Phys.
Thesis card

THE ELECTRODEPOSITION OF IRON
FROM
PERCHLORATE SOLUTIONS

THESIS

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INTRODUCTION

A great many methods have been tried for the electrolytic deposition of iron, some of which have proved successful and are in commercial operation at the present time, while others have never passed beyond the experimental stage.

However, as will be seen in the following pages, none of these methods is very satisfactory. For this reason, it seemed reasonable to suspect that some new method might yield better results. With this in view, this investigation was undertaken for the purpose of determining, if possible, whether iron could be successfully deposited from perchlorate solutions. The use of perchlorates was suggested by the fact that excellent deposits of lead are obtained from lead perchlorate and also because Dr. Walker stated in his thesis that ferrous perchlorate is unusually stable towards oxidation.

REVIEW OF PREVIOUS WORK

An exhaustive review of the literature shows that no work has ever been attempted for using salts of perchloric acid for the electrolytic deposition of iron. However, a digest of the other methods for plating out iron is both interesting and instructive as many of the difficulties to be overcome are common to all methods. For this reason, it was thought advisable to review the various methods for producing electrolytic iron.

The Burgess Process.

The best known and most widely used method is that developed by Burgess.(1) For electrolyte he used a neutral solution of ferrous sulphate and ammonium sulphate. The exact amounts are not given. Wrought iron or soft steel was used as anodes, and thin sheet iron served as the cathode starting sheets. A current density of 6 - 10 amperes per square foot (0.65 - 1.1 amperes per square decimeter) was used. The current efficiency was almost 100%. The iron obtained was exceedingly pure, the total impureties amounting to only 0.10 - 0.03% or even less. In common with all electrolytic, it did however contain considerable quantities of occluded or combined hydrogen. This made the iron very hard and brittle. If the iron were heated to 600 - 700 degrees Cent., all this hydrogen was driven off and the resultant iron became soft and ductile like the best Swedish iron. The iron first deposited was smooth but as the electrolysis progressed, the nodular structure increased and after about four weeks of steady electrolysis with a deposit almost one inch thick, the nodules had become so large that the cathodes had to be removed. Stirring reduced concentration changes and produced smoother deposits. It was found necessary to boil the electrolytes to remove dissolved gases. Otherwise pits were formed on the cathode due to the gas bubbles insulating small areas.

For several years, Burgess(2) carried on the deposition of iron on a semi-commercial scale. This time he used an electrolyte containing 40 grams of iron per liter in the form of ferrous sulphate and 40 grams of ammonium chloride. By maintaining the solution in proper condition, it was possible to conduct a continuous refining operation for many months at a cathodic current density of 6 - 10 amperes per square foot and with a current efficiency of very nearly 100 percent. The potential difference was about one volt. From these values he computed the power cost of iron refining as $5.00 per ton with power at 1/2¢ per kilowatt hour.

Soon after Burgess and Hambeuchen published their results, Neuburger(3) wrote an article stating that he and Klobukow had succeded in producing solid iron deposits for analytical purposes. They used a solution of crystallized ferrous sulphate. Any acidity was carefully neutralized by ammonia. Oxalic acid and a large amount of ammonium oxalate was then added. The current density used was 1.0 amp. per sq. dm. During the electrolysis a brown precipitate was formed. This was dissolved by the addition of more oxalic acid. They succeeded in obtaining a firm and solid deposit one centimeter thick.

The effect of addition agents on the Burgess process has been extensively studied by Watts and Li.(4) For a basic electrolyte, they chose one of the following composition: 150grams ferrous sulphate and 75 grams ferrous chloride per liter. They first tried the effect of additions of the sulphates of ammonium, sodium, magnesium, and aluminum, both neutral and slightly acidified to prevent the formation of precipitates. In both cases ammonium sulphate was far superior to the others. Then using the basic electrolyte:-

150 grams ferrous sulphate per liter
75 grams " chloride " "
120 grams ammonium sulphate " "

as a starting point, forty-eight different addition agents were tried. The average time of electrolysis was about 150 hours. Some of the addition agents improved the deposit noticeably, some were indifferent and others exerted a distinctly harmful influence on the nature of the deposit. They concluded that the best addition agents to use were:-

6.0 grams ammonium oxalate per liter
or 0.6 gram formin per liter.

With either of the above the deposit was decidedly superior to that of the plain solution.

Other Methods.

A method for making iron sheets and tubes from iron ore is described by Cowper-Coles.(5) and more fully by Palmaer and Brinell.(6) The electrolyte consists of a concentrated solution of ferrous chloride with some cresol-sulphonic acid and iron oxide added. A revolving cathode is used and the electrolysis is carried out near 100 degrees Cent. and with a current density of 7 amperes per sq. dm.. The refined iron contains considerably more impurities than that obtained by Burgess process, and also some occluded electrolyte which is very serious as it impairs the mechanical properties and promotes rusting. Pig iron is used for anodes.

Ramage(7) patented a process for making electrolytic iron in 1911. He proposes to dissolve the ferric iron ore in sulphuric acid and then reduce to ferrous by sulphur dioxide. This necessitates the use of a diaphragm to prevent the reduction of the sulphur dioxide by nascent hydrogen. Later(8) he devised a two cell affair. The electrolysis is carried out in one cell equipped with diaphragm and insoluble anode. After a certain time, the anolyte consisting of ferric iron and free acid is withdrawn and allowed to react,in a seperate tank or cell, with the impure iron to be refined. The resulting ferrous solution is then returned to the electrolysis cell and the operation is repeated.

