SOME FACTORS AFFECTING THE EFFICIENCY OF COPPER DEPOSITION FROM LEACHING SOLUTIONS RICH IN IRON

Thesis by

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ABSTRACT

Experimental work is described serving to identify eleven variable factors influencing the efficiency of operation of electrolytic cells operating with copper cathodes and lead anodes and fed with solutions containing relatively high concentrations of copper, iron, aluminum and sulfuric acid.

Results are given constituting a systematic investigation of the effect on anode and cathode efficiencies of three of these variables, and some work has been done on the effect of a fourth.

It is found that increasing temperature results in decreasing cathode efficiency with very little effect on the net anode efficiency.

It is found that increasing concentration of ferrous iron results in marked increase in net anode efficiencies and relatively small decreases in cathode efficiencies until a concentration of 19 grams per liter is reached. Further increase of ferrous iron results in marked increase in the cathode efficiency but also in pronounced decrease in the net anode efficiency.

It is found that increasing the concentration of ferric iron results in decreasing both cathode and net anode efficiencies. Investigation of this variable was not complete.

It is found that increasing concentration of aluminum results in marked increase in cathode efficiency after a poorly defined lower limit is passed. Small increases in the net anode efficiency with increasing aluminum concentration are found, the maximum gain being recorded at approximately the lower limit of concentration which has appreciable effect on the cathode efficiency.

The use of the glass electrode to determine the pH of the solution has been investigated and further work on the effect of varying alu-concentration involving pH control thru use of the glass electrode is outlined.

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I - Introduction

At the plant of the Inspiration Consolidated Copper Company, located at Inspiration, Arizona, copper of sufficient purity for marketing is produced by a process known as the "Leaching and Electrolytic Precipitation Process." The essentials of the process are as follows:-

First, the mined ore is crushed to approximately three eighths inch lumps and is subjected to the leaching or dissolving action of an aqueous solution containing as active ingredients sulfuric acid and ferric sulfate. Both of these materials are necessary to accomplish the complete solution of all the copper which is present in the ore, since the copper is present in several different chemical compounds which may be divided into two general classes; "oxide copper" and "sulfide copper." "Oxide copper" includes the oxides and silicates and other compounds which are dissolved by the action of the sulfuric acid alone according to the type reaction

$$\underline{CuO} + H_2^{+}SO_4^{=} \text{ ——— } Cu^{++}SO_4^{=} + H_2O.$$

"Sulfide copper" consists largely of chalcocite, Cu_2S, but includes all the copper compounds which are not attacked by the sulfuric acid alone but are dissolved by the combined action of the ferric sulfate and the acid, according to the type reactions

$$\underline{Cu_2S} + Fe_2^{+++}(SO_4)_3^{=} \text{ —— } \underline{CuS} + Cu^{++}SO_4^{=} + 2Fe^{++}SO_4^{=}$$

$$\underline{CuS} + Fe_2^{+++}(SO_4)_3^{=} \text{ —— } Cu^{++}SO_4^{=} + \underline{S} + 2Fe^{++}SO_4^{=}.$$

Also present in appreciable quantity in the leaching solution are copper sulfate, formed by the solution of the copper borne by the ore; ferrous sulfate, formed by the reduction of the ferric sulfate as indicated in (2) above; aluminum sulfate, arising from the partial solution of the clay and rocks forming the gangue of the mined material. Besides these there are a great number of other chemical substances present in very small amount, i.e., 1% or less of the total solids in the solution.

Second, this leaching solution, having dissolved all the copper values in the ore, is pumped into cells where it is electrolyzed. The anode is of 8% antimony lead and the cathode is of electrolytic copper. The anode is essentially inert chemically, becoming coated over the surface with PbO_2 after a short period of operation and undergoing no further change. During the electrolysis the ferrous sulfate in the leaching solution is oxidized to ferric sulfate at the surface of the anode. The copper of the leaching solution is deposited at the cathode during electrolysis.

In the commercial operation of this process it is very desirable that both of these things should be accomplished as completely and efficiently as possible since the copper plated out is the finished product of the whole process and the ferric sulfate thus generated is necessary to dissolve the "sulfide copper" present in the ore onto which this leaching solution is again pumped after its passage thru the cells.

II - Preliminary Considerations

The purpose of the research here described is to investigate the factors influencing the efficiency of each of the two electrode processes occurring during this electrolysis and to measure the extent of changes in these efficiencies caused by variations in these factors over a range covering possible commercial operating conditions.

In order to discuss the quantitative measurements which are the chief interest of the investigation it will be necessary to define the terms employed in the discussion.

By Cathode Efficiency is to be understood one hundred times the ratio of the weight of copper actually produced at the cathode by the passage of a certain amount of electricity to the weight of copper theoretically depositable by the same amount of electricity, according to Faraday's Law.

By Anode Efficiency is to be understood one hundred times the ratio of the weight of ferrous iron transformed to ferric iron by the passage of a certain amount of electricity to the weight of ferrous iron theoretically transformable by the same amount of electricity according to Faraday's Law.

A fairly thorough search of the literature revealed considerable work done on problems involved in the ore leaching part of the process, but nothing which appeared applicable to the electrolysis which constitutes the problem under consideration.

III - Experimental

In starting experimental work it was thought desirable for purposes of close control to use a cell containing only a single pair of electrodes. Accordingly the first cell set up consisted of a glass battery jar in which were hung a single pair of electrodes which were approximately four by six inches, with the long dimension vertical. Solution feed was by gravity, and the spent liquor was removed by overflow. The cell was set up on the work table and no attempt was made to regulate temperature.

Several difficulties appeared immediately,- for example, the action of the current was not confined to the face of the electrodes, but electrolysis also took place in considerable measure on the backs; the single gravity feed system was not subject to exact regulation, and the rate of feed was not readily reproducible. Also, temperature changes were found to be excessive, and the effect of temperature on the measured efficiencies was found to be quite marked.

A series of runs was made, the results of which were entirely inconclusive and consequently are not included here. As a result of this work the backs of the electrodes were insulated by painting, ordinary Duco being found to be most satisfactory, the feed and withdrawal system was refined and the construction of a constant temperature bath was undertaken. Considerable difficulty was had in correctly determining the sulphutic acid concentration in the solution, so a modified procedure for this determination was developed. In later work, however, it was found that the change in the sulphuric acid concentration caused by the action of the cell was less than the error in the determination, so the concentration of sulphuric acid was hereafter measured only in the original solution at the start of each experimental run.

At this time the following factors had been recognized as having effect on the efficiency of the cell:-

1. Temperature
2. Concentration of ferrous sulfate
3. Concentration of ferric sulfate
4. Concentration of copper sulfate
5. Concentration of sulfuric acid
6. Rate of passage of solution through cell
7. Rate of passage of electric current through cell

Consequently it was proposed to make a series of experimental runs in which all of these factors were held constant in each run and only the temperature was varied from run to run. This was expected to yield results from which the effect of the temperature on the cathode efficiency and the anode efficiency could be found. However, the results showed a marked change in efficiency with time of operation of the cell, which completely masked the effect sought. It was assumed that this effect was due to changes in the nature of the surface of the lead electrode, the anode.

It was then proposed to determine the change of the anode efficiency with time of use of the anode.

A run, starting with a freshly polished lead anode was made. The results showed a promising regularity and indicated a gradual decrease of anode efficiency with increasing time. The run was repeated at a higher temperature. In this case channelling on the surface of the cathode and sprouting along the bottom edge became so bad at the end of 44 hours of operation that a new copper cathode was installed. The effect of this was so profound both on the anode efficiency and cathode efficiency that it was recognized that some method of keeping the actual surface of the cathode exposed to the solution essentially constant was necessary.

Since the channelling of the surface of the cathode was apparently due to the rise of gas bubbles along it, it was felt that by artificially agitating the solution it should be possible to prevent the channelling and materially to reduce the sprouting. A motor driven glass stirrer was built into the cell and a trial run made. This gave a very much improved cathode surface and much more regularity in the calculated anode and cathode efficiencies. The apparatus was modified slightly and the run repeated with even better results. The anode efficiency and cathode efficiency reached essentially constant values in a comparatively short time under these conditions.

In order to avoid any errors introduced by the comparatively large quantities of solution which were present in the cell but not contained directly between the electrode faces in the battery jar cell, in June a cell was constructed in which the lead anode and copper cathode served as two walls of the cell. In this way there was no "dead" or inactive solution in the electrolysis cell.

While electrolysis progresses in a cell in which the liquor being electrolyzed contains ferric iron there is a certain amount of copper being dissolved off the cathode by the leaching or dissolving action of this ferric iron at the same time that metallic copper is being plated out on this cathode by the action of the current. As the ferric iron dissolves the copper it is converted into ferrous iron according to the equation

$$2Fe^{+++} + Cu\ (metal) = 2Fe^{++} + Cu^{++}$$

In order to calculate the amount of ferric iron actually made by the anode under any certain conditions the amount of ferric iron lost as a result of this reaction has been calculated and added to the net amount actually found as the increase. In making this calculation it had been assumed that the current was actually 100% effective in depositing copper and that any smaller value of cathode efficiency found was due entirely to the action of the ferric iron. This assumption was based on data of T.W.Richards for copper coulometers under conditions assumed to be comparable.(1) To check up on the validity of this assumption a run was made in which there was no iron present in the solution, only copper sulfate and sulfuric acid. At 30°C in the absence of iron the actual cathode efficiency was found to be only some 92%.

During June and July a series of test runs was made in the new cell described above, using the motor-driven stirrer mentioned. These runs were made at temperatures of 30°, 40° and 50°. At each temperature two runs were made, one with solution approximating the composition of Inspiration liquor and one with solution containing the same concentrations of copper sulfate and sulfuric acid but without any iron. Thus it was possible to find the decrease in copper deposited actually chargeable to the ferric iron and hence to calculate the cathode efficiency on the basis of the copper which could actually be produced in the absence of any iron. The figure thus found for the actual gross efficiency of the anode is called the "Corrected Anode Efficiency" and the value given for the cathode efficiency based on the amount of copper actually produced in the cell from iron-free liquor is called the "Corrected Cathode Efficiency."

A series of very fine cathode sheets was obtained and all results were very promising until the run at 50° with the iron-bearing solution was made. At this temperature the local eddy currents caused by the motor-driven stirrer apparently fed ferric iron up against the surface of the cathode too rapidly and holes were eaten clear thru the cathode sheet in two places. (see Fig. 10).

Since the amount of agitation had been shown to be a very important variable and since it was impossible to employ the motor stirrer at 50° the results of this series of runs were discarded.

The design of the cell was modified by drilling the bottom for a circulating system and for an outlet for the through flow. A portable air lift was designed to handle approximately 2 liters of solution per hour (compare with through flow of ca. 300 cc. per hour) which was withdrawn at the bottom and re-introduced at the top of the cell, thus providing the agitation. (see Figs. 1, 2, 3)

The series of runs at 30° (Run 6A, see Fig. 4), 40° (Run 7A, see Fig. 5), 50° (Run 5A, see Fig. 6) was repeated with this modified apparatus and again good cathodes were obtained (see Figs. 7, 8, 9).

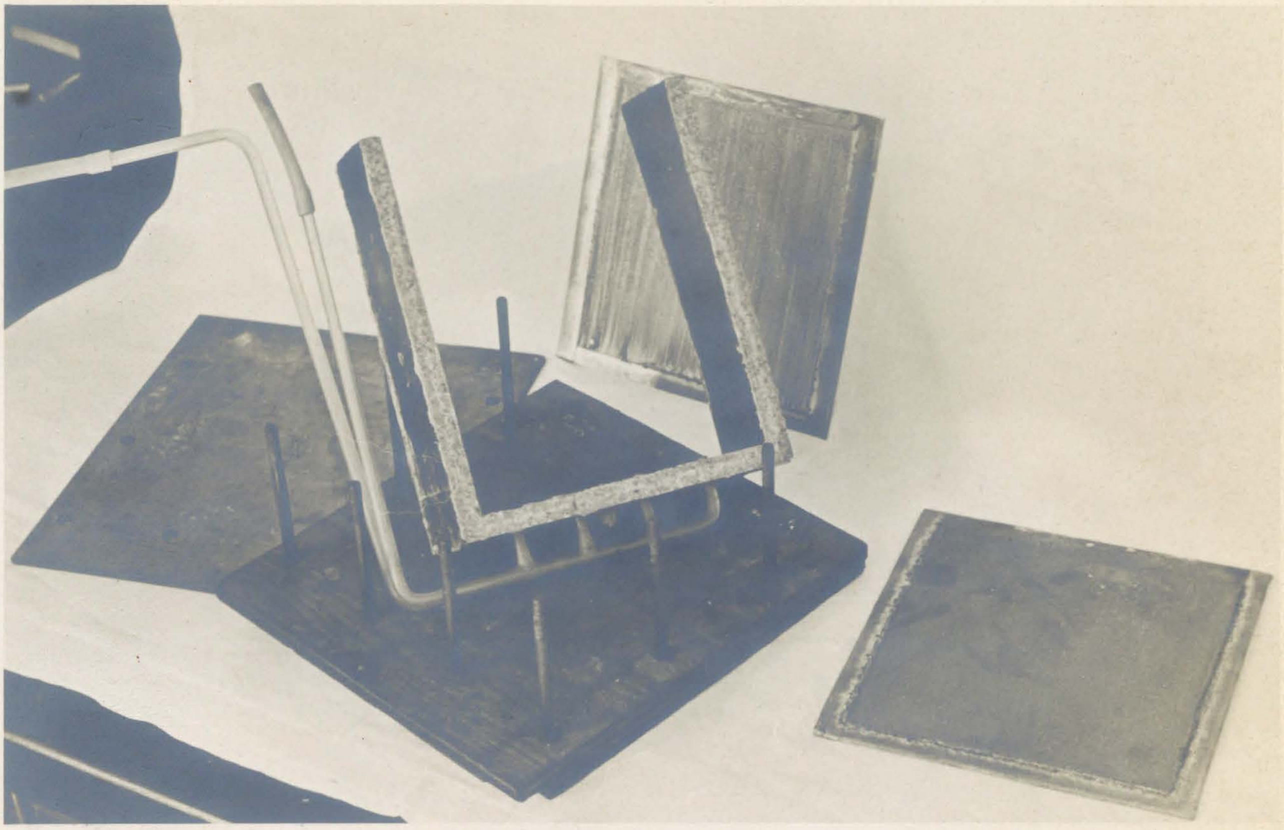


Fig. 1

Parts of Electrolysis Cell Ready for Assembly

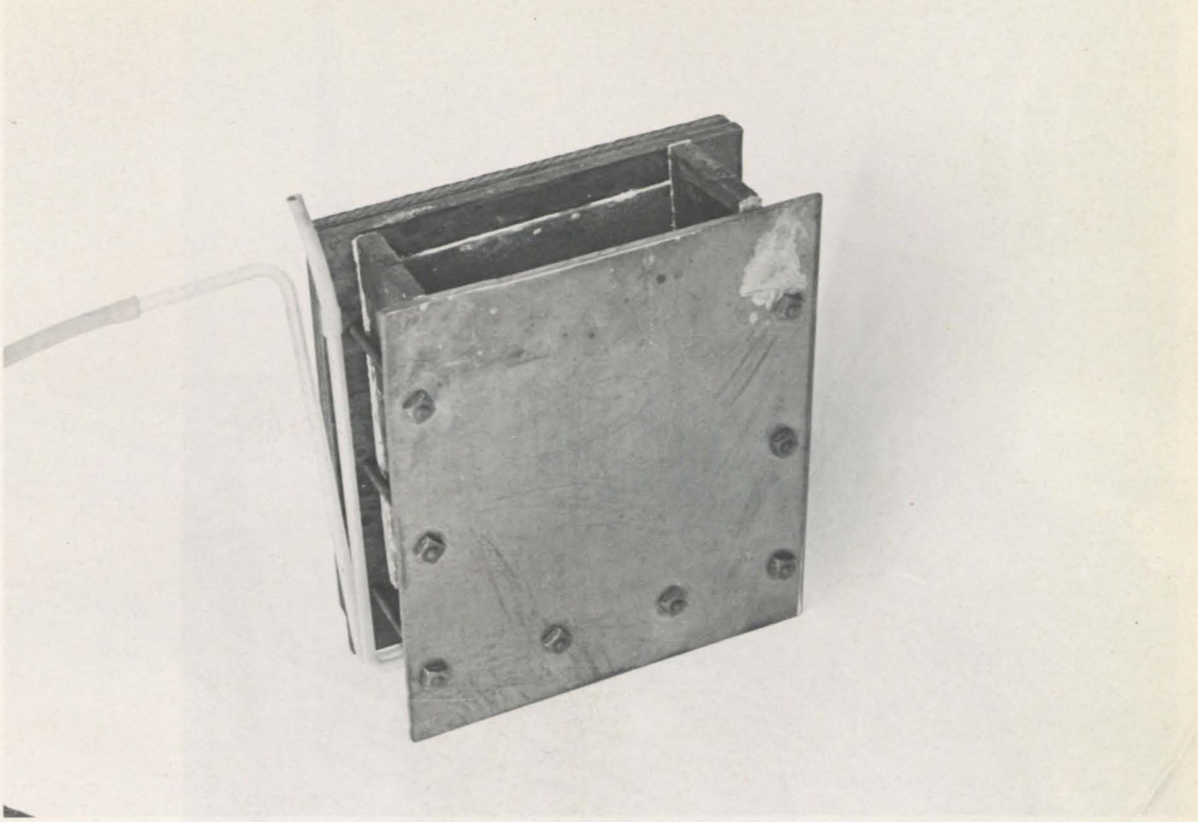


Fig. 2

Electrolysis Cell Assembled

Fig. 3

Assembled Apparatus, Showing Feed and Circulation Systems

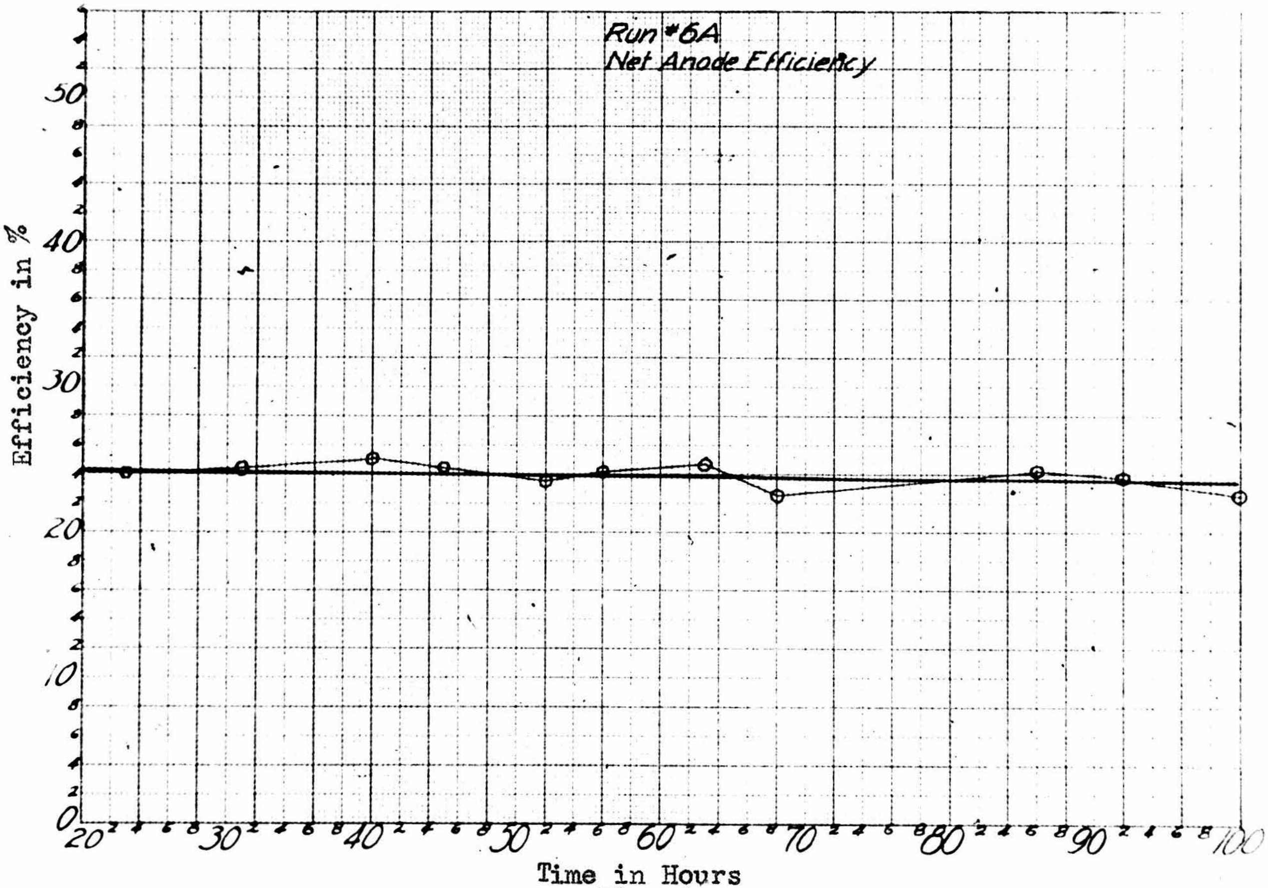

Run #6A
Net Anode Efficiency
Efficiency in %
0
10
20
30
40
50
20
30
40
50
60
70
80
90
100
Time in Hours

