

ELECTRODEPOSITION OF NICKEL

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A number of years ago, Calhane and Gammage¹ published some very interesting facts concerning the deposition of nickel from solutions of nickel ammonium sulphate. Although these experiments were made to study the impurities, such as iron, deposited with the nickel, they bring out some facts which may serve to throw light on the theory of nickel deposition.

In their work, the anodes used were the commercial ones, containing about 7.5 percent iron, and about 92 percent nickel. The first experiment consisted in the electrolysis of the nickel solution (containing about 80 grams of nickel ammonium sulphate per liter of water) using the nickel-iron anodes and platinum sheet cathodes. The current density was about 4 amperes per square decimeter, and the current efficiency on a one-hour run, was about 88 percent, the deposit containing about 0.15 percent iron. The effect of stirring was then tried by running two cells in series, one having a stirrer which rotated 130 revolutions per minute, while the other had a stationary electrolyte. The efficiency in the two cells was practically the same, being about 90 percent. The iron in the deposit from the still solution was 0.13 percent, and that from the stirred solution was 0.36 percent. The effect of rotating the cathode was then tried by running two cells in series, the conditions being the same with the exception that one held a stationary cathode while the other had the cathode rotated 130 revolutions per minute. The efficiency of deposition was 91 percent with the stationary and 12 percent with the rotating electrode. The iron contained in the deposit was 0.11 percent for the stationary, and 0.55 percent for the rotating cathode. Cathodes were used rotating 260, 519, 1041, and 2160 revolutions per minute, and

¹ Jour. Am. Chem. Soc., 29, 1268 (1907).

efficiencies of 69, 65, 55, and 40 percent, respectively, were obtained.

Unless the anodes were enclosed in bags, or the cathode placed in a porous cup, the iron content of the rotating cathode was always greater than that of the stationary ones.

In view of the fact that nothing has appeared, since this publication, to explain the seemingly specific effect, due to the rotation of the cathode, it was thought that an explanation should be sought with the idea of explaining some other facts found with rotating cathodes. Interest was also stimulated by the recent symposium on electroplating.

In checking up the work of Calhane and Gammage, the following curves of efficiency were obtained, which are plotted against time in minutes as ordinate. By running for fifteen minutes and weighing, and then continuing, the effect of time is shown very plainly. The rotating cathode shows a lower efficiency than the stationary. The solution used contained about 7 grams of crystallized nickel ammonium sulphate, and 1 gram of nickel chloride per 100 cc of water. The anodes contained about 0.75 percent of iron. The current density was 1.5 amperes per square decimeter. The run giving the third curve at the top of Fig. 1, was made with a solution

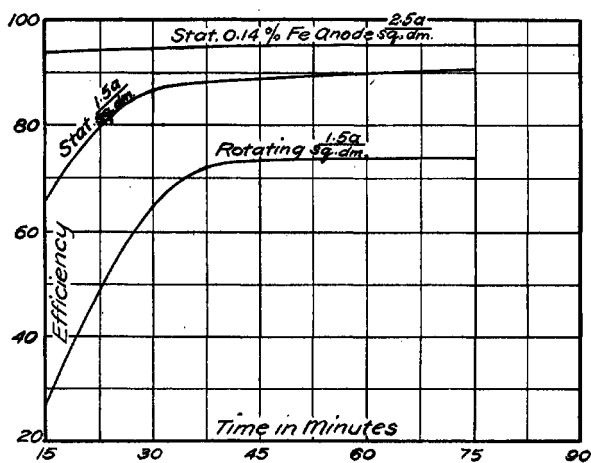


Fig. 1

containing 8 grams nickel ammonium sulphate crystalline, and 1 gram nickel chloride per 100 cc of water. The anode was 0.14 percent iron, the current density was about 3 amperes per square decimeter. Here the anode having the least iron content is in the cell which gives the highest efficiency. It was therefore thought that iron had something to do with the lowering of the efficiency. Attempts were made to obtain pure nickel plate which contained no trace of iron for use as anode for an efficiency test to see if rotation would have the same effect here. It was thought possible that the voltage relation might be changed so that iron could be reduced and oxidized more easily than nickel deposited and dissolved, respectively, and therefore, that these reactions would go on more readily than the normal deposition of metal. The alternate oxidation and reduction of the iron, if this is the important factor, would be greatly increased by the rapid stirring and consequent mixing of the anode and cathode compartment occasioned by the rotating cathode. Attempts, however, to get a large amount of pure nickel were futile, more or less, so it was decided to change the plan.