Fischer(9) claims that he was able to produce ductile electrolytic iron. A highly concentrated mixture of ferrous chloride and some hydroscopic salt as calcium chloride is used as electrolyte. To get the desired ductility the solution must be operated at a very high temperature (100 - 120 deg. Cent.). This also makes it possible to work at very high current density (20 amperes per sq. dm.). Duisberg(10) confirms Fischer's claims and states that iron deposited by this method is free of hydrogen and its hardness is less than that of pure silver or gold.

A very ambitious scheme for making electrolytic iron and sulphuric acid simultaneously was patented by Reed(11) in 1913. He proposes to electrolyze ferrous sulphate using spongy lead as anode. The anode gradually becomes sulphated and is then removed to a separate vessel where the sulphuric acid is recovered. Due to the fact that there is no free acid in the electrolyzing cell, it is claimed that the iron produced is free of hydrogen.

Cowper-Coles(12) patented another method for electrodepositing iron wherein he claims to be able to deposit iron which is not brittle. The electrolyte is a concentrated solution of ferrous sulphate or chloride in which is suspended an iron sponge, made by reducing the ore below the melting point of iron by means of a gas.

Using a boiling electrolyte the current density may run as high as 4.5 amps. per sq. dm. He claims to make finnished articles as sheets and tubes directly from the ores.

Very similar to the above is a process used in France and described by Guillet.(13) Using pig iron as raw material, finished articles as tubes and sheets or iron to be melted are manufactured. A neutral solution of iron salts, charged with iron oxide as depolarizer, is used as electrolyte. the current density is very high. (10 amps. per sq. dm.) Stirring or revolving cathode is resorted to. To expel hydrogen the iron is annealed at 900deg. Cent. It is then soft and ductile and can be readily worked. If the refining is carried out at the current density mentioned above, the yield is about 2 tons per kilowatt year. Using half the current density, the yield is doubled . The best current density to use is therefore determined by the relative cost of power and that of labor and interest on investment.

Probably the most complicated process of all is that patented by Boucher.(14) He uses cast iron as anodes and for electrolyte a mixture of ferrous sulphate and chloride. The mixture is stirred in contact with air in order to form an oxychloride which depolarizes the cathode by reacting with the hydrogen formed there. The electrolyte is continuously circulated and passed into a seperate tank where any ferric salts are reduced by scrap iron. The speed of circulation is proportional to the current density used. The cathode is rotated at a speed proportional to the current density. The temperature is also raised when high current densities are used. The amount of air supplied to form the oxychloride is determined by the concentration of the solution.

This method in common with many of the others described above, has the advantage over the Burgess process of using cast or pig iron or even iron ore as raw material. It should be kept in mind,however,that this advantage is not as material as first thought might indicate. These materials contain considerable impurities which either contaminate the electrolyte, therefore requiring frequent purification and regeneration, or collect at bottom of cell as anode mud, necessitating frequent draining,cleaning and flushing. Moreover, revolving cathodes, stirring devices, regenerating cells and other auxiliary apparatus are required. All these items increase the labor cost very materially. For this reason, especially in the United States, such methods as Burgess' that are designed for fairly pure iron as wrought iron or mild steel, are very probably the cheaper to operate. Besides,the electrolytic iron obtained by using fairly pure anodes is generally purer than the yield from those processes that use crude iron.

Both lead and nickle are deposited with great success from fluosilicate solutions. An attempt to deposit iron from the same solution was made by Kern(15) in 1908. He prepared a solution of ferrous fluosilicate which he used as electrolyte. Sheets of wrought iron served as anodes. The current density was about 2 amps. per sq. dm. During the electrolysis a large amount of silica was precipitated and also collected on the electrodes. The deposit obtained was smooth and solid but contained considerable silica. O. P. Watts also tried this method for plating out iron. He electrolyzed a solution ferrous ammonium fluosilicate for 170 hours at a current density of 1.1 amps. per sq. dm. The deposit was gray streaky and very irregular. At the end the cell was half full of precipitated silica.

An interesting article on alleged allotropic forms of iron was published by Skrabal.(16) He deposited iron from various electrolytes as ferrous sulphate and ferrous chloride, together with ammonium and magnesium sulphate and chloride. No other data concerning the electrolysis are given. The two allotropic forms of deposited iron were called A-iron and B-iron. The A-iron was produced by using an iron anode and working at a low current density and at a low voltage. This form of iron was of a beautiful silver-white color, extremely hard and probably of a crystaline structure. The B-iron was obtained by using a platinum anode and electrolyzing at high current density and high voltage. This form of iron was of a grayish color, less compact and less hard than A-iron. Skrabal obtained in some cases iron which was extremely resistant against chemical action. He attributed the difference in hardness of ordinary electrolytic iron before and after heating as due not entirely to the difference of hydrogen content but also to the presence of two allotropic forms of iron.

Now that the various methods of depositing iron have been reviewed, it seems advisable to devote a little space to properties and uses of electrolytic iron.