Fig. 4a

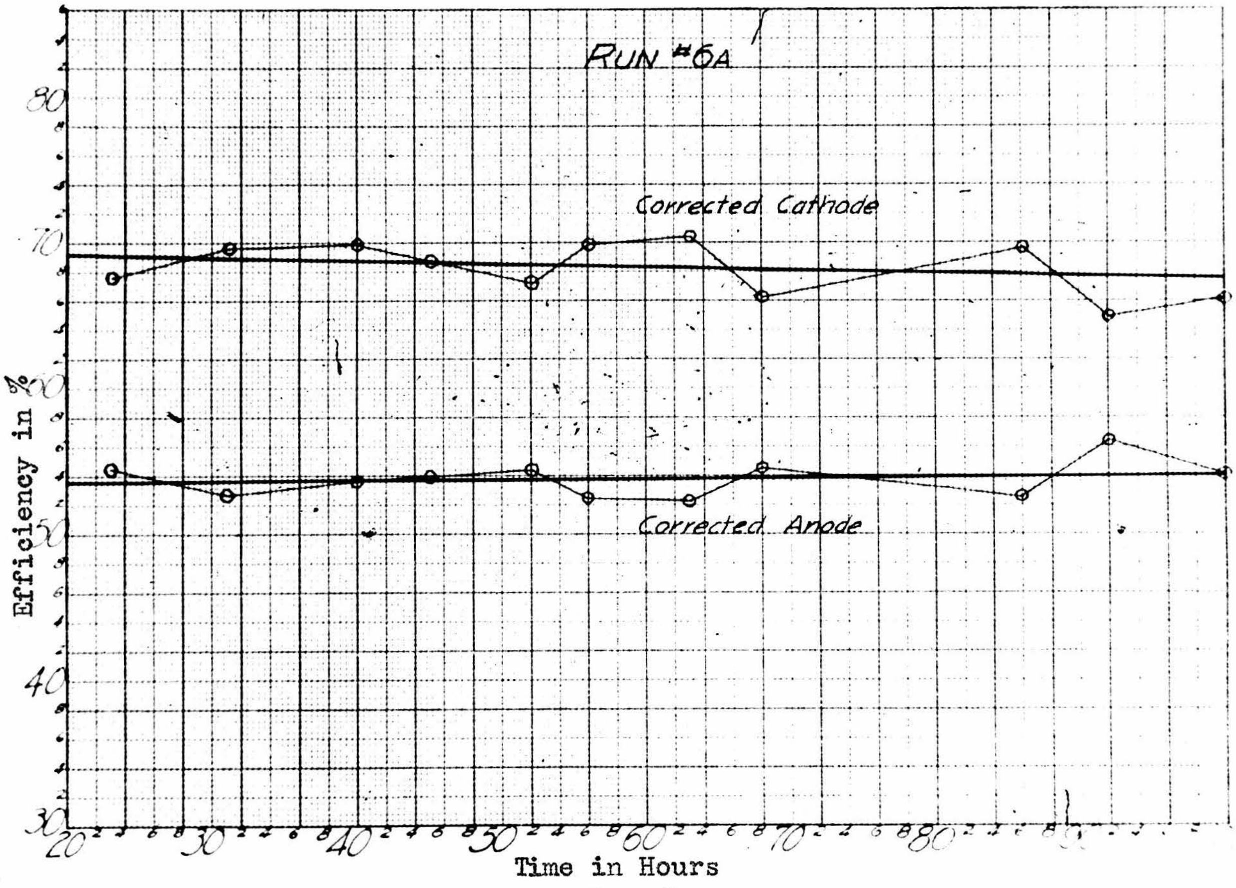

RUN #6A
Corrected Cathode
Corrected Anode
Efficiency in %
30
40
50
60
70
80
20
30
40
50
60
70
80
Time in Hours

Fig. 4b

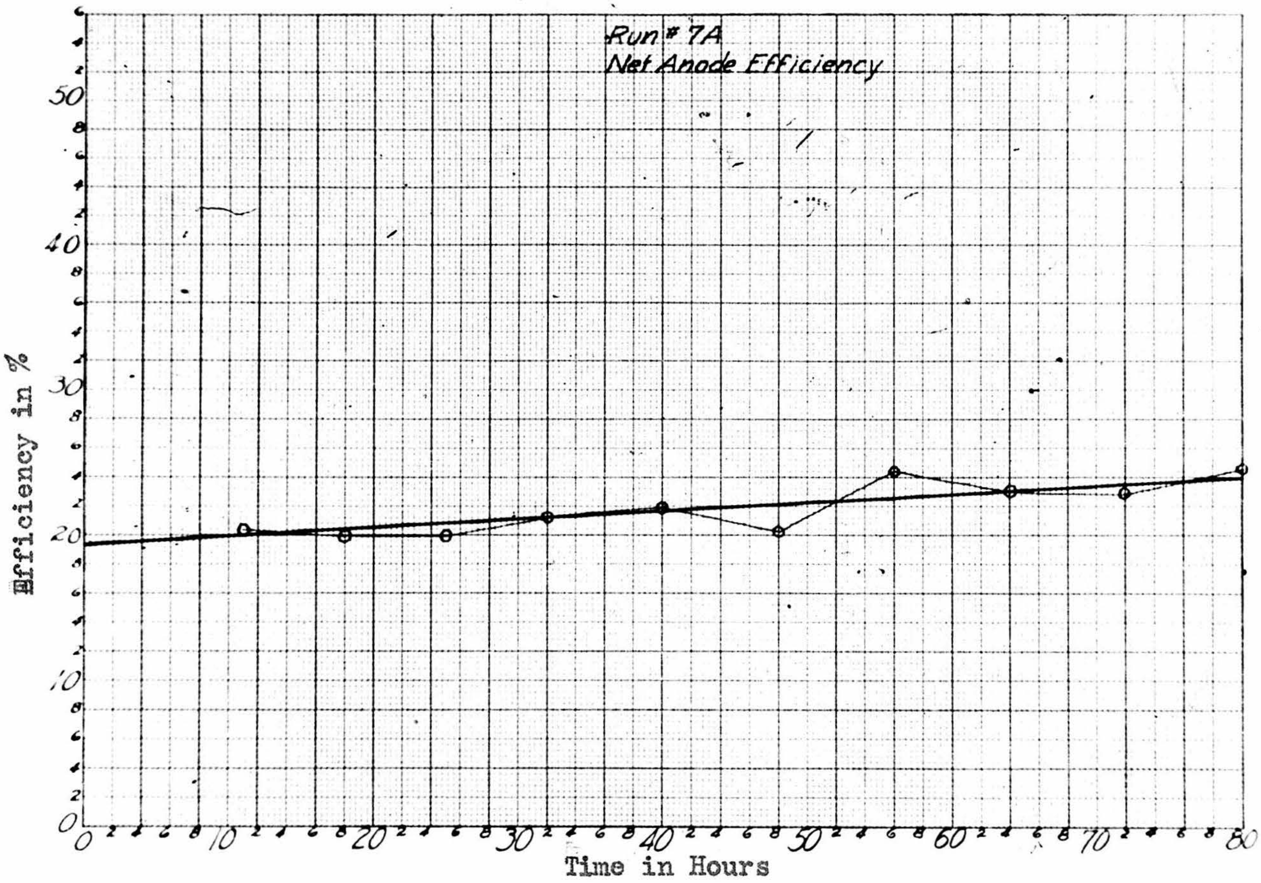

Run # 7A
Net Anode Efficiency
Efficiency in %
0
10
20
30
40
50
0
10
20
30
40
50
60
70
80
Time in Hours

Fig. 5a

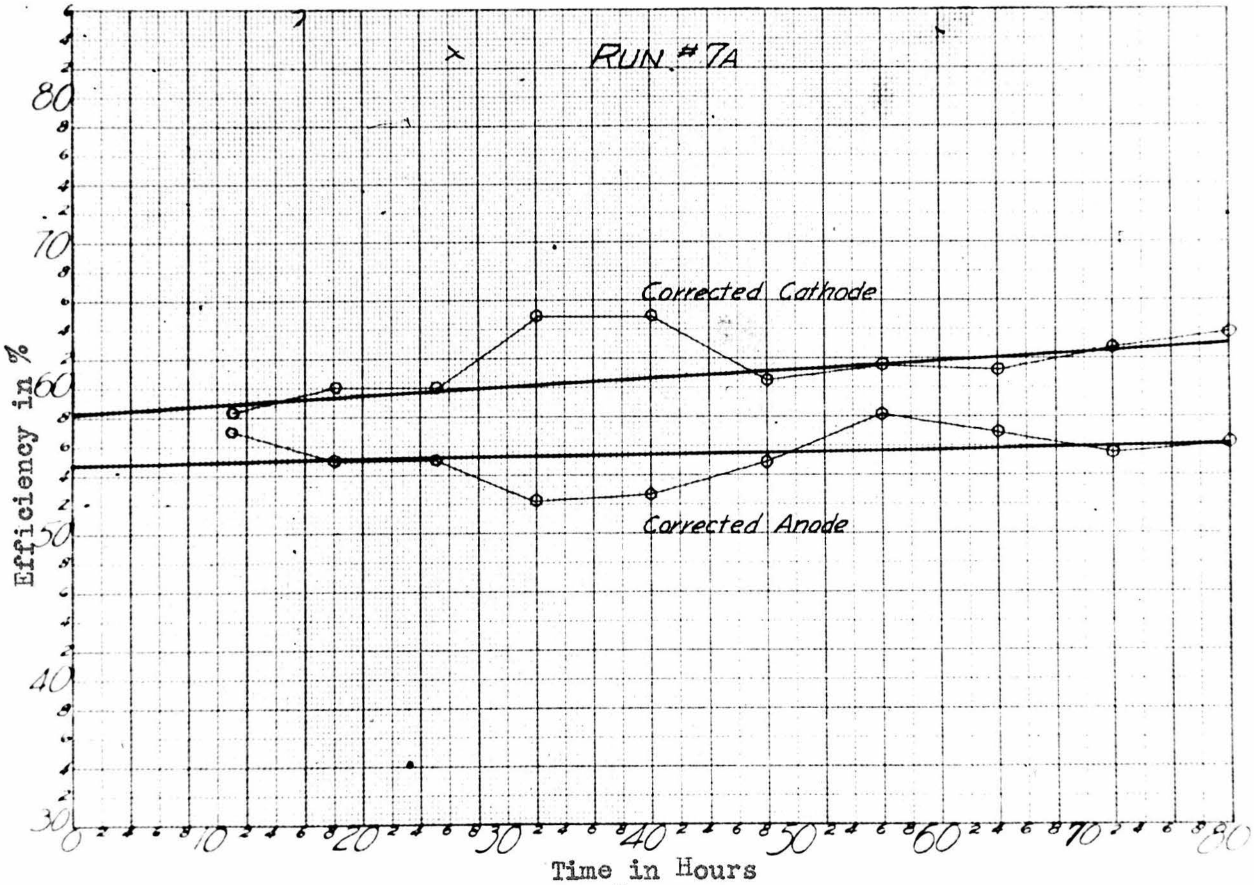

RUN # 7A
Corrected Cathode
Corrected Anode
Efficiency in %
30
40
50
60
70
80
0
10
20
30
40
50
60
70
80
Time in Hours

Fig. 5b

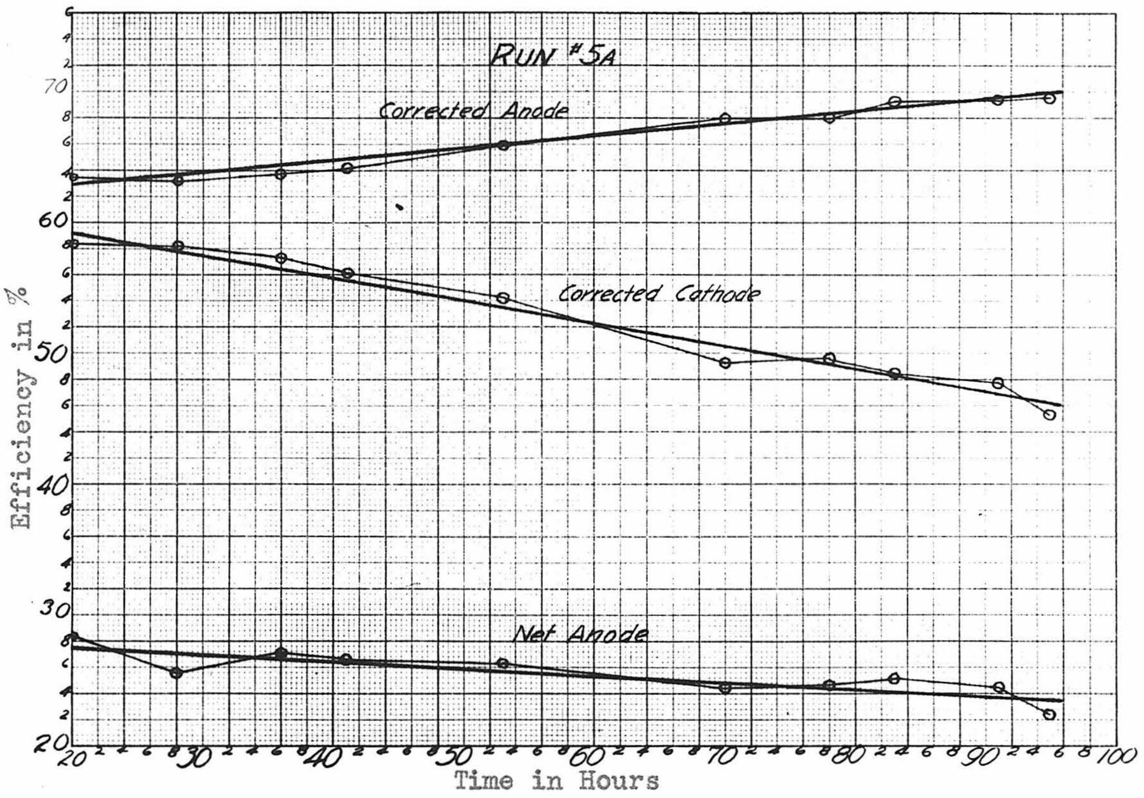

RUN #5A
Corrected Anode
Corrected Cathode
Net Anode
Efficiency in %
70
60
50
40
30
20
20
30
40
50
60
70
80
90
100
Time in Hours

Fig. 6

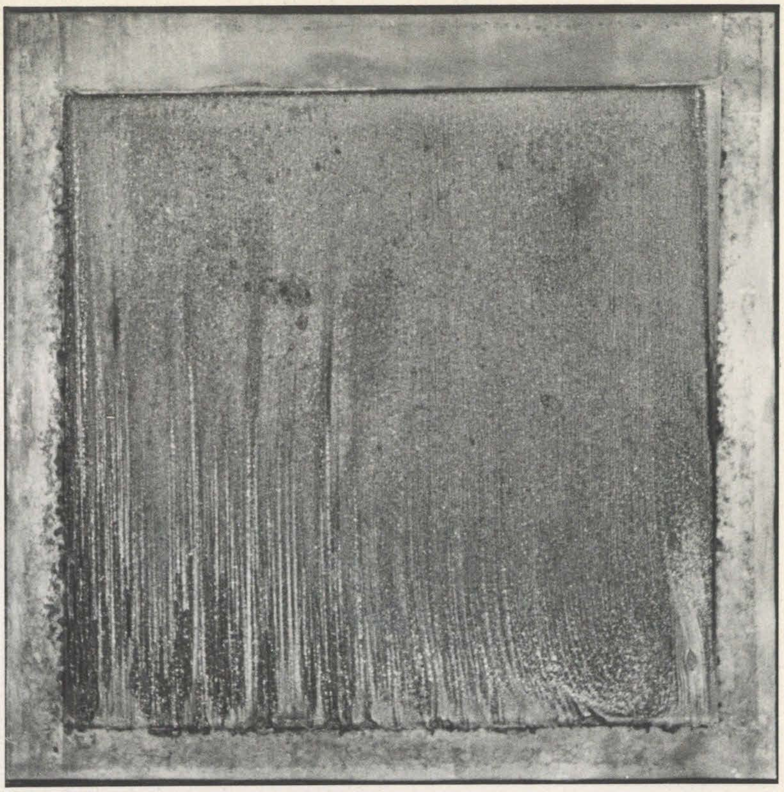


Fig. 7
Cathode Sheet Run No. 6A

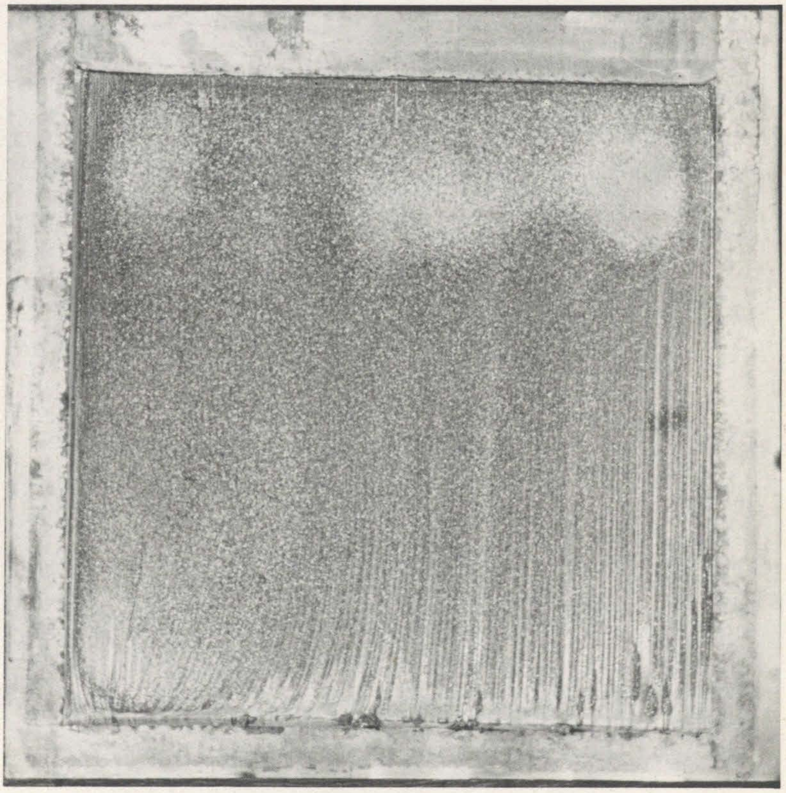


Fig. 8
Cathode Sheet Run No. 7A

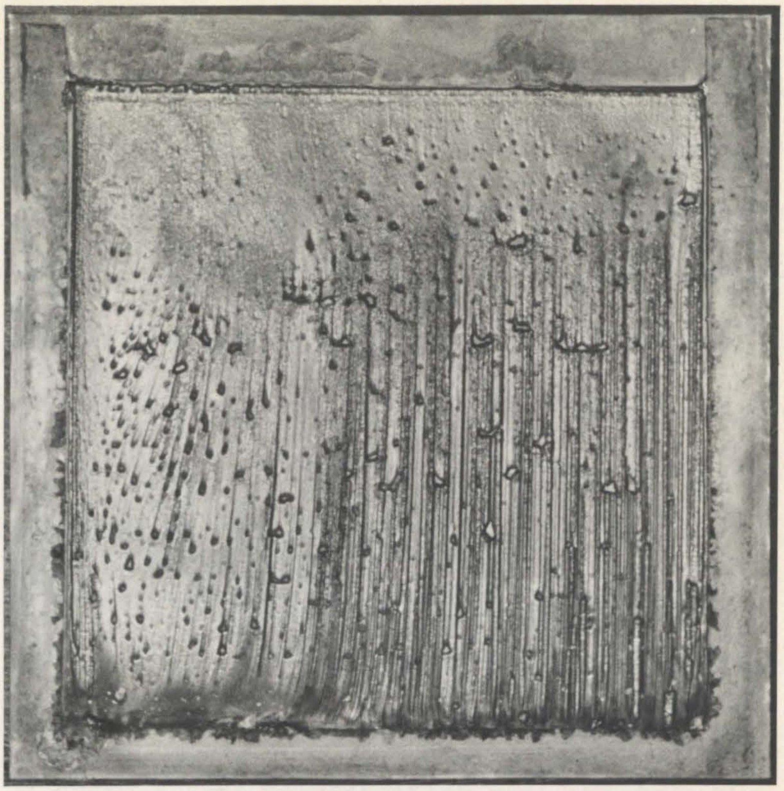


Fig. 9
Cathode Sheet Run No. 5A

Fig. 10
Cathode Sheet Run No. 4A

These results serving to indicate the effect of temperature, it was now thought desirable to investigate the effect of changing concentration of ferrous iron on the cathode and anode efficiencies. A series of runs was therefore undertaken in which the temperature was fixed at 40°C, the ferric iron concentration at 5.5 grams per liter, the copper concentration at 33 grams per liter, and sulfuric acid concentration at 33 grams per liter, and in which the change of anode and cathode efficiencies with the time of cell operation at each of a series of values of ferrous iron concentration was to be determined.

It was expected that the cathode and anode efficiencies would remain practically constant during the course of any one run and that higher values of ferrous iron concentration would produce higher anode efficiencies, both net and corrected. Runs were proposed at ferrous iron concentrations approximating 13, 16, 20, 23 and 25 grams per liter as it was felt that this was the range most interesting from the commercial viewpoint.

The first run made in this series, Run 10A (see Fig. 11), in which the ferrous iron concentration was 20.6 grams per liter, however, showed a very unexpected effect. The anode efficiency at the beginning was, as expected, considerably higher than the value obtained with ferrous iron at 10.1 grams per liter in Run 7A (see Fig. 5). However, as the run progressed the anode efficiency fell off quite markedly, till after sixty hours of operation it was less than a third of its starting value and somewhat less than half that obtained in Run 7A.

It was observed that as the anode efficiency decreased, the cathode efficiency increased and thruout this series of runs it was

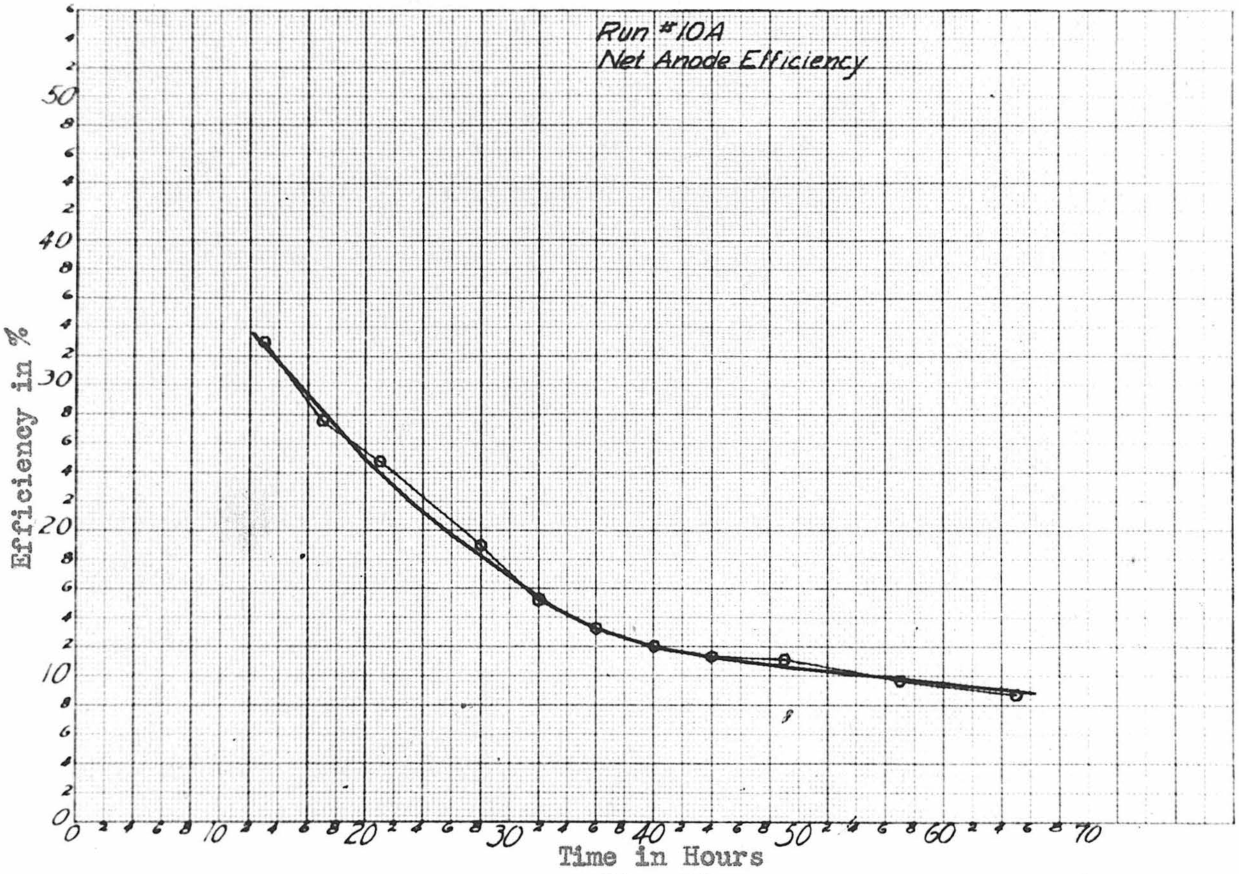


Fig. 11a

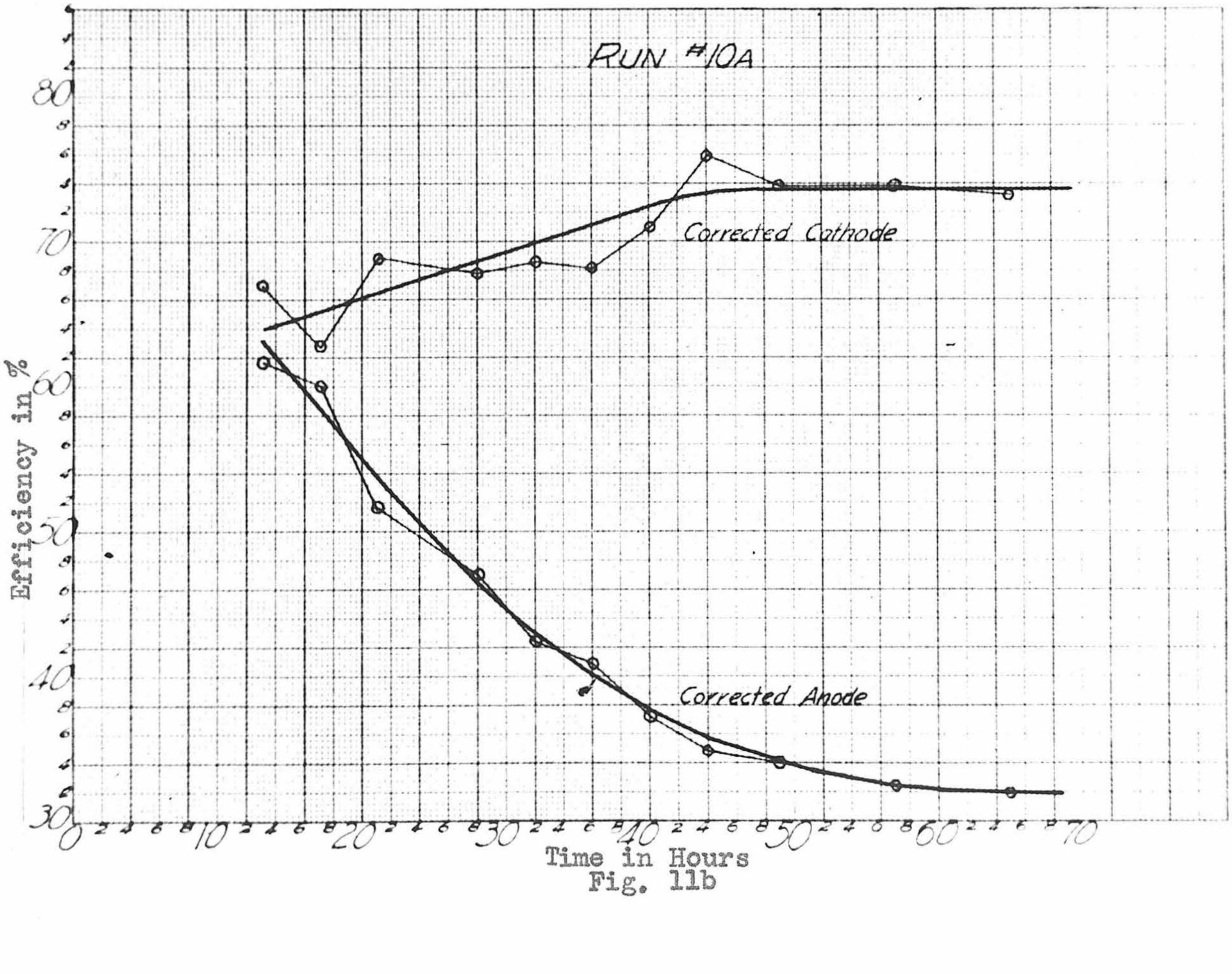


Fig. 11b

noted that any variation of ferrous iron concentration which caused decreased anode efficiencies also caused increased cathode efficiencies and vice versa. Consequently in the following discussion only anode efficiencies are mentioned although the graphs showing the course of the cathode efficiencies are also included.

The ferrous iron concentration was increased to a value of 24.6 grams per liter for the next run (Run 11A) and again the anode efficiency was found to decrease as the time of operation increased. See Fig. 12.

The next run, 12A, was made with the ferrous iron concentration at 16.3 grams per liter. The relatively high anode efficiency attained at the start was maintained throughout the course of the run. See Fig. 13.

A run, 13A, was next made with ferrous iron concentration at 19.3 grams per liter. The anode efficiency was higher than in the previous run and again this was maintained throughout the course of the run. See Fig. 14.

Considerable uncertainty as to the reality of the effect observed in Runs 10A and 11A was felt, inasmuch as the observed decrease of anode efficiency with increasing time was totally unexpected and no reason for this could be given, so Run 15A with ferrous iron concentration at 23.0 grams per liter was made. Again the anode efficiency started at the expected high value and continually fell off with increasing time of cell operation. See Fig. 15.

Run 16A was an attempt to duplicate Run 15A in order to discover just how reproducible the results of a run are. Ferrous iron con-