Properties and Uses of Electrolytic Iron.

Probably the most noticeable property of electrolytic iron, aside from its purity, is its brittleness. This, however, is often an asset, for such iron may be readily broken up into small pieces for introduction into crucibles when making high grade steels. It may thus be used for such purposes as require the best Swedish iron. Its high purity makes it an ideal substance for making chemical and pharmaceutical preperations requiring very pure iron. The iron first deposited is almost always very smooth. Hence thin tubes and sheets of iron can be manufactured much more uniformly electrolytically than by mechanical means. In fact the thinner the required coating, the smoother and more uniform it will be.

The physical constants of electrolytic iron have been extensively investigated by Yensen.(17) He prepared extremely pure electrolytic iron by double refining and melting in a vacuum furnace. The average maximum permeability was 19,000 for a corresponding $B_{max.}$ of 9,500 gausses. The hysteresis loss of electrolytic iron was only 50% of that of ordinary iron, and its specific resistance was 9.96 microhms per cm. cube. The mechanical properties depend on the heat treatment used, although all heat treatments give an ultimate strength and stress at yield point lower than ordinary iron, but elongation and percent reduction of area is about the same as for ordinary iron.

These results indicate that electrolytic iron may compete with soft iron for electro-magnetic purposes because of its high permeability and low hysteresis loss. A distinct disadvantage, however, as compared with silicon steel, is its high electrical conductivity which will very materially increase the eddy current losses.

DESCRIPTION OF METHOD AND APPARATUS

Preparation of Solutions.

The ferrous perchlorate to be used is not a commercial salt and therefore had to be prepared. Chemically pure perchloric acid was used as the starting point. For preparing the ferruos perchlorate, two methods of preparing this salt were available: namely, neutralization of the acid by (1) metallic iron, or by (2) ferrous hydroxide.

Of these two, the neutralization by pure iron is by far the simpler method, provided the reaction can be made to take place. In order to get a pure salt, it is of course necessary to use pure iron, as any impurities present in the iron are directly introduced into the salt, unless subsequently purified. For this reason two spools of C. P. iron wire were obtained, such as are used for standardization purposes, with analysis of 99.7% Fe. When this wire was put into the acid, there was at first no reaction, probably due to a thin film of oil or grease on the wire. After about fifteen minutes, however, the reaction started and then proceeded violently. Ferrous perchlorate can therefore be prepared by direct neutralization. Nevertheless it was decided to try the second method also.

The general method, used by Mr. Wilson in his thesis for preparing perchlorates by reaction with the hydroxide, was followed. A rather dilute solution of ferruos sulphate was prepared. This was treated with iron wire and sulphuric acid to reduce any ferric salts present. Ferrous hydroxide was then precipitated by adding, in slight excess, a dilute solution of potassium hydroxide, followed by gentle boiling. Potassium hydroxide was used because any potassium salts, adsorbed by the ferrous hydroxide and not removed by washing, would be precipitated by the perchloric acid as insoluble potassium perchlorate. It is therefore only necessary to continue washing until wash-water gives no test for sulphate. In this case however, this general method could not be used because of the frightful oxidation of the ferrous hydroxide. Even on the slightest exposure to air, the ferric salt would form. Hence this method was rejected. The preparation of chromium perchlorate, however, for which Mr. Wilson used this method, was a different case, first because metallic chromium would not dissolve in perchloric acid, and secondly because chromium hydroxide was not oxidized by the air.

As was said before, there was no trouble experienced in dissloving iron wire in the acid. The reactoin, however, could not be allowed to go to completion. If this were done, then oxidation would take place and the bluish-green ferrous sulphate sloution would change to a yellow or brownish color, with the simultaneous precipitation of basic salts of uncertain composition. Whenever this oxidation occurred, the solution could be readily restored by adding iron wire and perchloric acid. The ferrous perchlorate was therefore poured off while it yet contained a little free acid. This was then filtered to remove the free carbon introduced from the iron wire.

It was decided to purify the salt by crystalization. The solution was first concentrated by boiling in the air. Unfortunately, oxidation soon set in. Adding iron wire did not improve matters. It was evident that the solution could be concentrated only by heating in a neutral or reducing atmosphere or in a vacuum. The latter method, being simpler, was used. To this end the solution was poured into an Erlenmeyer flask which was evacuated by means of a high vacuum aspirator. In this way, the concentrated solution could be kept boiling at a temperature of 40 - 50 degrees Cent. After the solution had become very concentrated, it was allowed to cool slowly, when long needle-like crystals of $Fe(ClO_4)_2 \cdot 3H_2O$ separated. The mother liquor was then drained off by inverting the flask in a vacuum dessicator. It was, however, impossible to remove all of the mother liquor in this way. The long slender crystals of ferrous perchlorate formed an interlacing network full of little interstices where small amounts of the thick and viscous mother liquor were tenaciously held. After all that would drain off had been thus removed, the crystals were transfered to a watch-glass and placed in the same vacuum dessicator to dry. The vacuum, however, was a poor one and after some hours the adhering mother liquor was found to be oxidized on the surface layer of crystals. Hence this method was abandoned. Other ways of separating crystals from mother liquor were tried, but these were even less successful due largely to the fact that the slender crystals of ferrous were so fragile that they would break up into a fine mush whenever handled.