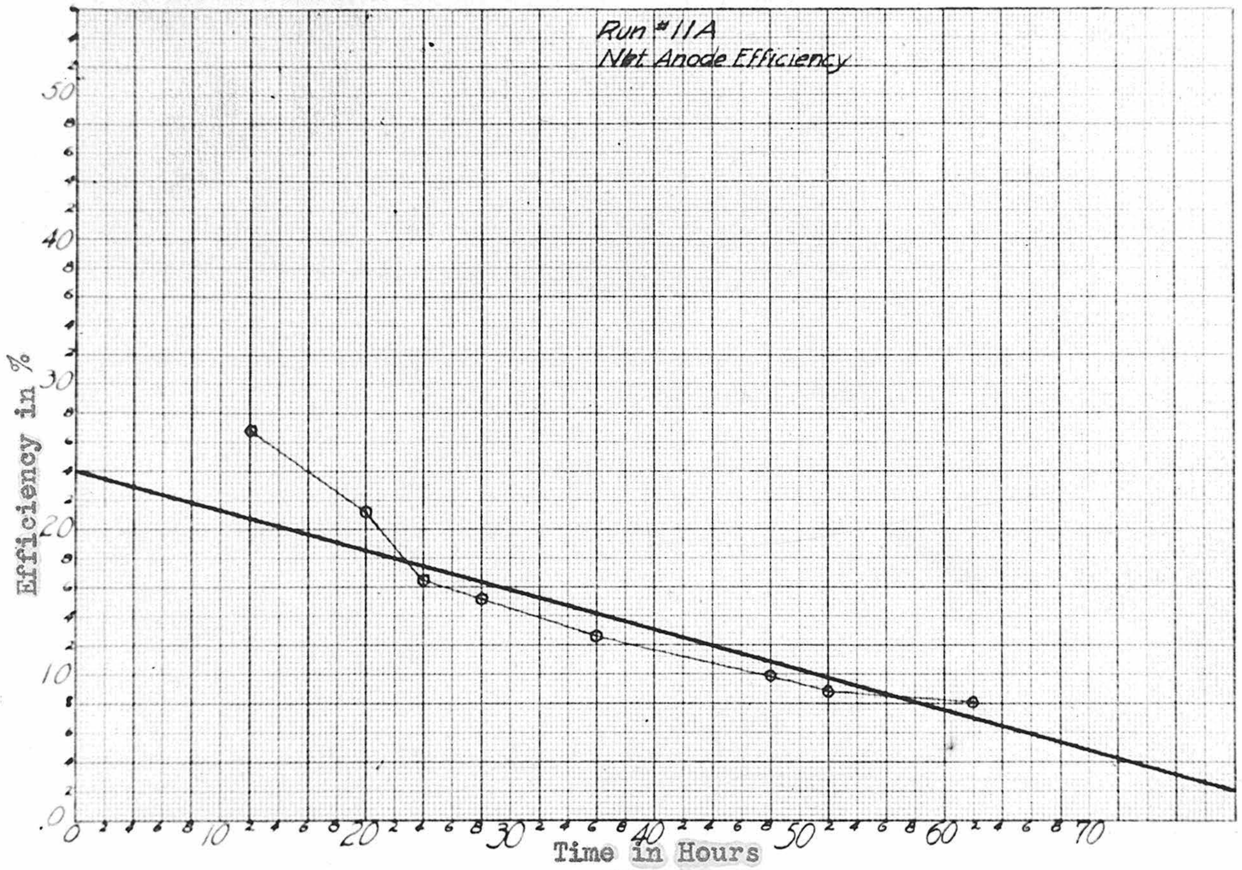


Fig. 12a

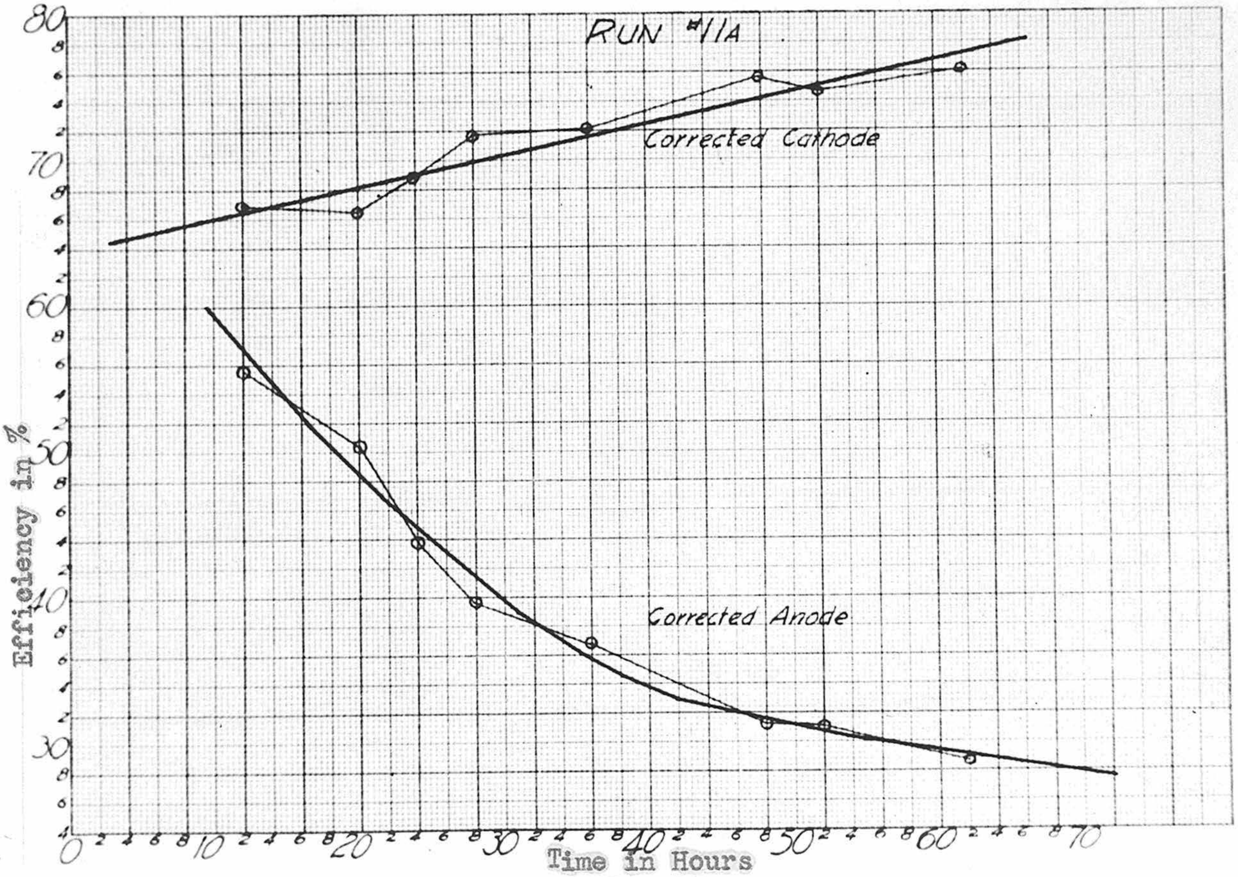


Fig. 12a

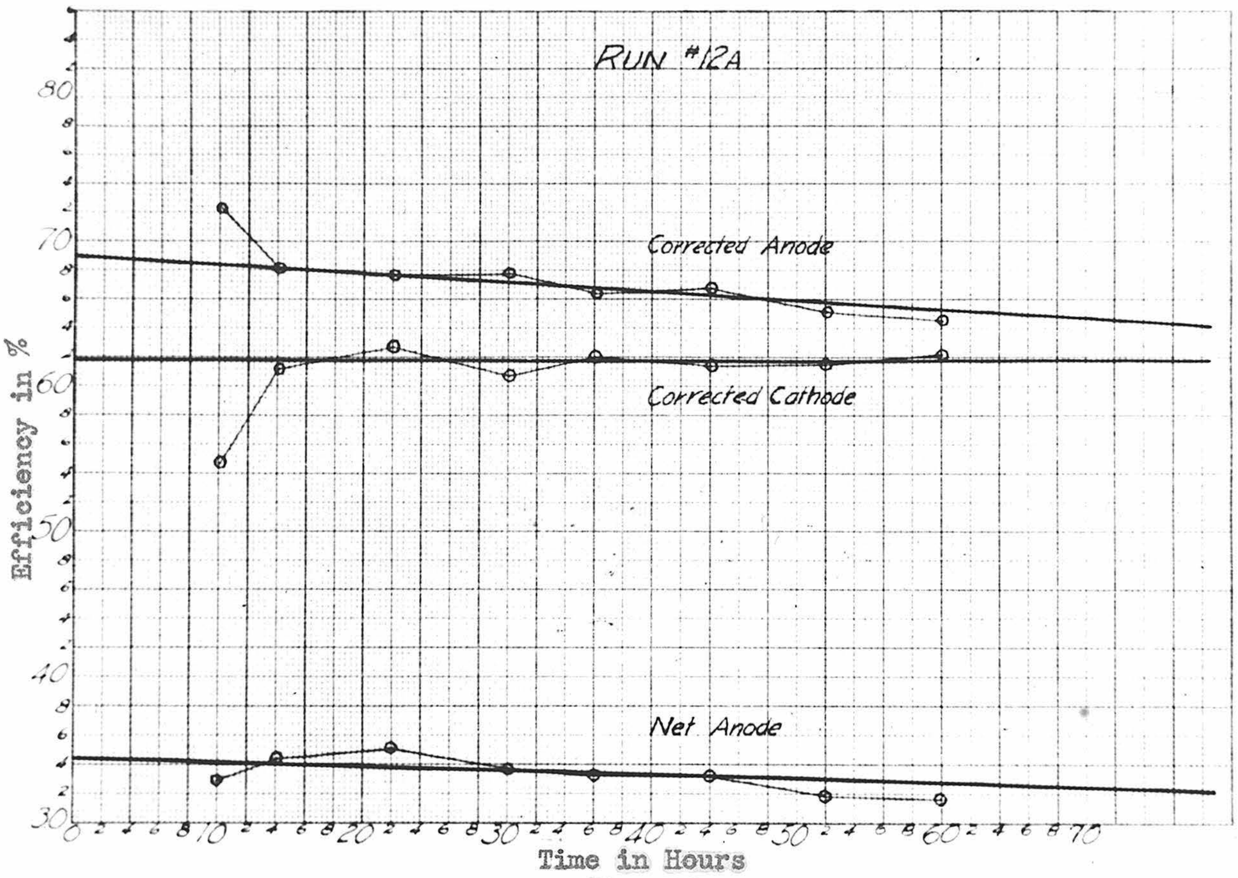

RUN #12A
Corrected Anode
Corrected Cathode
Net Anode
Efficiency in %
30
40
50
60
70
80
0
10
20
30
40
50
60
70
Time in Hours

Fig. 13

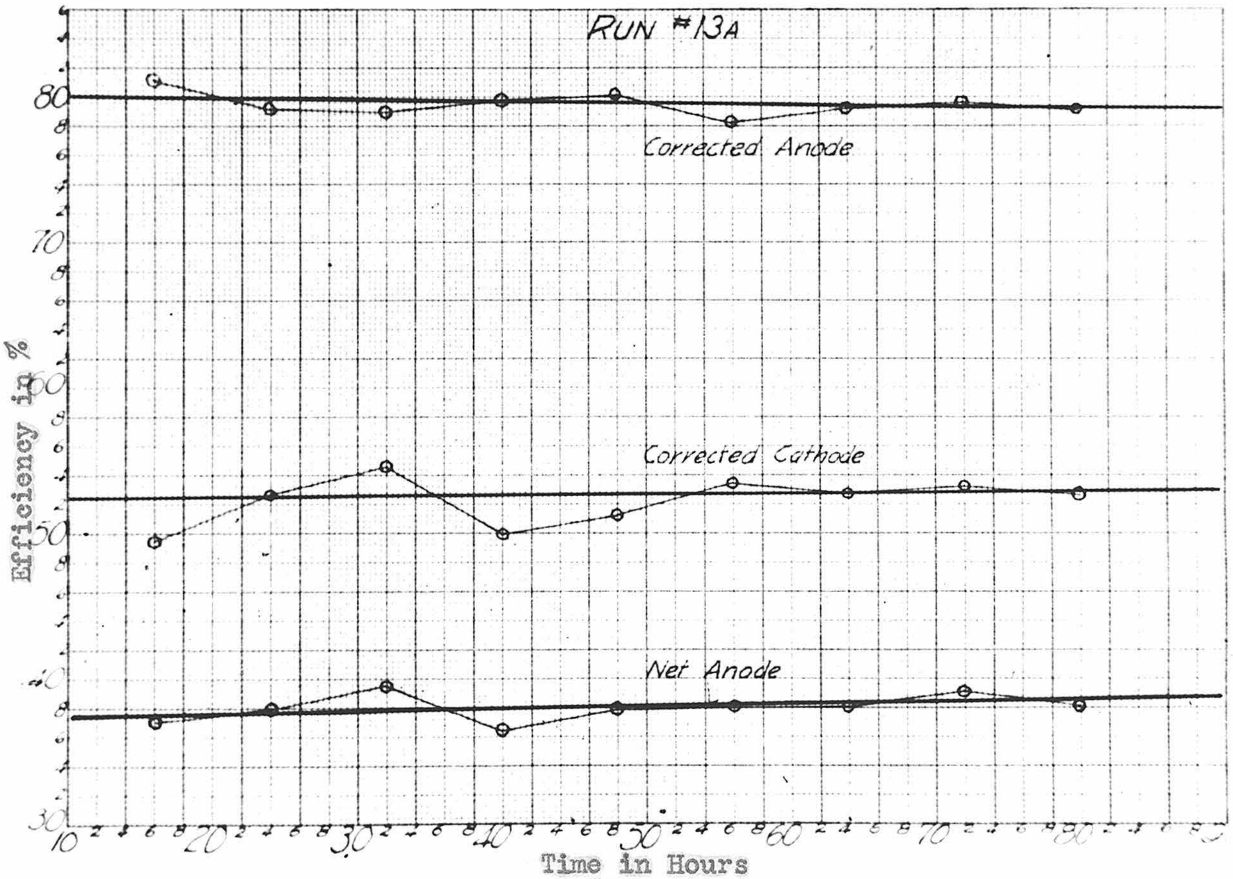

RUN #13A
Corrected Anode
Corrected Cathode
Net Anode
Efficiency in %
30
40
50
60
70
80
10
20
30
40
50
60
70
80
Time in Hours

Fig. 14

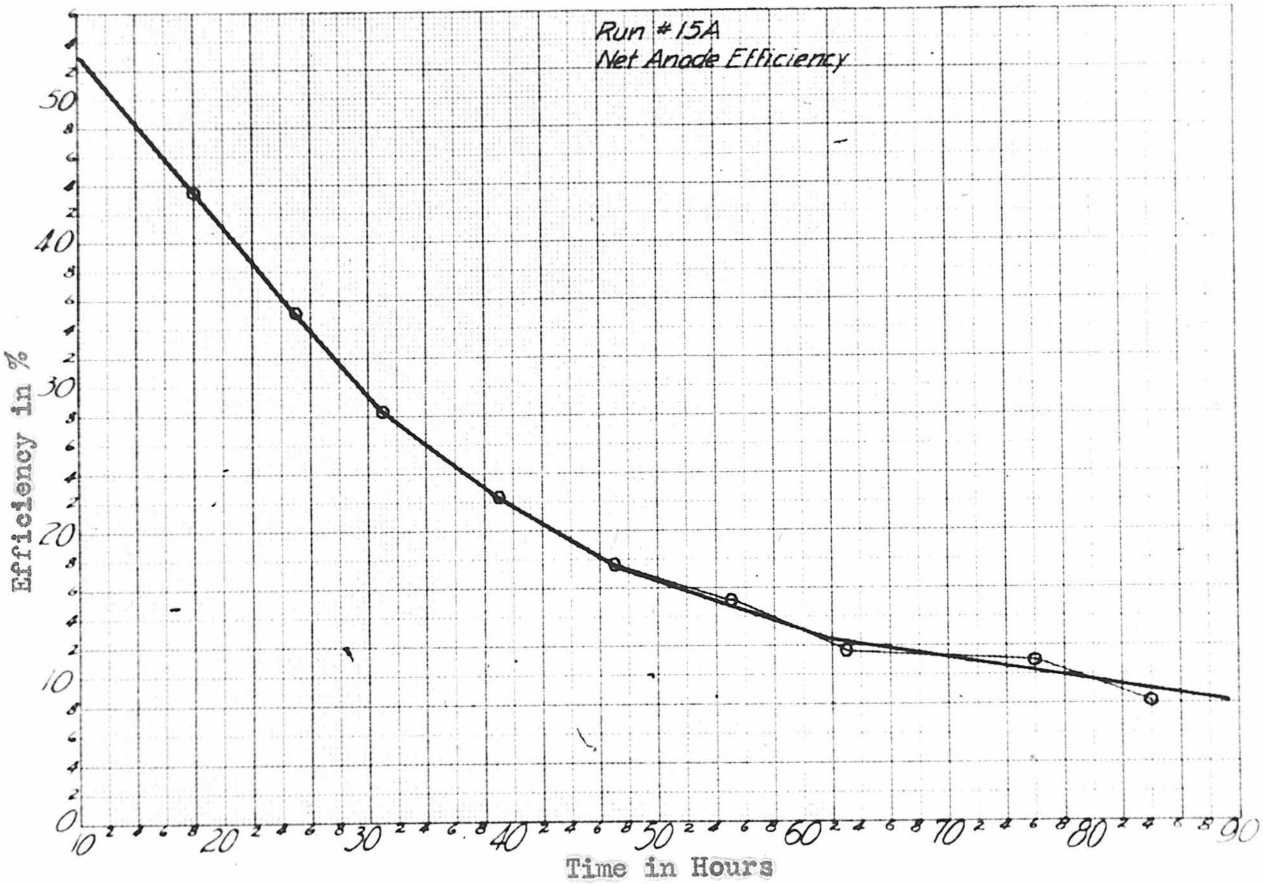


Fig. 15a

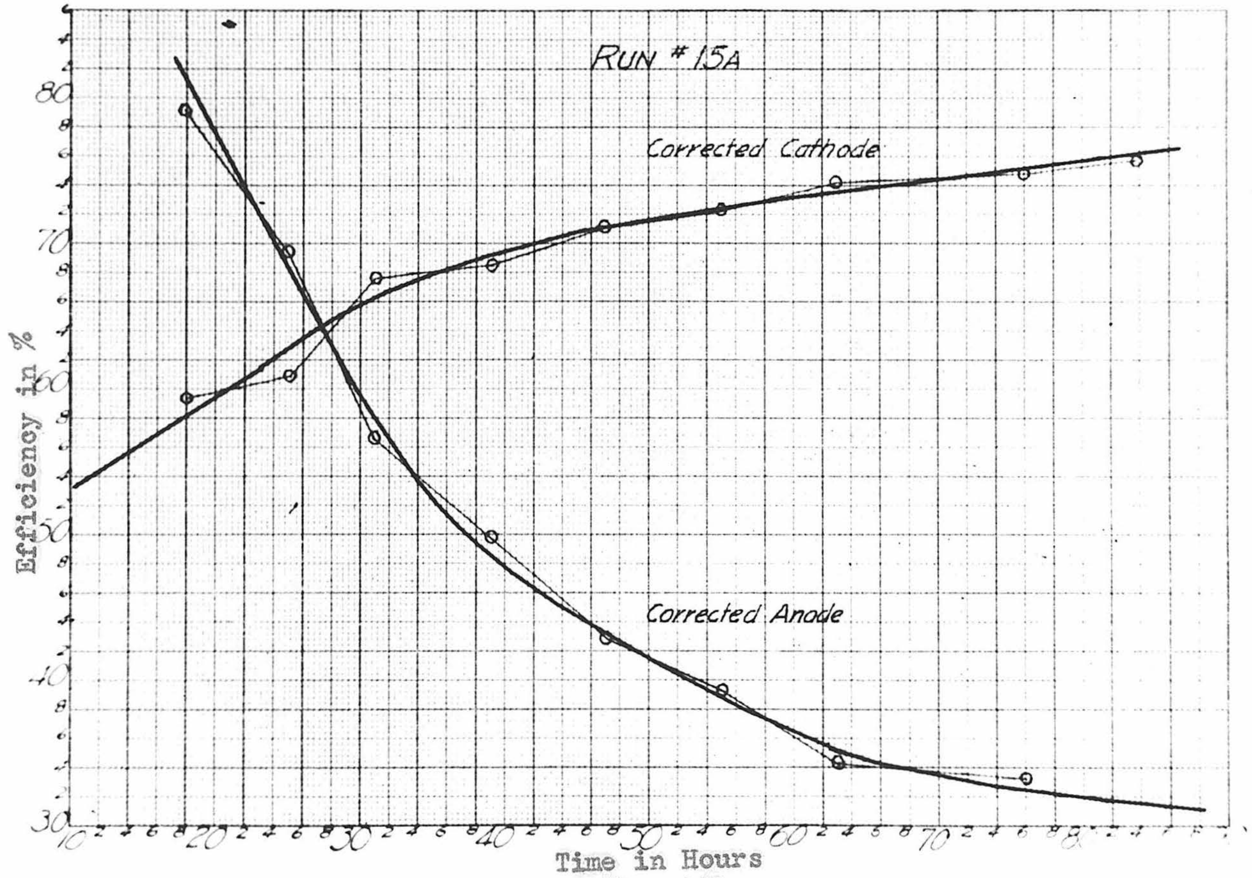
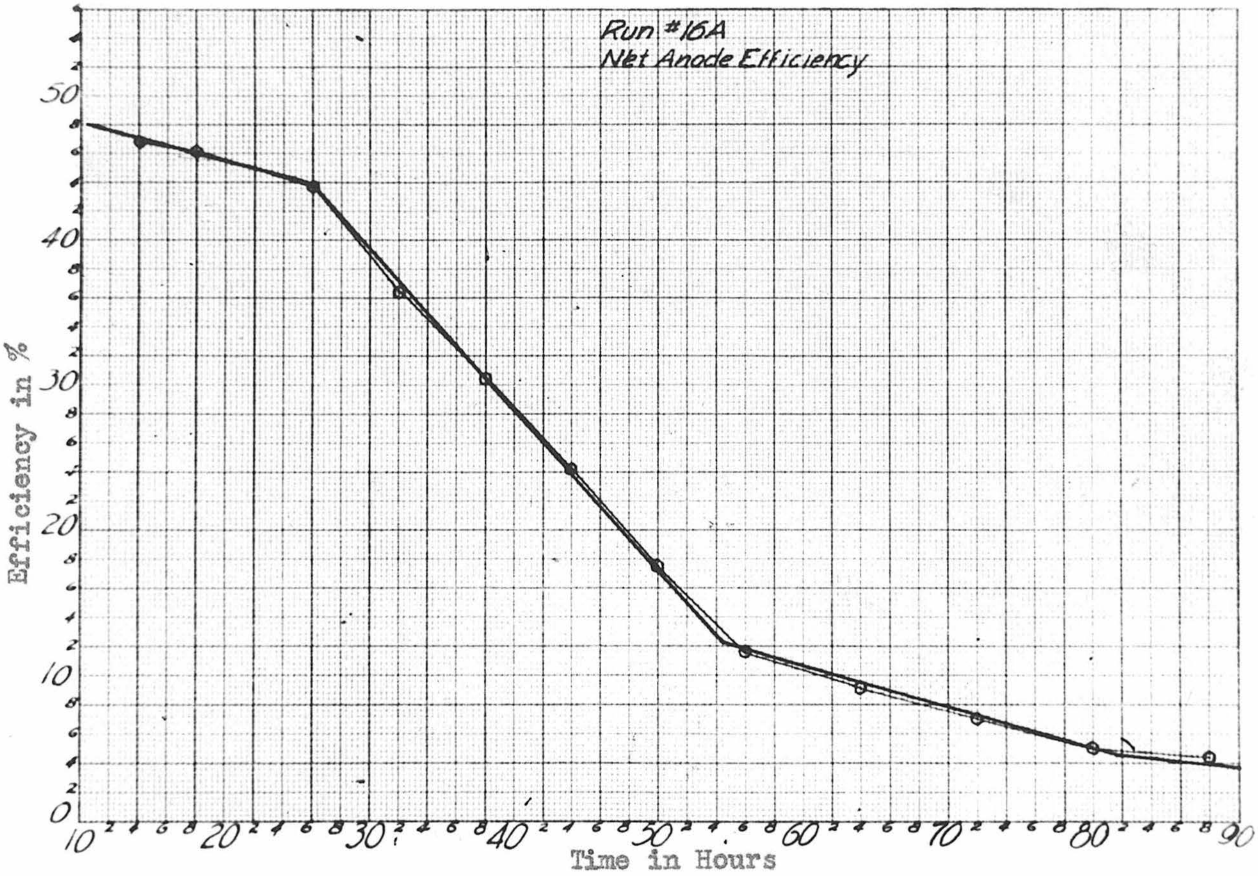