No further attempts to crystalize the ferrous sulphate were made at this time. Instead the salt was always kept in solution.

Nevertheless, some means of determining the strength of the solution had to be devised. The best method seemed to be the determination of total iron by titration with potassium permanganate. The analysis was carried out as follows: A definite quantity of the solution, 1 or 2 cc. depending on concentration, was withdrawn by means of a pipette and put into an Erlenmeyer flask. About 25cc water and 5 cc HCl conc. were added and the whole heated to boiling point. While still hot, any ferric salts were reduced by adding stannous chloride. The flask was then cooled by running water and when cold, 10 cc of $HgCl_2$ solution were added quickly. This solution was then washed into a large beaker with about 300 cc of water and 10 cc of manganese sulphate solution added. (20 gms. $MnSO_4$, 220 cc H_2O and 40 cc H_2SO_4 conc.) This was then titrated with $KMnO_4$ previously standardized against pure sodium oxatate. It was at first feared that the $SnCl_2$ would react with the ClO_4^- ion, but this did not happen even in the boiling solution, thus showing as is well known that the perchlorate ion is very stable towards reduction.

The method of analysis given above, closely follows the so-called Zimmermann-Reinhardt method given in Fay's "Quantitative Analysis". On the whole, this method was so satisfactory that it was used throughout whenever the strength of the solution was desired.

In the later runs, ammonium perchlorate was used. No trouble was experienced in preparing and purifying this salt. Perchloric acid was neutralized by ammonium hydroxide and the neutral solution concentrated by boiling. Upon cooling crystals of NH_4ClO_4 separated and these were removed by filtering through a suction filter. The crystals were again dissolved by pouring hot water over the filter, thus leaving behind any dirt present. This solution was again concentrated, cooled and the crystals filtered off on a porcelain filter plate. These were sucked as dry as possible, transferred to a watch-glass, and placed in drying-closet to dry. A perfectly pure salt resulted which could be weighed out whenever wanted.

Other Apparatus.

Wrought iron was sought for as anode material. However, the search through the various metal dealers of Boston proved unsuccessful and soft steel had to be used instead. A strip about 2 ft. long 1 3/4 in. wide and 3/16 in. thick was procured from the Technology workshop and sawed up into convenient lengths. Copper wire was soldered on for electrical connection and the upper part of the anode,that was not submerged when the electrolysis was in progress, was covered with paraffin.

In the runs proper, the single electrode potentials of anode and cathode were measured. Evidently, the KCl of the calomel electrode, against which these potentials were measured, could not dip directly into the ferrous perchlorate lest a precipitate of potassium perchlorate be formed. To obviate this, a connecting liquid of normal NH_4NO_3 was used. A half-normal electrode vessel provided with a glass tube drawn out to a point, was used to contain the connecting liquid. The end of the glass tube could then be pressed closely up against the electrodes, in this way reducing the error due to resistance drop. As two anodes were used with a cathode in the center, it was not possible to introduce the tube behind the electrodes as would be the case if only one anode had been used. Both the normal electrode proper and the connecting vessel were made airtight to prevent any syphoning action, thus making it unnecessary to adjust all liquids to same level.

In all the runs except one, where iron was used, copper sheet served as cathodes. Copper was selected because it was of a different color from iron, enabling any irregularity of deposit to be easily seen; it was also convenient and easily cleaned.

Wiring.

The wiring was laid out for the simultaneous operation of two cells. Both of these cells were , however, only used in the preliminary runs. In the remaining runs, only one cell could be used at a time due to the necessity of taking the electrode measurements.

As it was connected, one drop wire served both cells. Each cell does, however, have independent rheostatic control. The drop wire was normally connected across the storage battery circuit, but when this was being charged, the capacity of the wire rack used as drop wire was great enough to permit it to be operated across the 110 volt circuit. A small motor enabled one of the cells to be operated with a revolving cathode or stirring apparatus. The electrode potentials were measured by the Poggendorf potentiometer method.

PRELIMINARY RUNS

After the solutions and alectrodes had been prepared, the following series of runs were started. These preliminary runs were for qualitative purposes only. No attempt to get quantitative results were made. The object was simply to get idea as to the general conditions for depositing iron. This was necessary because of the fact that no work had been done before using ferrous perchlorate as electrolyte for plating out iron. Later, the runs proper were started and complete data taken for determining current efficiencies, electrode potentials etc.

All runs were carried out at room temperature.

Prelim. Run 1.

Electrolyte:- Fairly concentrated solution of $Fe(ClO_4)_2$ slightly acidified. This solution was prepared as described under "Preparations of Solutions" (see pages 12&13).

Anode..............Platinum sheet
Cathode.(stationary) Copper sheet
Current density.....1.6 amps. per sq. dm.
Voltage.............1.52
Time................2.0 hours

As the first deposit obtained from an hitherto untried electrolyte, the deposit was remarkably good. It was solid,uniform and adherent. When removed from the cell it was black on the surface, but could be polished bright by emery cloth. Under the microscope, no holes could be detected. The black color was seen to be due to minute irregularities of surface.