Fig. 15b

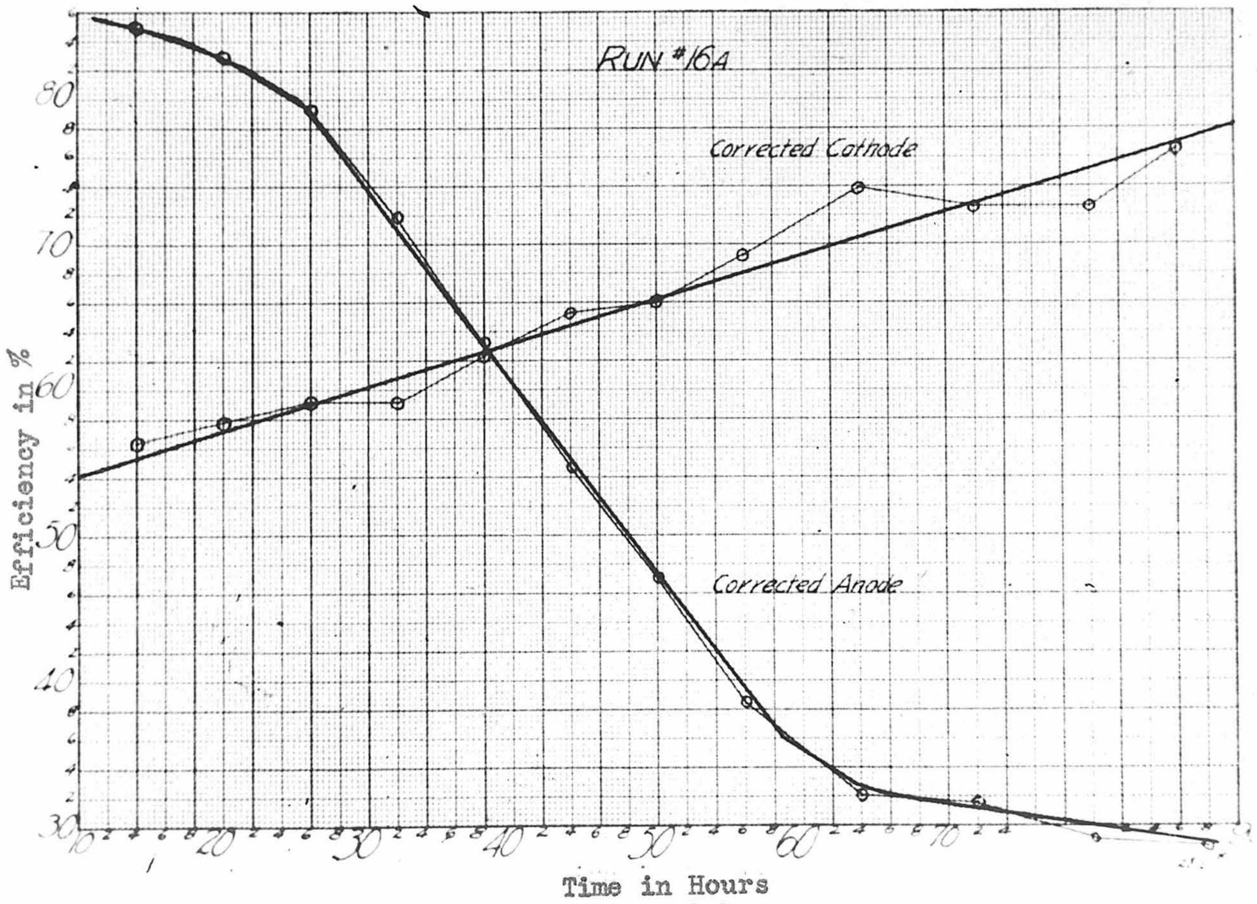
centration was 23.1 grams per liter. The plotted curves of efficiency vs. time differed somewhat between the two runs (see Fig. 16), but the same anomalous effect of decreasing anode efficiency with increasing time was noted and in both cases the curves levelled off at approximately the same low value after some sixty or seventy hours of operation.

As a result of the runs made in this series up to this point it had been found that as ferrous iron was increased up to a value of 19.3 grams per liter an increase in the anode efficiency was achieved and this increased efficiency was maintained at least through a hundred hours of cell operation. At values of ferrous iron concentration higher than 20.6 grams per liter a temporary gain in anode efficiency was made but the efficiency fell off with increasing time until it was absurdly small. Apparently there exists a certain "critical value" of ferrous iron concentration, at least for the other conditions of this series of runs, beyond which an entirely new effect enters. It was considered desirable to locate more definitely this "critical value," so Run 17A (See Fig. 17) with ferrous iron concentration at 19.2 grams per liter was made. This was practically a duplication of the conditions of Run 13A. For over fifty hours of operation the course of the efficiency vs. time curves of the two runs were almost identical but at this time the anode efficiency in Run 17A suddenly started to fall, with no apparent cause. It continually decreased and was still falling at 102 hours when the run was ended. It was concluded from these results that the "critical value" of ferrous concentration under these conditions is slightly greater than 19 grams per liter, probably 19.1 although this was not further tested. Before a conclusive report on this point can be made more work in this range must be carried out.



Time in Hours

Fig. 16a



Time in Hours

Fig. 16b

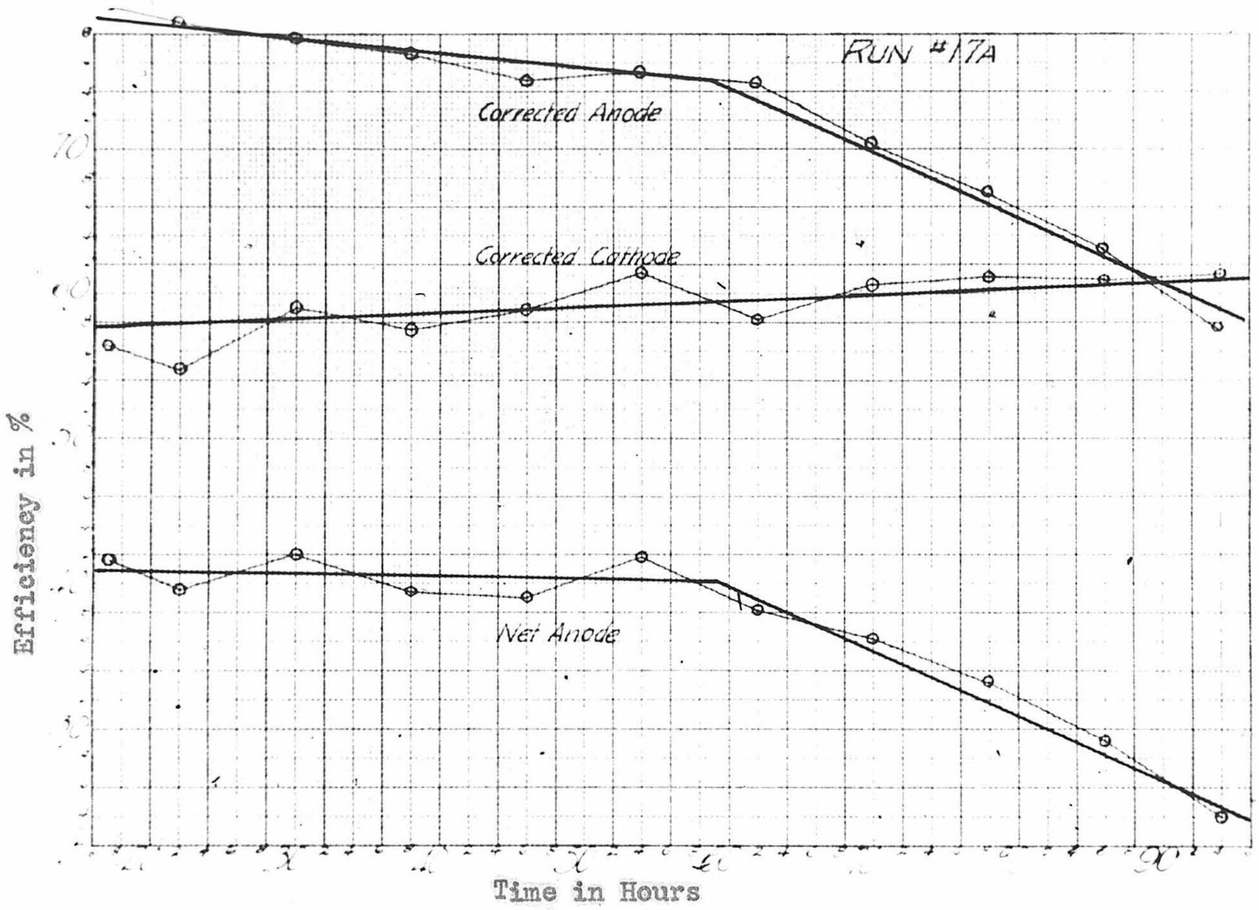

RUN #17A
Corrected Anode
Corrected Cathode
Net Anode
Efficiency in %
70
60
50
40
30
20
30
40
50
60
70
80
90
Time in Hours

Fig. 17

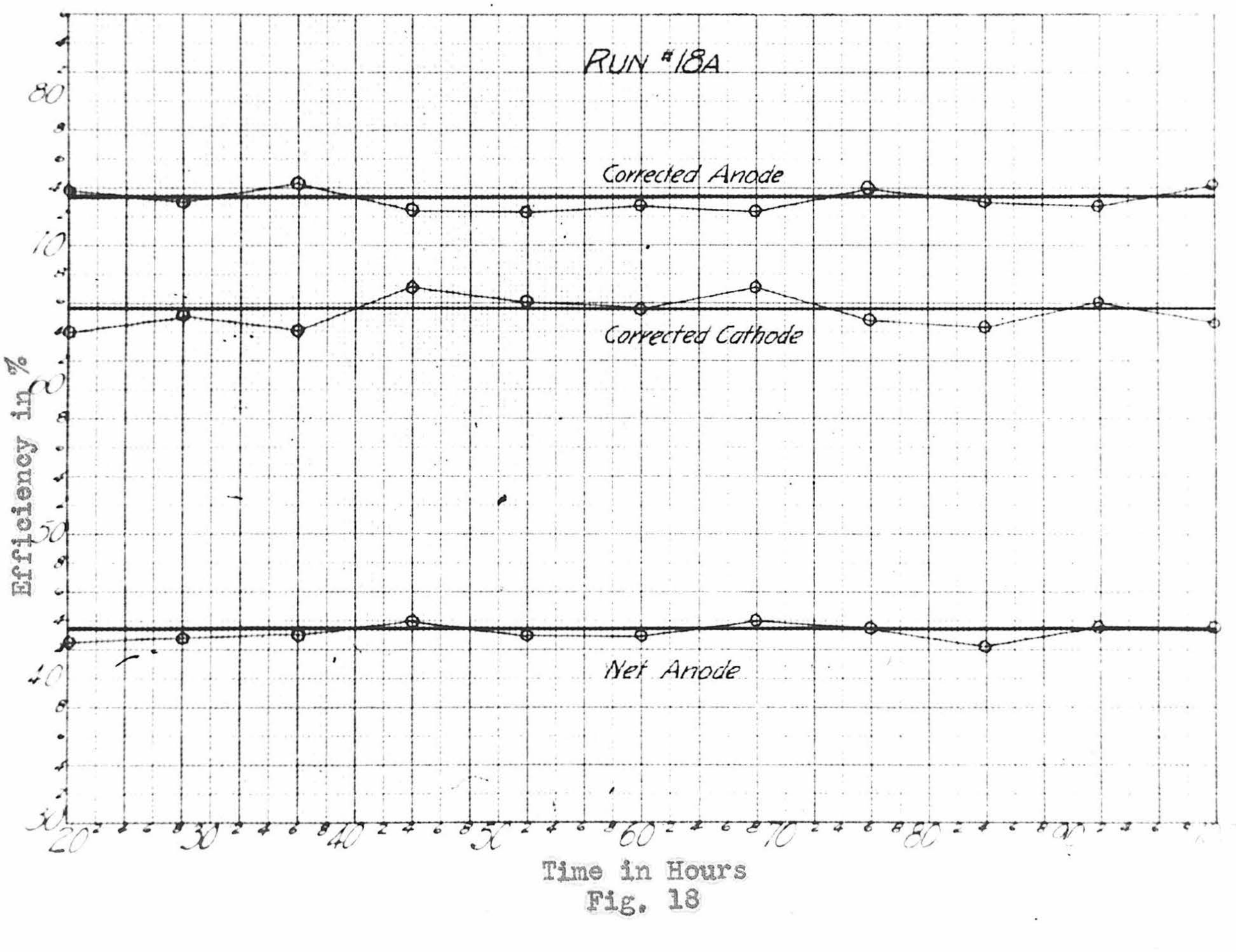

RUN #18A
Corrected Anode
Corrected Cathode
Net Anode
Efficiency in %
80
70
60
50
40
30
20
30
40
50
60
70
80
90
Time in Hours

Fig. 18

It was considered desirable to investigate the effect of changes in the ferric iron concentration in the same manner that the ferrous iron concentration had been investigated. The other conditions being the same as given for the series on ferrous iron concentration effect, i.e., copper concentration 33 grams per liter, sulfuric acid concentration 33 grams per liter, temperature 40°C, the ferrous iron concentration was fixed at 16.3 grams per liter for this series.

Run 18A was made with ferric iron concentration at 2.75 grams per liter, in comparison with 5.5 grams per liter in Run 12A. Both the anode efficiency and the cathode efficiency were increased in comparison with the values obtained in Run 12A. See Fig. 18.

Run 19A was made with ferric iron concentration at 8.55 grams per liter. As expected, the net anode efficiency was lower than in Run 18A, but unexpectedly, it was higher than in Run 12A. The corrected anode efficiency in this run was even higher than in Run 18A. This was even more unexpected but seems to indicate that the anode is more efficient in converting ferrous iron to ferric iron in the presence of higher concentrations of ferric iron. This is the reverse of what would be expected from the mass action law but agrees with the anomalous effect of ferrous iron noted above. For results of Run 19A see Fig. 19; and for comparison with results of Runs 18A and 12A see Fig. 20. The cathode efficiency in Run 19A was lower than in either Run 18A or 12A, as expected.

It is felt that more work on the effect of ferric iron on the anode efficiency should be done.

At the suggestion of Dr. Ricketts the effect of the presence of aluminum sulfate on the efficiencies was now undertaken. Run 20A was

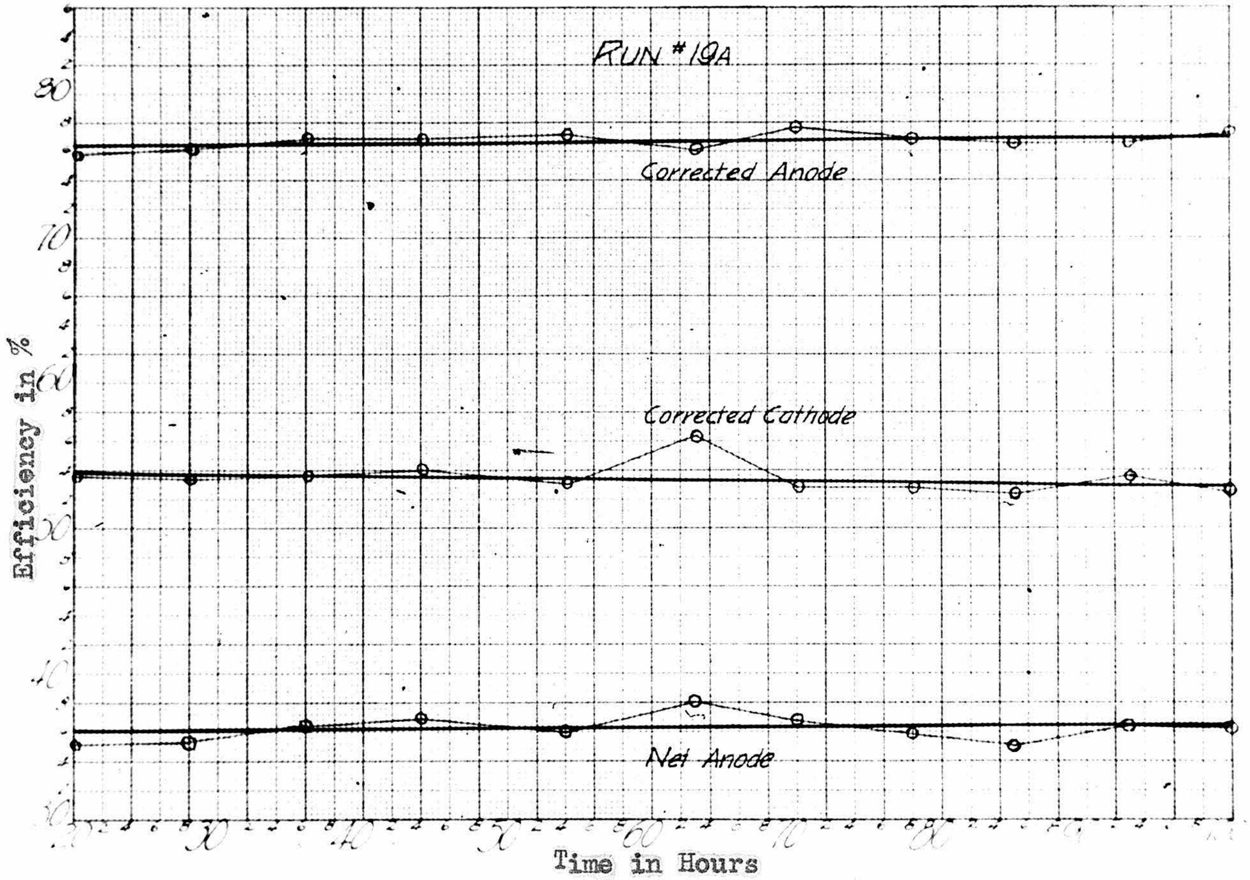

RUN #19A
Efficiency in %
80
70
60
50
40
30
Corrected Anode
Corrected Cathode
Net Anode
20
30
40
50
60
70
80
90
Time in Hours

Fig. 19

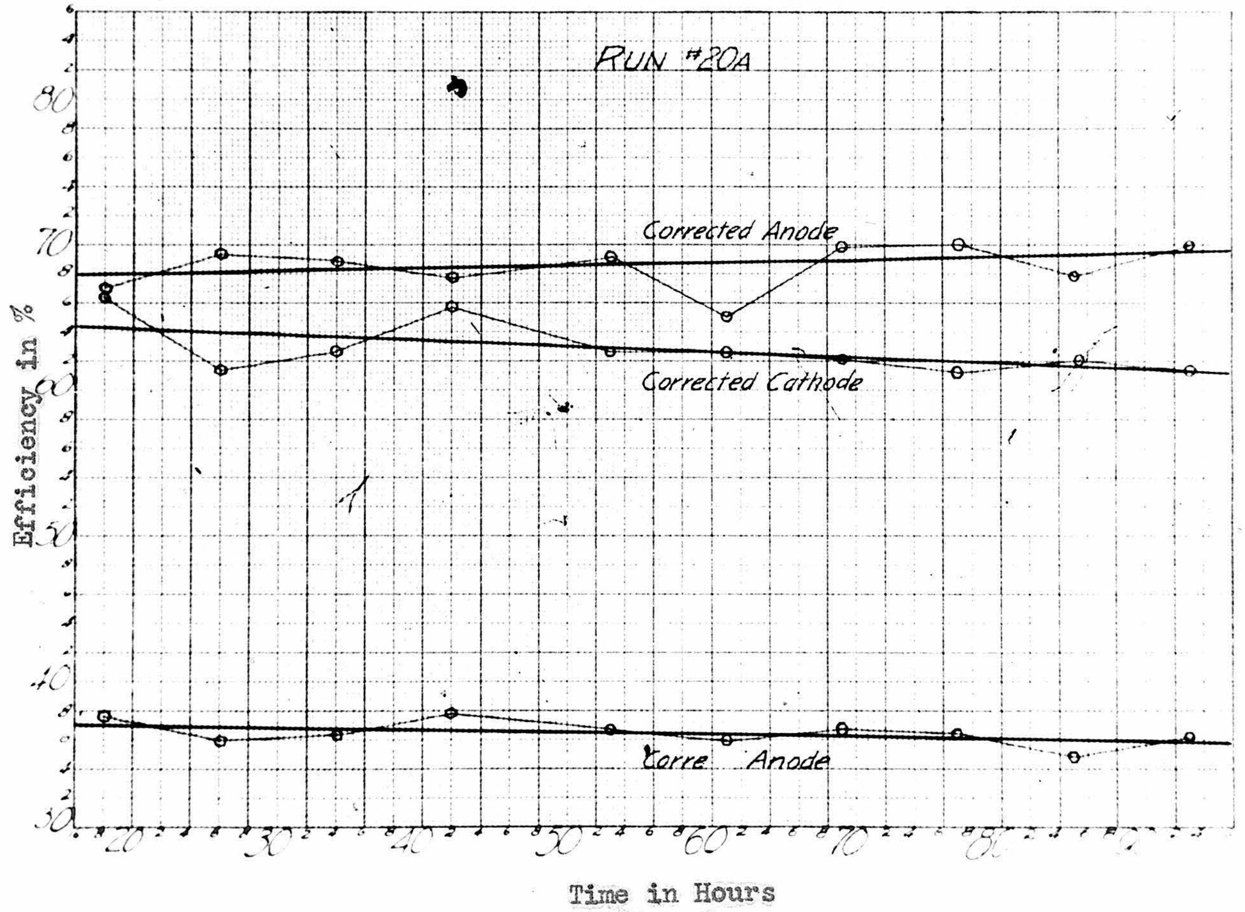

RUN #20A
Efficiency in %
80
70
60
50
40
30
Corrected Anode
Corrected Cathode
Corre Anode
20
30
40
50
60
70
80
90
Time in Hours