During the electrolysis, hydrogen gas was evolved continuously from the cathode due to the acidity of the solution. No gas was evolved on the platinum anode. Instead the current was used up in oxidizing the ferrous ions. A thin layer of the yellow-brownish salt could be distinctly seen forming next the anode. As the electrolysis progressed, this gradually diffused throughout the electrolyte. In its final condition, the electrolyte was a clear yellow-brownish solution. It was regenerated for future use as described in "Preparation of Solutions". (see page 13)

Prelim. Run 2.

This run was started in the hope of getting a thick deposit with iron anode.

Electrolyte:- Regenerated solution from run 1.
Anode .... Platinum
Cathode (stationary) .. Copper sheet
Current density .... 1.6 amps. per sq. dm.
Voltage .... 0.60 - 0.42
Time .... 16 hours

The deposit was soft, spongy and black throughout. It was worthless.

Gassing took place on both electrodes but only slightly on anode. Atthe end there was a considerable semi-colloidal precipitate in the solution.

Prelim. Run 3.

It was decided to try again the effect of platinum anodes. This time two anodes were used with the cathode in between. In this way an even deposit could be obtained on both sides.

Electrolyte:- Regenerated solution.

Anodes .... Plat. sheets

Cathode (stationary) .. Copper sheets

Current density .... 1.0 amps. per sq. dm.

Voltage 1.4

The deposit was solid, adherent and hard but streaky and nodular in certain places.

Gas was evolved as in run 1. The final condition of electrolyte was also similar to run 1, although more pronounced because of longer time of electrolysis.

Prelim. Run 4.

Runs 4 and 5 were undertaken for the purpose of determining the effect of revolving cathode. In order to get similar conditions, portions of the same solution were used as electrolyte in both runs.

Electrolyte:- Solution of $Fe(ClO_4)_2$ slightly acidified.

Anodes .... Iron.
Cathode (revolving) ... Round copper bar
Current density .... 2.0 amps per sq. dm.
Voltage 0.64

The deposit started well but soon began to peel off in flakes.

Prelim. Run 5.

Electrolyzed under same conditions as in run 4 except that stationary cathode is used.

In this run also, the first deposit was good but peeled off later.

Evidently, the fundamental nature of the deposit was mot effected by using a revolving cathode.

Prelim. Run 6.

Up to this point,all deposits with platinum anodes had been consistently good, and all deposits with iron anodes as consistently poor. This run was made for the purpose of finding out if the use of platinum had a direct influence on the nature of the deposit. Therefore the solution left over from run 5 from which a very poor deposit was obtained, was used as electrolyte.

Electrolyte:- Solution left over from run 5 without being regenerated.

Anodes .... Plat. sheets
Cathode (stationary) .. Copper sheet
Current density ...... 0.5 amps. per sq. dm.
Voltage 1.24

The deposit was quite similar to that obtained in run 5. It was certainly not better.

Gas was evolved throughout the run, and the solution which contained a fairly large precipitate from run 5, did not change appreciably during the run.

It is interesting to note that the first layer deposited from this solution was apparently good. Iron was allowed to plate out for about ten minutes, and the cathode was then removed. The deposit, though very thin and of a black color, was uniform and very adherent. This seemed at first to be a big improvement over run 5. In order to get a complete test, however, another cathode was substituted and electrolyzed for about two hours. This was covered with a black, porous and soft deposit. Both of these cathodes were washed and left on the desk. After about a day, the black and porous deposit was completely oxidized, while the thin deposit was not effected.

This run shows that the platinum anodes do not have a direct influence on the nature of the deposit.

<u>Prelim</u>. <u>Run 7</u>.

This run was an attempt to duplicate run 1.

Electrolyte:- Solution of $Fe(ClO_4)_2$ slightly acidified. (regenerated from previous runs).

Anodes .... Platinum sheets
Cathode (stationary) .. Copper sheet
Current density .... 1.0 amp. per sq. dm.
Voltage 1.42

This run was unsuccessful. There was an excessive evolution of gas throughout the run and almost no iron was deposited. This was caused by the fact that the solution was too acid. It had been regenerated in the usual manner, but too much acid had been added and insufficient time had been allowed to permit the excess to react with the iron wire. Consequently almost nothing but hydrogen deposited on the cathode. It was apparent that the acidity of the solution had a marked influence on the deposit.

Prelim. Run 8.

It was decided to attempt electrolysis with a perfectly neutral solution. It was explained on page 13 that neutral solution could not be obtained by allowing iron wire to react with the acid to completion. Instead, excess acid was neutralized by carefully adding small amounts of KOH. The OH^- ions neutralized any H^+ ions present. Any excess would be precipitated as $Fe(OH)_2$. All of the K^+ ions introduced were precipitated as $KClO_4$. The precipitate consisting of $KClO_4$ and some $Fe(OH)_2$ was then filtered off leaving a clear solution.

Electrolyte:- Prepared as explained above.
Anodes .... Iron
Cathode (stationary) .. Copper
Current density .... 0.5 amp. per sq. dm.

No gas whatsoever was evolved. This was the first run in which this was the case. The deposit , however, was black porous and worthless. It resembled that obtained in run 2. Although the deposit from this run was useless, the results proved, as had already been suspected, that no gassing would take place in a neutral solution.