Fig. 21

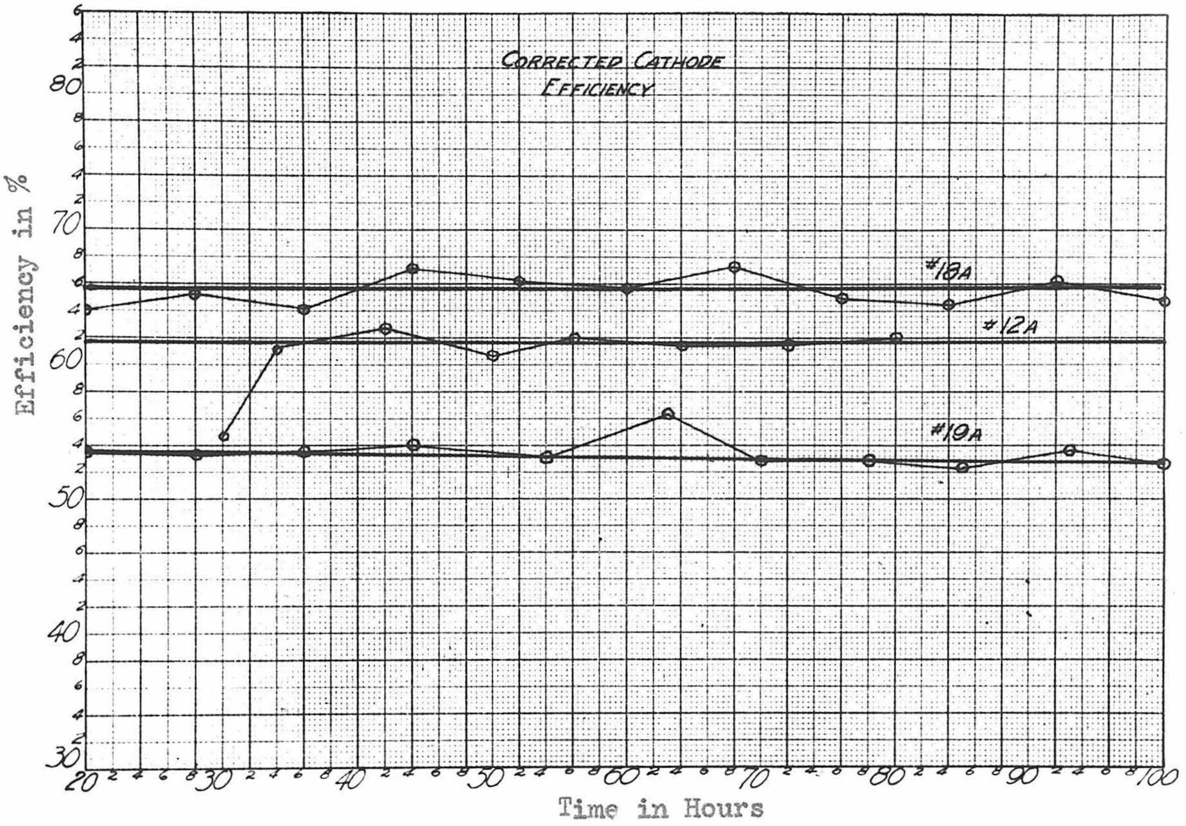


Fig. 20a

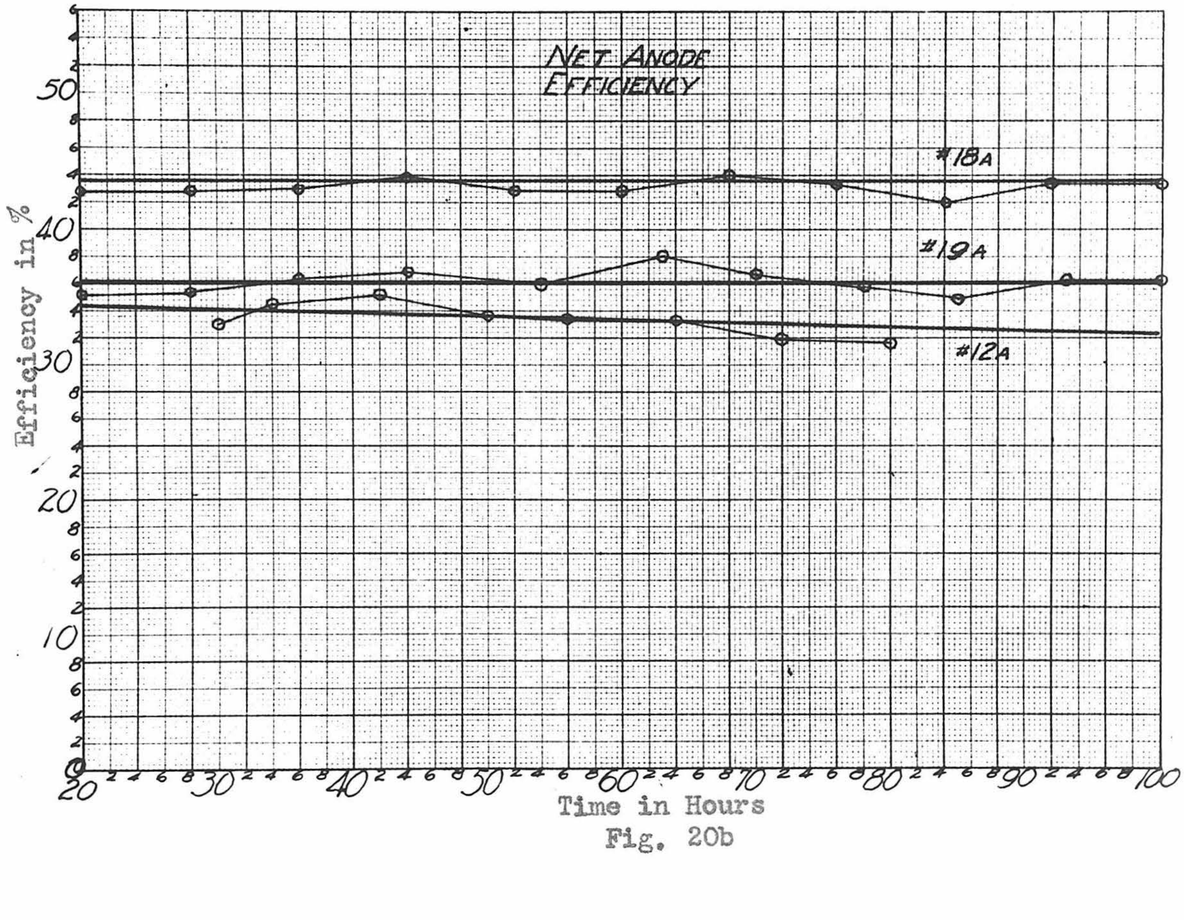


Fig. 20b

made with sufficient aluminum sulfate added to bring the alumina content of the solution to 14.9 grams per liter while the other conditions were the same as in Run 12A. The cathode efficiency was almost exactly the same as in Run 12A, while both the net and corrected anode efficiencies were noticeably higher. See Figure 21 for results of Run 20A and Figure 22 for comparison with Run 12A.

Run 21A, in which the alumina content was raised to 27.5 grams per liter was made next. Due to an error in analysis for the copper in the original solution, the copper content was too high by approximately 5 grams per liter, being 39 grams per liter. The combined effect of the two simultaneous variations was, however, of some interest so the results are included here. The cathode efficiency was increased remarkably, attaining a value of 75.4% in comparison with the figure 62.8% of the previous run. The net anode efficiency was slightly decreased and the corrected anode efficiency, in consequence of the high cathode figure, was reduced to 55.2%. See Fig.23.

In Run 22A, the alumina content was 24.0 grams per liter. The cathode efficiency was some 10% higher than in Run 12A, q.v., while the net anode efficiency was slightly lower than in Run 20A, although still above the figure attained in the absence of aluminum. The corrected anode efficiency was essentially equal to that maintained under conditions of Run 20A. See Figure 24.

In Run 23A an attempt was made to duplicate the condition of Run 20A. It was hoped to confirm the fact indicated in that run that concentration of aluminum approximating 15 grams per liter had no appreciable effect on the cathode efficiency. In this run, however,

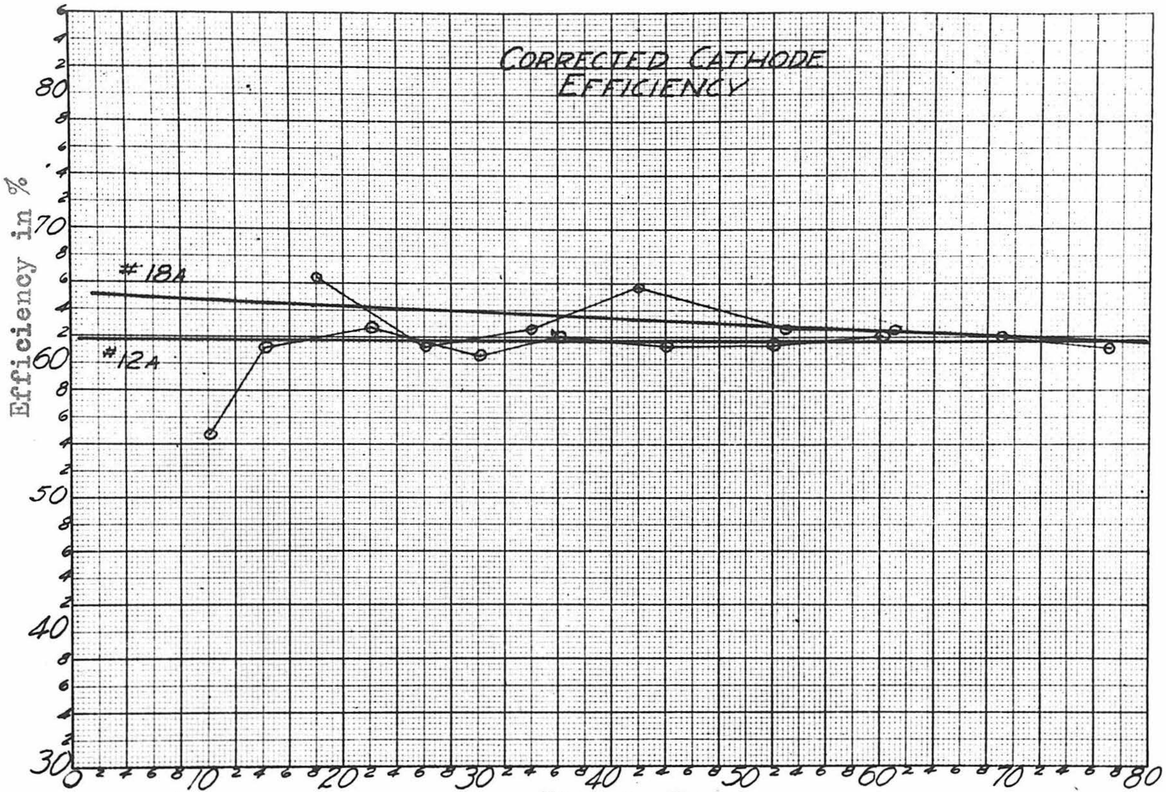


Fig. 22a

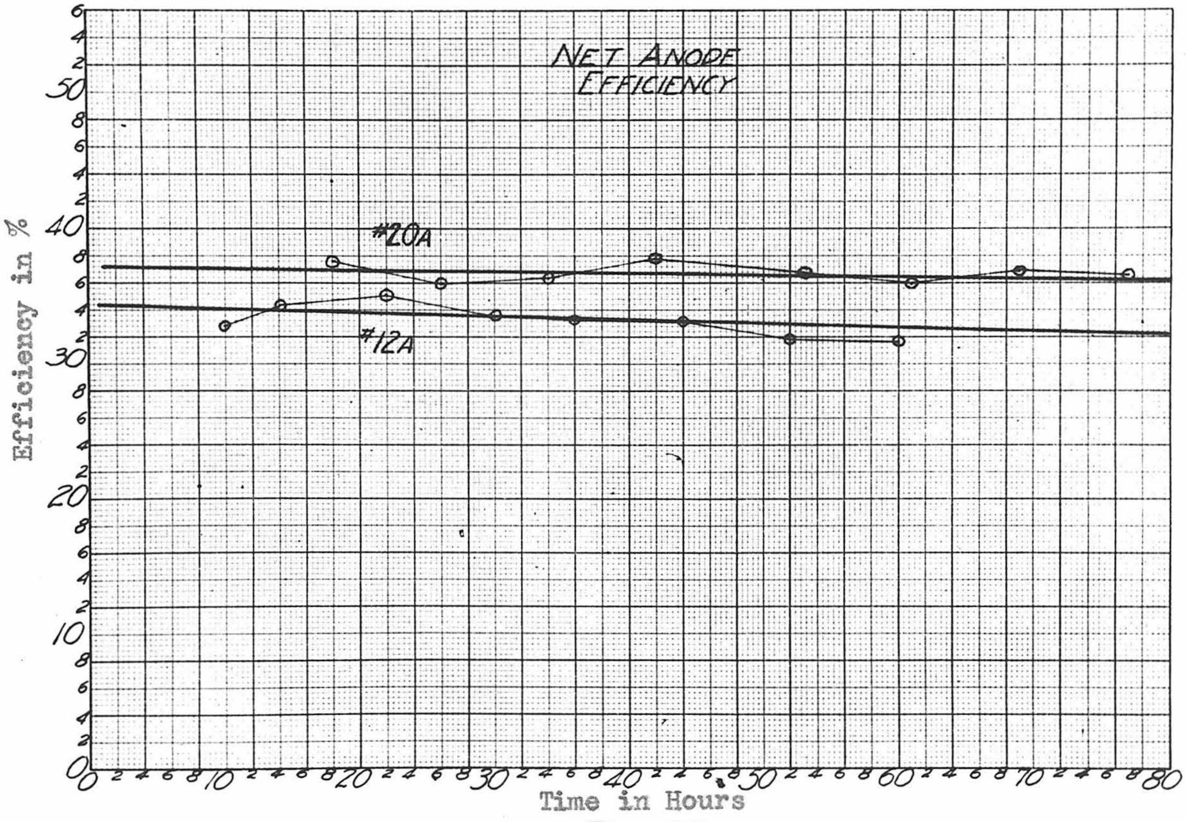


Fig. 22b

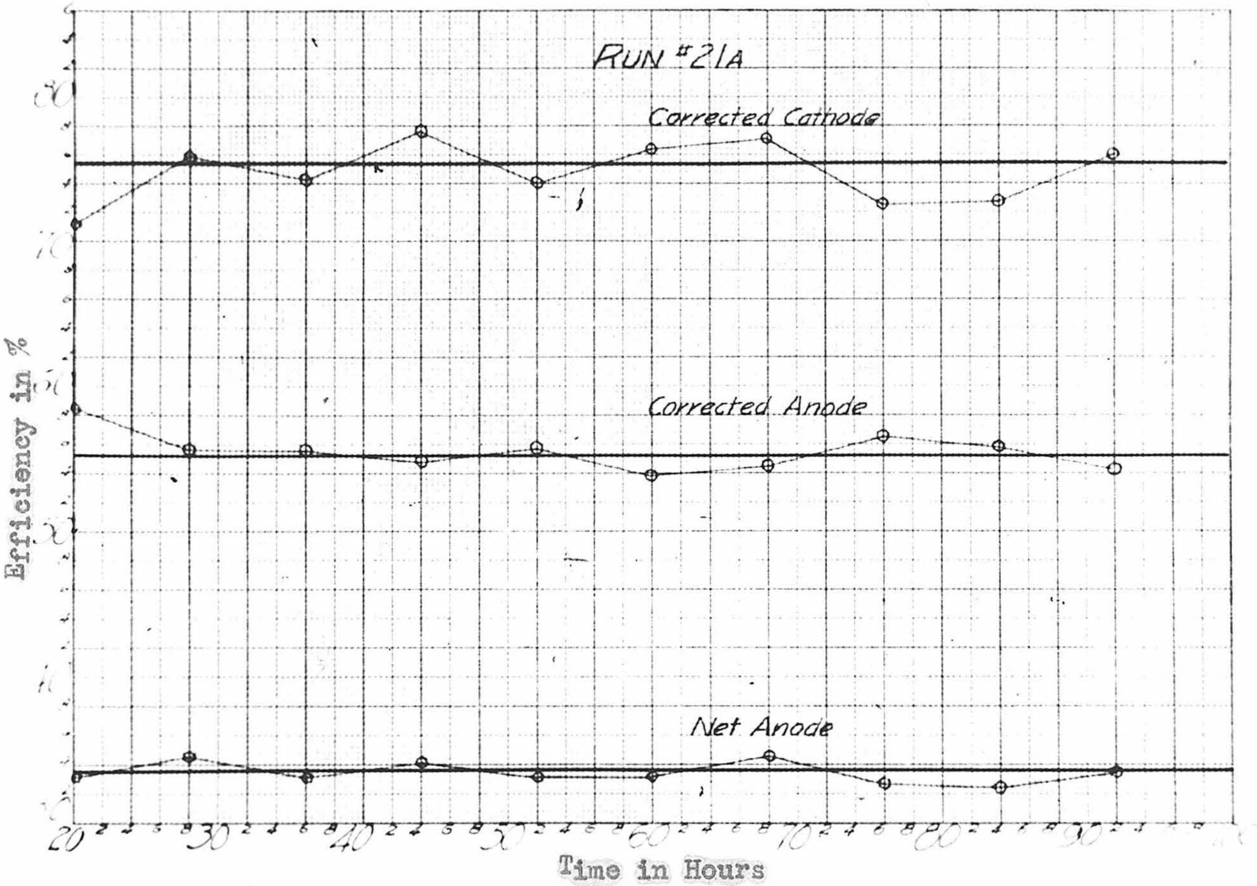

RUN #21A
Corrected Cathode
Corrected Anode
Net Anode
Efficiency in %
80
70
60
50
40
30
20
30
40
50
60
70
80
90
100
Time in Hours