DISCUSSION OF PRELIMINARY RUNS

As a whole, the results from the preliminary runs were discouraging. No deposit equalling that of run 1 had been obtained, not even by using platinum anodes. In all runs with iron anodes, black and worthless deposits had been obtained, and a basic precipitate was always formed in the solution. It was certainly basic as it would always dissolve on addition of acid. With platinum anodes no precipitate was obtained except in run 6 where the solution already contained a precipitate from the beginning. Moreover, with platinum anodes, the solution was always oxidized, and could be restored only by adding iron wire. To summarize, the solutions obtained from platinum and iron anodes uniformly differed in two main respects. (1) The platinum anode solution was always oxidized. (2) The iron anode solution always became turpid from basic precipitate. To be sure , it too would oxidize on prolonged electrolysis, but the precipitate was formed long before any oxidation was perceptible.

This difference in the nature of the deposits might be due to two causes: (1) The helpful influence of the ferric salt, or (2) the detrimental influence of the basic precipitate. The first assumption seemed untenable because the deposit with platinum anodes as it first comes down is good, long before any ferric salt could have diffused from anode to cathode. Hence it seemed reasonable to suppose that the formation of the basic precipitate is the cause of the poor deposit obtained with iron anodes. This was confirmed by the results of run 6.

Up to this point, attempts to get good deposits had been made on what might be called a hit and miss method. Although deductions had been arrived at,that were very helpfull, yet it was evident that only by carrying on the work on a more quantitative basis could anything definite be accomplished. For this purpose,the following runs were made.

FINAL RUNS

In the following runs, the cathodic and anodic polarizations were determined throughout each run at intervals of 30 minutes.

The current efficiencies were determined by weighing the cathode before and after each run on an analytical balance. It would have been very desirable to also determine the anodic current efficiencies. This, however, was impractable due to their great weight. No balance of sufficient capacity was sensitive enough to detect the small differences in wieght with sufficient accuracy to be of any value.

The concentration of the ferrous perchlorate solution was determined as explained on page 15. This solution was either used full strength or diluted to any desired concentration. In this way concentrations were determined. For uniformity with current practice, these have been transformed into grams of the crystalized salt per liter. This is the form used to express concentrations throughout the subsequent runs.

All runs were carried out at room temperature.

<u>Run 1</u>.

Runs 1 and 2 were for the purpose of definitely settling the question of the influence of the platinum anodes on the cathode deposit. Portions of the same solution were used as electrolyte in both runs.

Electrolyte:-	880 gm $Fe(ClO_4)_2 \cdot 3H_2O$ per liter (slightly acid)
Anodes	Plat.
Cathode (stationary) ..	Copper sheet
Current density	0.36 amp. per sq. dm.
Anodic Polarization ...	+.508 volt
Cathodic " ...	-.778 "
Voltage	1.31
Time	3 hours
Current efficiency	14.1 %

The deposit was smooth, uniform and adherent, but very thin. It had the color of polished iron.

Gas was continuously evolved on cathode. The solution gradually turned yellow-brown but remained clear.

Run 2.

Electrolyte:- Same as run 1.

*Anodes	Iron
Cathode	Copper
Current density	0.30 amp. per sq. dm.
Anodic polar.	-0.390
Cathodic "	-0.794
Voltage	0.41
Time	3.0 hours
Current eff.	34.3 %

The deposit was solid and adherent but not as uniform as in run 1.

Gas was evolved on cathode. The solution did not change color but a flocculent precipitate was formed.

The deposit with platinum anodes is not unlike that obtained in the preliminary runs. That with iron anodes, however, is much better. This improvement may be due to the decreased current density or to a different acid concentration.

*In all subsequent runs, iron, in the form of soft steel, was used as anode.

It will be seen that by using platinum anodes an anodic polarization about 0.90 volt higher than that with iron anodes, was obtained. This is due to the fact that with platinum anodes, the reaction at the anode is $Fe^{++} - e = Fe^{+++}$, while with iron anodes, the reaction is $Fe - 2e = Fe^{++}$. The free energies of these reactions, and therefore the electromotive forces, are different.

Run 3.

From the preceding runs, it was evident that the acid concentration was too high. It was thought that this could be reduced effectively by adding a salt of a very weak acid. For this purpose, ammonium acetate was selected. The hydrogen ion concentration would then be limited to that of acetic acid, which is very low.

Electrolyte:- 220 gm. $Fe(ClO_4)_2$ per liter
70 " $NH_4C_2H_3O_2$ " "
Cathode .... Copper
Current density .... 0.2 amp. per sq. dm.
Anodic polar. ....-0.587
Cathodic " ....-0.962
Voltage 0.39
Time .... 2 hours
Current efficiency .... 47.2 %

The deposit was black, soft and worthless except near top where it was hard and compact.

Immediately upon adding the

ammonium acetate, the solution turned brown. Considerable gas was evolved during the electrolysis, though less than in runs 1 and 2. A froth was formed on the surface and a black precipitate was thrown down.

The results from this run did not look promising, and therefore further use of ammonium acetate was discontinued.

<u>Run 4</u>.

All attempts to get a good deposit using iron anodes had been unsuccessful. Apperently some new scheme must be tried. As ammonium salts very materially improve the deposit in the Burbess process, it was decided to try ammonium perchlorate. This salt was prepared as explained on page 16. The ferrous and ammonium perchlorate were mixed in molecular proportions.