Fig. 23

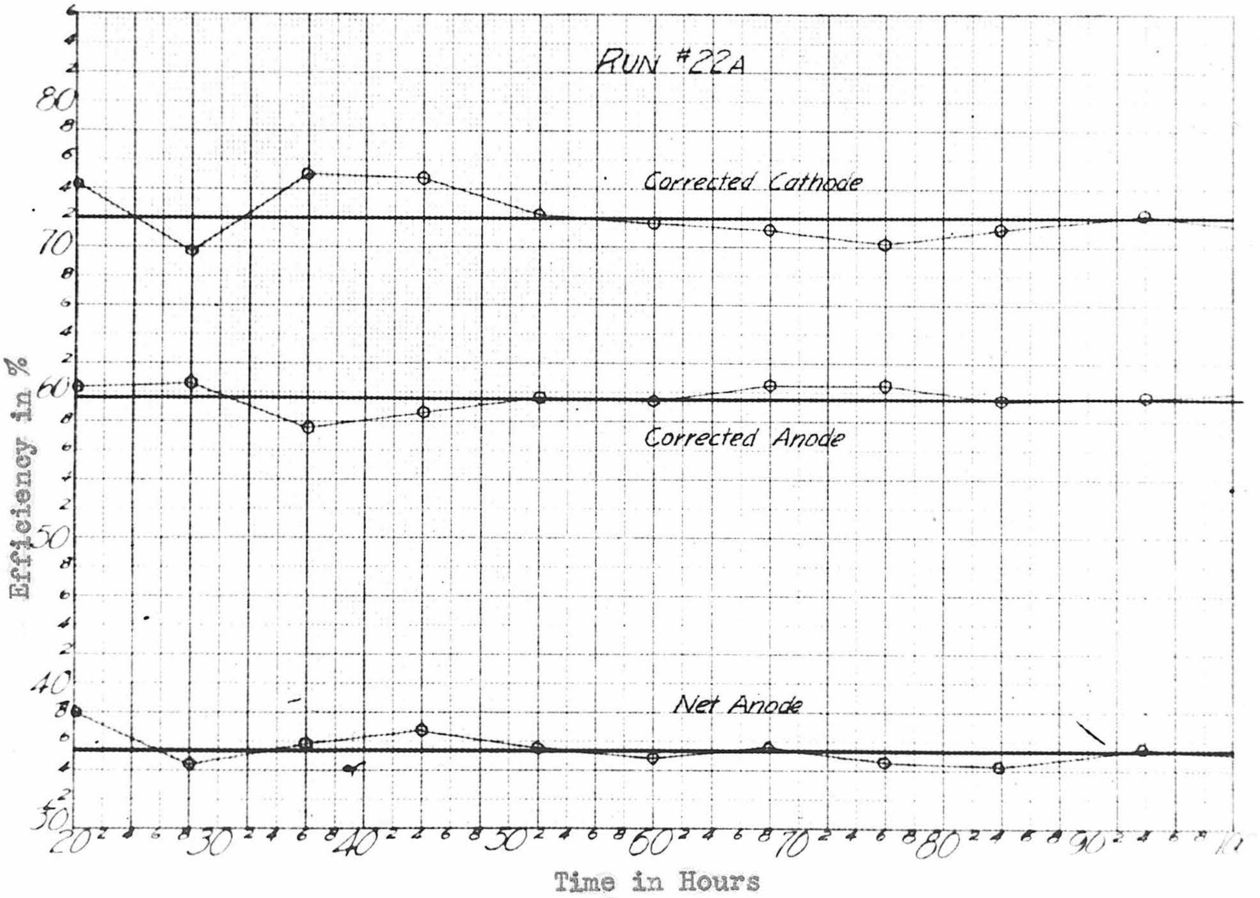

RUN #22A
Corrected Cathode
Corrected Anode
Net Anode
Efficiency in %
80
70
60
50
40
30
20
30
40
50
60
70
80
90
100
Time in Hours

Fig. 24

both the corrected cathode efficiency and the net anode efficiency were found to be some 3.5% higher than under the essentially identical conditions of Run 20A. See Figure 25.

In Run 24A the aluminum content was reduced from the immediately preceding runs to a value of 9.8 grams per liter, expressed as Al_2O_3. The corrected anode efficiency remained approximately the same as in the three runs, 20A, 22A, and 23A. The net anode efficiency was some 3% higher than that attained in the absence of aluminum. The cathode efficiency was approximately the same as that of Run 12A, i.e. in the absence of aluminum. See Figure 26.

Run 25A was made next with aluminum concentration 19.8 grams per liter. In this case the corrected anode efficiency was found to be much lower than that in either Run 22A, where aluminum concentration was 24.0 grams per liter or Runs 20A and 23A in which the aluminum concentration was ca. 15 grams per liter. The net anode efficiency was also found to be appreciably lower than had been attained in any other run in which the liquor contained aluminum. (With the exception of Run 21A, in which the copper concentration was abnormally high.) The corrected cathode efficiency was, however, raised considerably, the value attained being in good agreement with the results of the previous runs. See Figure 27.

A consideration of the variation in the several calculated efficiencies with variations in the aluminum content of the solution showed so many inexplicable irregularities and a clear failure of reproducibility in the case of Run 20A and 23A that it was felt that some uncontrolled variable must be present. The most likely thing appeared

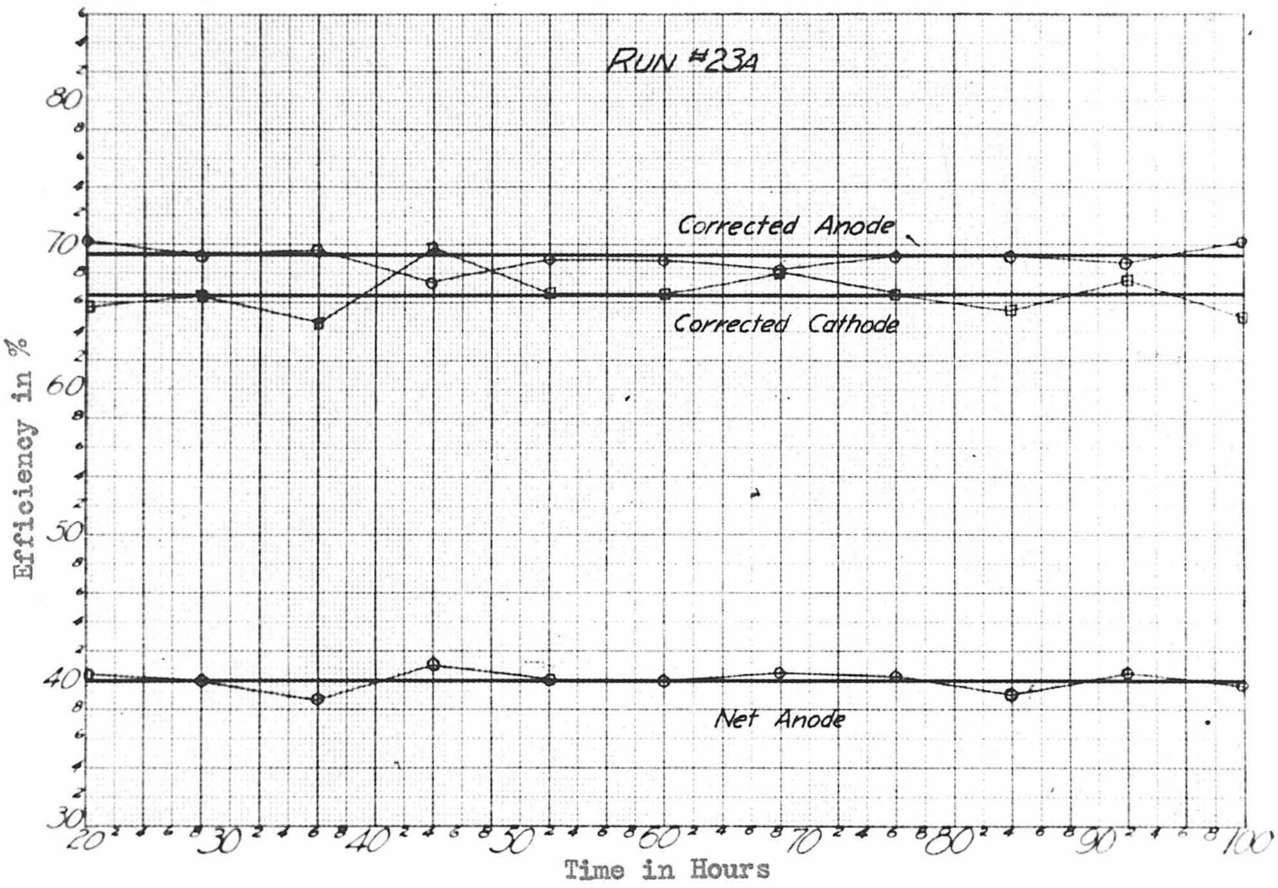

RUN #23A
Corrected Anode
Corrected Cathode
Net Anode
Efficiency in %
80
70
60
50
40
30
20
30
40
50
60
70
80
90
100
Time in Hours

Fig. 25

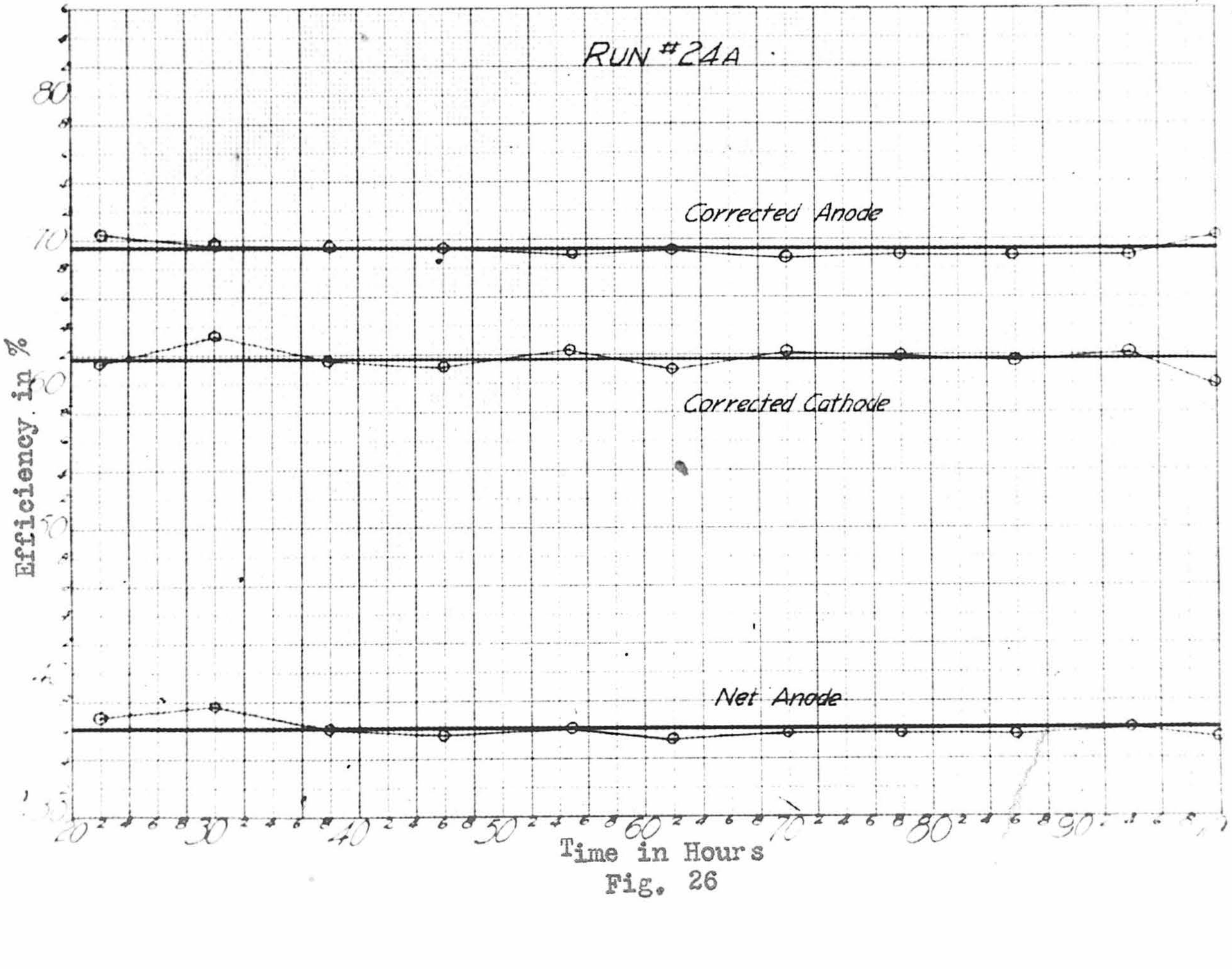

RUN #24A
Corrected Anode
Corrected Cathode
Net Anode
Efficiency in %
80
70
60
50
20
30
40
50
60
70
80
90
Time in Hours

Fig. 26

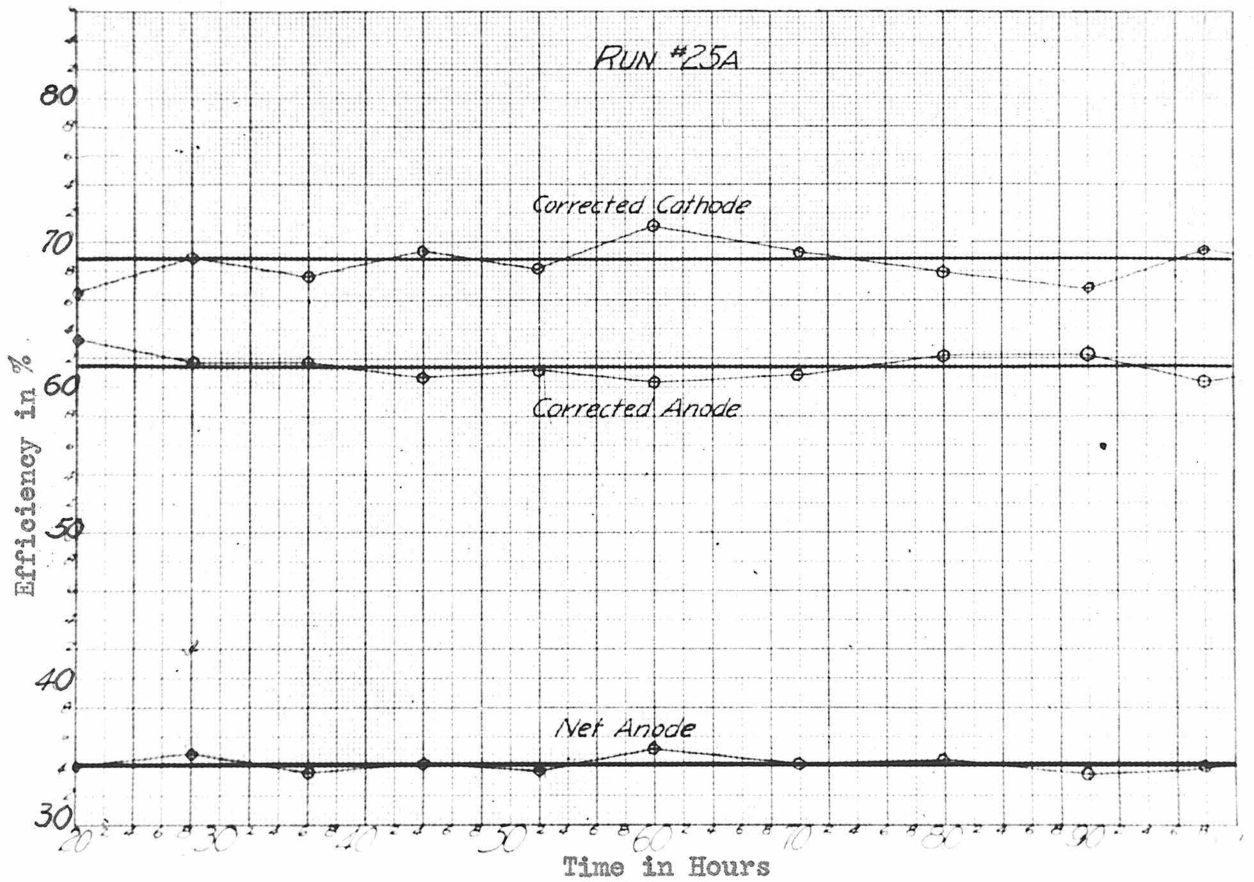

RUN #25A
Corrected Cathode
Corrected Anode
Net Anode
Efficiency in %
80
70
60
50
40
30
20
30
40
50
60
70
80
90
Time in Hours

Fig. 27

to be the hydrogen ion concentration. While the total H_2SO_4 was maintained constant through this series of runs, the hydrolysis of aluminum sulfate is considerable, and nothing can be said concerning the activity of hydrogen ion in solutions as concentrated and as complex as those under consideration so it was felt necessary to determine the hydrogen ion activity experimentally and to fix it at the value obtaining in the solution before the additions of the aluminum sulfate.

The only method of pH control which offered any promise was the use of the glass electrode. Considerable difficulty was experienced in obtaining reproducible results in the pH range which is of interest in this problem and the probable error of measurement of the E.M.F. of the cell was so great using apparatus suited to the conditions of vibration existing in the laboratory that no results were obtained with electrodes blown from "Corning O 15" glass.

A glass electrode was purchased from Leeds and Northrup, however, which was found to be satisfactory in its response. The following table shows results obtained by the use of the electrode. The solutions used were HCl, the values for a_{H^+} were those given by Lewis and Randall (Thermodynamics, page 336).

TABLE I

Conc. HCl N	A_{H^+}	pH	E M F v
1.875	1.95	-0.29	0.441
0.750	0.59	+0.23	0.430
0.375	0.265	+0.58	0.412
0.1875	0.15	+0.82	0.398
0.094	0.093	+1.03	0.389

The shape of the curve showing the relationship between pH and E M F indicates that linear interpolation is reasonably accurate up to the values of pH approximately 0.2, and the sensitivity of the cell is sufficient to insure reproducing the pH as between two solutions with less than 0.1 pH error. With this technique it is proposed to repeat the runs dealing with the effect of aluminum, with pH held constant at the value obtaining in solutions to which no aluminum has been added.

IV - Conclusion

As a result of the investigations here reported, the following factors have been found to affect the efficiency of operation of electrolytic cells fed with leaching solutions comparatively rich in iron:-

1. Temperature,
2. Concentration of ferrous iron,
3. Concentration of ferric iron,
4. Concentration of copper,
5. Concentration of sulfuric acid,
6. Concentration of aluminum,
7. Rate of solution flow,
8. Current density,
9. Degree of agitation,
10. Condition of surface of anode,
11. Condition of surface of cathode.

A technique has been developed and apparatus devised making it possible to vary each of these variables independently and thus follow the effect of each individually on the several calculated efficiencies. Of the eleven variables listed above, three have been systematically investigated: temperature, concentration of ferrous iron, and concentration of aluminum. Some work has also been done on the effect of variation of the concentration of ferric iron.

The effect of temperature variation on the various efficiencies is shown in the following table. The values given are taken from the curves showing the results of Runs 5A, 6A and 7A, being the values obtaining after sixty hours of operation. The concentration of copper was 33 grams per liter, the concentration of ferrous iron 10.5 grams per liter, the concentration of ferric iron 5.5 grams per liter, concentration of sulfuric acid 33 grams per liter, and no aluminum was present.

TABLE II

Run	Temperature °C	Efficiency Corrected Cathode	Corrected Anode	Net Anode
6A	30	68	54	24
7A	40	62	56	23
8A	50	52	67	25

It should be noted also that, while an increase of 10° from 30° to 40°C results in a 6% decrease in the corrected cathode efficiency and a 10° increase from 40° to 50°C results in a further 10% drop, these figures are referred to separate standards and the theoretical efficiency also decreases with increasing temperature so that the net loss in copper actually produced is greater than these figures indicate. Furthermore, this effect is also reflected in the corrected anode efficiencies. Very little change is noted in the net anode efficiency as a result of temperature variation, so the amount of ferric iron actually gained in the electrolysis is practically independent of the temperature.

The effect of variation in ferrous iron concentration is shown in the following table. The values given are obtained in the same manner as described for the previous table. All runs were made at 40°C, and the concentrations of the various substances were as previously given.

TABLE III

Run	Conc. of Ferrous Iron g/ℓ	Efficiency in % Corrected Cathode	Corrected Anode	Net Anode
7A	10.1	62	56	23
12A	16.3	62	65	32
17A	19.2 (60 hrs)	59.5	75	40
17A	19.2 (95 hrs)	61	58	4
13A	19.3	53	79.5	38
10A	20.6	74	32	9
15A	23.0	75	33	9
16A	23.1	74	30	6
11A	24.6	75.5	29	8

These results show a very interesting phenomenon, namely that increasing the concentration of ferrous iron is effective in raising the net anode efficiency, i.e., in actually producing more ferric iron at the anode, until a certain critical concentration is reached. Beyond this critical concentration, increase in the concentration of ferrous iron apparently inhibits the reaction

$$Fe^{++} = Fe^{+++} + \ominus$$

which presumably takes place at the anode surface. A graphical representation of this is given in Figure 28, where the variation of net anode efficiency and corrected cathode efficiency with concentration are plotted.

No theoretical explanation of this phenomenon is advanced and it is felt that further work should be carried out, with solutions containing the impurities ordinarily found in commercial practice, especially aluminum.

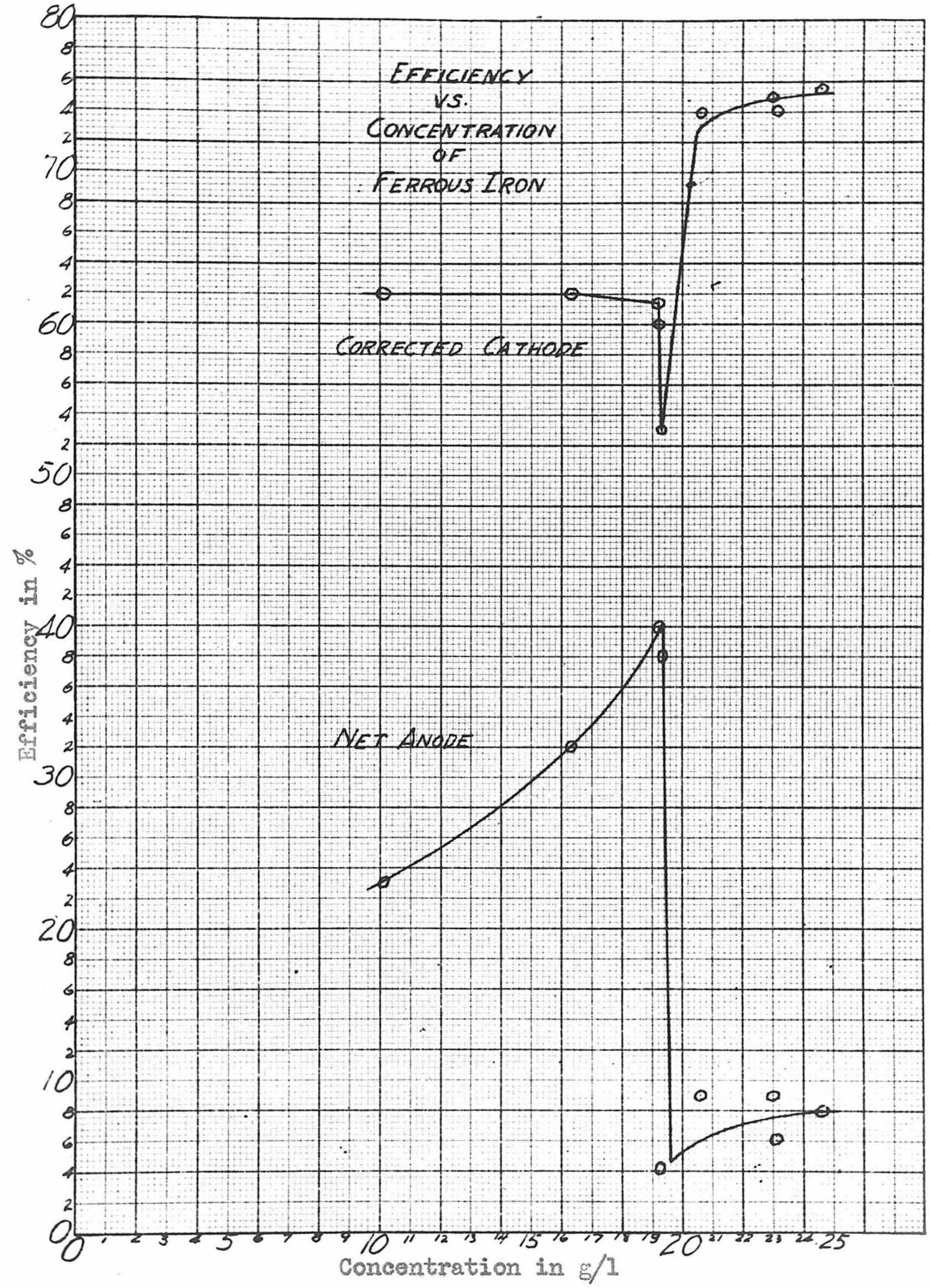

EFFICIENCY VS. CONCENTRATION OF FERROUS IRON
CORRECTED CATHODE
NET ANODE
Efficiency in %
Concentration in g/l
0
10
20
30
40
50
60
70
80
0
5
10
15
20
25

Fig. 28

An indication of the effect of variation in ferric iron concentration on the calculated efficiencies is given in the following table. The results do not represent a systematic investigation of the effect of variations in ferric iron concentration but are given here as a record of preliminary work. No further work was carried out on this phase of the problem because the effect of variations in aluminum concentration was next undertaken at the request of Dr. L.D.Ricketts. Temperature was 40°C in these runs, the concentration of ferrous iron was 16.3 grams per liter. All other concentrations were as noted previuusly.

TABLE IV

Run	Conc. of Ferrous Iron g/ℓ	Efficiency Corrected Cathode	Efficiency Corrected Anode	Efficiency Net Anode
18A	2.86	65.6	75.4	43.5
12A	5.31	62.0	65.0	32.0
19A	8.55	53.5	76.5	36.0

Curves showing the relations between the corrected cathode and net anode efficiencies and concentration of ferric iron are given in Figure 29.

The effect of variations in the concentration of aluminum on the various efficiencies is shown in the following table. The values given are obtained from the experimental curves as previously described. Temperature of all runs was 40°C, ferrous iron concentration 16.3 grams per liter, ferric iron concentration 5.3 grams per liter and other conditions as previousl̶y noted.

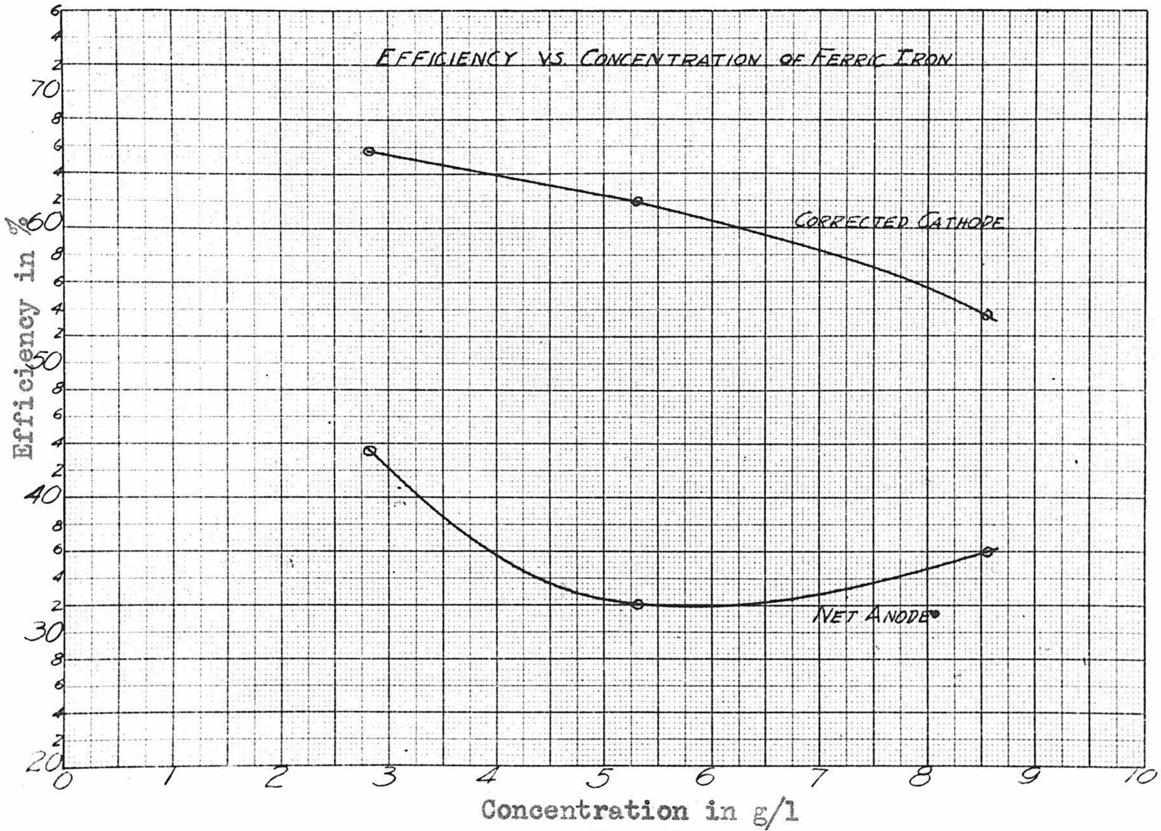

EFFICIENCY VS. CONCENTRATION OF FERRIC IRON
CORRECTED CATHODE
NET ANODE
Efficiency in %
Concentration in g/l
20
30
40
50
60
70
0
1
2
3
4
5
6
7
8
9
10

Fig. 29

TABLE V

Run	Conc. of Aluminum*	Efficiency Corrected Cathode	Corrected Anode	Net Anode
12A	0	62	65	32
24A	9.8	61.8	69.5	36.0
20A	14.9	62.0	69.0	36.0
23A	15.1	66.4	69.2	40.0
25A	19.8	69.0	61.5	34.0
22A	24.0	72.0	59.5	35.2
21A	27.5$^{\Delta}$	75.5	55	33.5

* Expressed as Al_2O_3

Δ Concentration of copper higher than normal

Curves showing the relation between concentration of aluminum and the corrected cathode and net anode efficiencies are given in Figure 30.

The discrepancy between Runs 20A and 23A makes it somewhat difficult to establish a lower limit at which the effect of aluminum becomes appreciable on the cathode efficiency but apparently the aluminum has little or no effect on the cathode efficiency unless it is present at concentrations greater than 10 grams per liter. Above this concentration, increase of the aluminum concentration is accompanied by a very definite increase in the cathode efficiency and this effect continues thru the upper limit of the range of concentrations investigated.

In contrast the net anode efficiency achieves a maximum value in the neighborhood of 15 grams per liter of Al_2O_3 and at higher concentrations falls back to approximately the value attained in the absence of aluminum. The corrected anode efficiency consequently goes thru a rather flat maximum between 10 and 15 grams per liter of alumina and then falls off sharply at higher concentrations.

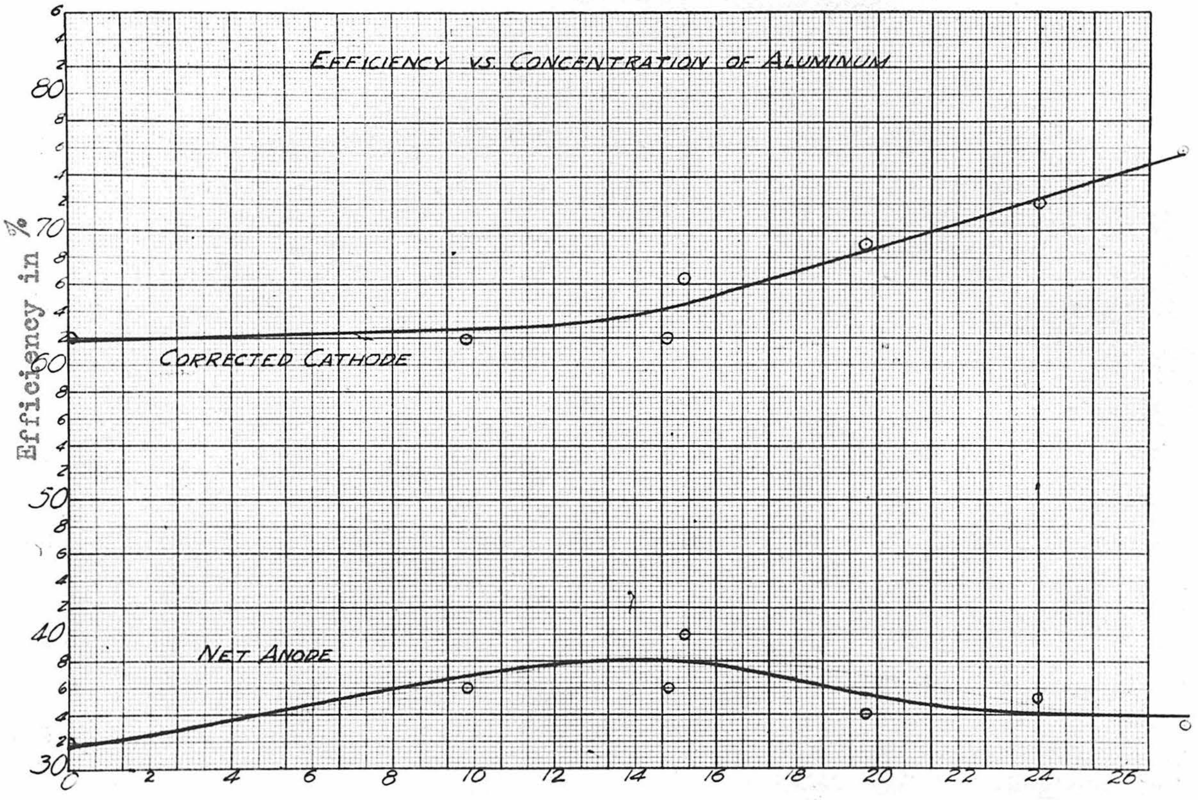

EFFICIENCY VS. CONCENTRATION OF ALUMINUM
Efficiency in %
CORRECTED CATHODE
NET ANODE
30
40
50
60
70
80
0
2
4
6
8
10
12
14
16
18
20
22
24
26
Concentration in g/l

Fig. 30

It is felt that the general trends indicated by these results are real but that too much importance should not be ascribed to small variations, until the results of the series of runs at constant pH are available.

ACKNOWLEDGEMENT

This work has been made possible by funds contributed by the Inspiration Consolidated Copper Company.

The author wishes to express his indebtedness to Dr. W.N.Lacey, under whose supervision the work has been done, and to thank Dr. L.D.Ricketts for his interest and cooperation thruout the entire project.

APPENDIX A

Sample of Calculation

The following calculation will serve to illustrate the method by which the points plotted on the curves representing the results of a run were arrived at.

The point chosen is that corresponding to 60 hours operation in Run 22A.

Analysis of Solution Fed to Cell.

Fe^{++} (Titration vs. $KMnO_4$)

0.00 - 16.31 = 16.31 x 1.025 = 16.75 g/ℓ
16.40 - 32.71 = 16.31

Total Iron (Solution reduced with metallic aluminum and titrated with $KMnO_4$)

0.00 - 21.30 = 21.30 = 21.87 g/ℓ
21.29 - 42.58 = 21.29

Copper (Electrolytic deposition from 10 cc. sample)

9.8819 - 9.5284 = 0.3535 = 35.35 g/ℓ
9.7971 - 9.4437 = 0.3534

Aluminum (Precipitation with NH_4OH of total iron plus aluminum. Aluminum by difference)

20.9484 - 20.3924 = 0.5560 Al_2O_3 = 24.0 g/ℓ
24.6181 - 24.0569 = 0.5512

Analysis of Sample

(Sample collected over 8-hour period ending at 60 hours)

Fe^{++}

0.00 - 9.14 = 9.14 = 9.42 g/ℓ

9.14 - 18.30 = 9.16

Total Iron

0.15 - 21.70 = 21.55 = 22.15 g/ℓ

21.70 - 43.25 = 21.55

Copper

9.7242 - 9.4437 = 0.2805 = 28.05 g/ℓ

9.8089 - 9.5284 = 0.2805

Volume of Sample = 2320 cc.

Correction for evaporation

$$Fe^{++} \text{ corrected} = 9.42 \times \frac{21.87}{22.15} = 9.32 \text{ g/}\ell$$

$$Cu^{++} \text{ corrected} = 28.05 \times \frac{21.87}{22.15} = 27.75 \text{ g/}\ell$$

$$\text{Volume of sample corrected} = 2320 \times \frac{22.15}{21.87} = 2340 \text{ cc.}$$

Theoretical weight of copper deposited in 8 hours at 3 amperes and 87% (due to presence of O_2) efficiency is

$$8 \times \frac{3 \times 3600}{96{,}500} \times 31.8 \times 0.87 = 24.80 \text{ g.}$$

Theoretical weight of Fe^{++} converted to Fe^{+++} in the same time under the same conditions

$$8 \times \frac{3 \times 3600}{96{,}500} \times 55.84 = 50.00 \text{ g.}$$

Actual weight of copper deposited = (35.35 - 27.75) x 2.34 = 17.77 g.

Actual net weight of Fe^{++} converted to Fe^{+++} =

(16.75 - 9.32) x 2.34 = 17.37 g.

Copper lost by dissolving according to the reaction

$$Cu + 2Fe^{+++} = Cu^{++} + 2Fe^{++}$$

is therefore = 24.80 - 17.77 = 7.03 g.

Which is equivalent to 7.03 x 1.757 = 12.35 g. Fe^{+++} lost.

So total Fe^{+++} made = 17.37 + 12.35 = 29.72 g.

Corrected Cathode Efficiency = $\frac{17.77}{24.80}$ = 71.6%

Corrected Anode Efficiency = $\frac{29.72}{50.00}$ = 59.4%

Net Anode Efficiency = $\frac{17.37}{50.00}$ = 34.7%