Electrolyte:- 200 gm. $Fe(ClO_4)_2 \cdot 3H_2O$ per liter
slightly acidified.
80 gm. NH_4ClO_4 per liter.

Cathode .... Copper
Cur. dens. .... 0.33 amp. per sq dm.
Anodic polar. ....*(-.500) - (-.550)
Cathodic " .... (-.946) - (-.903)
Voltage .... 0.45 - 0.36
Time .... 2.5 hours
Current efficiency .... 88.0 %

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* Means that it changed, during run, from -.500 to -.550

The deposit was smooth, solid, adherent, uniform, and had the color of polished iron. Microscopic examination of surface, even with high power (500x) only a very slight irregularity of surface could be detected.

During the electrolysis, the electrolyte turned slightly yellow-brown and a small brownish precipitate was formed. There was only a slight evolution of gas on the cathode. The beneficial effect of the ammonium perchlorate was very marked. Both the nature of the deposit and the current efficiency were improved enormously by its use.

This electrolyte was so successful, that in all subsequent runs, the ferrous perchlorate and ammonium perchlorate were in the same proportions. The only improvement to be desired was to raise the current efficiency to a better figure.

Run 5.

It had already been concluded that the cause of low current efficiency was excessive acidity of the electrolyte. Therefore it was decided to make a perfectly neutral solution by crystalizing out the salt. Some oxidation was of course inevitable. Nevertheless, in spite of the objections stated on page 13, this method was used as the results of the previous runs had shown that the presence of small amounts of the ferric salt is certainly not harmful. The solution was evaporated in vacuum and allowed to crystalize on cooling. The crystals were sucked as dry as possible on a porcelain filter plate, redissolved in water and the concentration determined by analysis.

Up to this point, the current efficiencies had been determined from ammeter readings. This was not very accurate, however, and in all subsequent runs, a silver voltammeter was used instead. The voltammeter was connected and operated in the usual manner.

Electrolyte:- 155gm. $Fe(ClO_4)_2$ per liter (neutral).
60 gm. NH_4ClO_4 per liter
Cathode .... Copper
Current dens. .... 0.30 amp. per sq dm.
Anodic polar. .... -.600 (constant)
Cathodic polar. ......(-0.908) - (-0.883)
Voltage .... 0.34 - 0.28
Time .... 2.5 hours
Current eff. .... 94.6 %

The iron deposited only in streaks or blotches. Where it did deposit, however, the deposit was solid, hard, and adherent. It was of a silvery color. Microscopic examination revealed a scintillating field at low and medium power. At 500x it could be distinctly seen that the deposit was crystaline.

A small amount of gas was evolved during electrolysis. The solution turned yellow and a yellow-brown precipitate was formed early.

The results from this run were most unexpected as regards the nature of the deposit. Why the deposit should form over only half the cathode surface seemed to be a riddle. The thorough cleaning before electrolysis, eliminated any possible unevenness due to this source. Still it seemed possible that the iron deposited best on iron in preference to copper; then as soon as a molecular layer of iron had deposited on one spot, the iron would continue to depisit there in preference to a neighboring spot of pure copper. The following run was made to test this hypothesis.

<u>Run 6</u>.

A cathode of iron was used. Any unevenness due to copper cathode was therefore avoided.

Electrolyte:-	THat left over from run 5, unchanged
Cathode	Iron
Current dens.	0.30 amp. per sq. dm.
Anodic polar.	(-0.608) - (-0.588)
Cathodic "	(-0.890) - (-0.868)
Voltage	0.28 (constant)
Time	2.0 hours
Current eff.	100%?

The fundamental nature of the deposit was not changed. It did cover a little more of the cathode surface, but otherwise it was similar to that of run 5 in every respect. Hence the hypothesis that the nature of the deposit is influenced by the copper cathode can be safely rejected.

Run 7.

It was decided to try another salt of a weak acid as addition agent. Ammonium oxalate was used. Watts had found (see page 4) that it was very beneficial in the case of the Burgess process.

Electrolyte:- 150 gm. $Fe(ClO_4)_2$ per liter. (neutral)
60 gm. NH_4ClO_4 per liter
6 gm. $(NH_4)_2C_2O_4 \cdot H_2O$ per liter

Cathode .... Copper
Current dens. .... 0.30 amp. per sq.dm.
Anodic polar. .... -0.605 (constant)
Cathodic " .... (-0.905) - (-0.888)
Voltage .... 0.30 - 0.29
Time .... 2.6 hours
Cur. eff. .... 100 %

The deposit was distinctly crystaline. It was hard, solid, and adherent, uniform at bottom but slightly streaky at top of cathode. Microscopic examination confirmed the crystaline structure.

During electrolysis, there was no gas evolved on the cathode. A rather large yellow-brownish precipitate was formed.

Run 8.

The solution used in run 6 from which the best deposit was obtained, was slightly acid. Hence it was decided to try adding a little acid to see if the deposit could be improved thereby. This was carried out by adding successive portions of 1 cc each of 5% $HClO_4$ and electrolyzing for about 1 minute after each addition, cleaning the electrode before each electrolysis. When a layer was deposited that looked uniform, the cathode was removed, cleaned and weighed, the voltameter placed in series, and the run proper was begun.

Electrolyte:- same as in run 8, with 5 cc 5% $HClO_4$ added
Cathode .... Copper sheet
Current density........0.9 amp. per sq. dm.
Anodic polar........(-0.515)-(-0.570)
Cathodic " ....(-0.995)-(0.940)
Voltage .... 0.50 - 0.38
Time .... 2 hours
Cur. eff............. 97%

The deposit was firm, solid and adherent, but slightly pitted. The deposit showed a marked improvement over that obtained in run 7. Microscopic examination at 500x revealed the presence of small protrusions like small rounded off crystals or nodules.

During electrolysis a slight amount of gas was evolved and a yellow precipitate settled out.

By adding acid, the nature of the deposite and keeping qualitites of solution had improved, but the current efficiency had been lowered.

Run 9.

It was decided to try a slightly acidified solution without the addition of ammonium oxalate. The neutral solution prepared by crystallization (see page 30), had been all used up. Hence the slightly acid solution attained by regenerating ferrous perchlorate was used without the further addition of any acid. This solution had been treated in the same way as that used in run 4, but its acidity was less as determined by gas evolution during electrolysis.

Electrolyte; - 160 gm. $Fe(ClO_4)_2 : 3H_2O$ per liter
(slightly acidified)
60 gm. $NH_4 ClO_4$ per liter.

Cathode ....Copper

Current density...........6 amp. per sq. dm.

Anode polar ....(-550)-(-.575)

Cathode polar ....(.966)-(.918)

Voltage.................. .44 - .38

Time......................2 hours

Current eff...............95%

The deposit was smooth, solid, and adherent. It had a lustrous sheen almost like silk. Microscopic examination showed at high magnification, very small incipient nodules. They were very small, much smaller than crystals in run 7.

During electrolysis, there was a slight evolution of gas which gradually decreased. A small yellow-brown precipitate formed.

DISCUSSION OF RUNS.

It is not difficult to obtain good deposits by using platinum anodes. What is desired is the production of good deposits when iron anodes are used to keep the concentration of the solution constant. Any process using platinum anodes necessarily involves the use of regenerating cells which is a distinct disadvantage. The process would then be like that patented by Ramage (see page 5). On the other hand, what is desired is a continuous electtrolysis where iron dissolves from anode at same rate as it is deposited on cathode. For this reason whenever platinum anodes were resorted to they were simply used for purposes of comparison.

By far the most promising electrolyte is that of ferrous and ammonium perchlorate. The addition of ammonium perchlorate changed the nature of the deposit entirely. The two salts were used in molecular proportions.

Whether this was the optimum amount, cannot be foretold as time did not permit my experimentation with different proportions.

As far as results show, addition of ammonium oxalate does not effect the deposit to any marked extent.

The anodic polarization was greater with platinum than with iron anodes, as was expected. With iron anodes it decreased when another salt as ammonium perchlorate was added, probably due to the change in concentration of the ferrous ions due to the common ion effect. By a decrease is meant, decrease in the positive sense; e.g. the polarization decreased from -0.39 to -0.60.

The acid concentration seems to have an influence on the nature of the deposit. That free acid would lower the current efficiency by plating out hydrogen, and improve the keeping qualities of the solution by preventing the formation of basic precipitates, is perfectly natural; but why non-uniform deposits are obtained in the absence of any free acid seems unexplainable.

CONCLUSIONS

(1) Iron can be electrolytically deposited from perchlorate solutions.

(2) The best deposits are obtained from a 20% solution of ferrous perchlorate and 8% ammonium perchlorate with a slight amount of free acid present.

(3) By using platinum anodes, good deposits can be obtained from the plain ferrous perchlorate solution.

(4) In solution at least, ferrous perchlorate is more stable than either sulphate or chloride. This verifies Dr. Walker's statement. As pure crystals free from mother liquor were not isolated, its stability in crystaline forms was never tested.

(5) Besides affecting current efficiency, and keeping qualities of solutions, the acid concentration also seems to effect the nature of the deposit.

(6) Electrolysis with 100% current efficiency, with good keeping qualities of solution, and with good deposits were obtained, but not all at the same time. The best compromises were runs 4, 9, and 8.

(7) Extent of work done does not justify critical comparison with other methods of plating out iron, as the Burgess process.

SUMMARY.

It was found impracticable to separate ferrous perchlorate crystals, due to their fragile nature and to adherence of mother liquor.

A series of preliminary runs were made for the purpose of finding out the general condition for electrolysis. On the basis of the results obtained from these runs, another series of final runs were made of a more quantitative character.

At first good deposits were obtained only by using platinum anodes. Later, however, by adding ammonium perchlorate, many good deposits were obtained with iron anodes.

Lack of time prevented any thick deposits from being made. For this reason no definite statement as to the adaptability of the method to commercial practice, is possible. As far as the thin deposits obtained show, however, the ferrous and ammonium perchlorate solution compares favorably with other methods for plating out iron. When comparing with other methods, it should be kept in mind that most of these methods, noticeably the Burgess process, have been experimented upon for years by various investigators, while no work at all has been done before with perchlorates.

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