If the cathode is enclosed in a porous cup, the iron will be almost wholly kept out, so that some factors would be changed with a probable change in the results. Consequently, two cells were run in series, one with, and the other without the porous cup. The solutions were iron-free, and contained, as all solutions henceforth, 8 grams of nickel ammonium sulphate and 1 gram nickel chloride per 100 cc of water. The chloride was added to aid the solution of the anodes (0.14 percent iron) which were used in several runs. The anodes used here, however, contained 7.6 percent iron. The current was as before. The deposits were weighed every fifteen minutes for one hour and at longer intervals after that, giving the time-efficiency curves shown in Fig. 2. The efficiency in the ordinary cell increases continuously, while that of the porous cup cell increases, reaches a maximum, and then falls off. Inside of the porous cup, the cathode compartment, after 15 hours' run, the solution consisted essentially of a

rather concentrated solution of ammonium hydroxide, the nickel being almost wholly removed from the compartment by deposition. The cathode in the ordinary cell contained about 3.5 percent iron, the one in the porous cup containing only 0.15 percent. After the run the solution in the ordinary cell, 400 cc, had 0.4 gram of iron present. In the porous cup cell, 1.6 grams of iron were found inside the cup and 2.1 grams outside. The iron had practically all been precipitated by the ammonium hydroxide inside the porous cup. It was deposited before it reached the cathode and hence the iron content of the cathode in the cup was low.

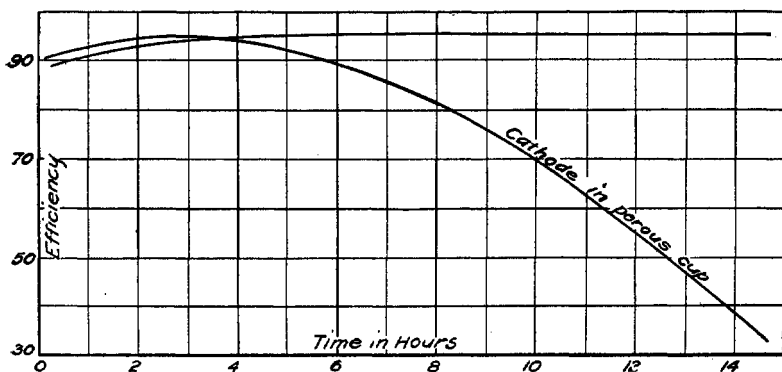


Fig. 2

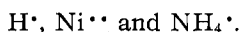
The fact that the cathode compartment becomes alkaline leads one at once to an important consideration which probably throws light on the deposition of several of the metals more electropositive than hydrogen. If the measurement of the voltage required to deposit nickel,¹ 0.228 volt, and the measurement of the overvoltage of hydrogen² at the surface of a nickel cathode, 0.14 to 0.21 volt, mean anything, the fact that nickel is deposited instead of hydrogen from a solution giving a slight acid reaction, cannot be ascribed to the overvoltage of hydrogen, for the balance is in the other direc-

¹ Wilsmore: *Zeit. phys. Chem.*, **35**, 318 (1900).

² Coehn: *Zeit. phys. Chem.*, **38**, 618 (1901); Caspari: *Ibid.*, **30**, 93 (1899).

tion. It is not going too far, probably, to say that hydrogen is liberated at a nickel electrode with a smaller expenditure of energy, than that required to deposit nickel. This leads directly, then, to the obvious conclusion that nickel cannot be deposited from an acid solution. When, however, the solution becomes slightly alkaline the nickel may be deposited, for the concentration of hydrogen as ion becomes practically zero in the alkaline solution. In interpreting this statement, it must be borne in mind that the acidity of the solution from which the actual deposition takes place is considered, and not that of the solution out between the two electrodes. The reference is, therefore, to the film of solution which is in actual contact with the cathode.

Under this condition, suppose an electrolysis is begun with nickel ammonium sulphate solution with nickel electrodes. The solution being neutral or slightly acid will contain the following positive ions,



These ions will all take part in carrying the current to the cathode. At the cathode hydrogen will be liberated, which removal leaves an excess of hydroxyl ions which with the NH_4^+ ions corresponds to the ammonium hydroxide which accumulates at the cathode. No deposition of nickel can take place until the hydrogen is removed and the solution becomes alkaline. When this occurs nickel may deposit, and the efficiency of deposition will depend on the maintenance of a cathode film which is alkaline. The facts exhibited in the curves, Fig. 1, are intelligible from this viewpoint. When the electrolysis is started, the efficiency is low at first, due to the fact that much of the current is used up in liberating hydrogen. When these ions are removed, the cathode film is alkaline, and nickel deposits with an efficiency which gradually increases as the electrolysis proceeds, until practically a maximum value is reached, when the cathode film of solution is most favorable for the production of the best deposit.

The tendency to deposit hydrogen is greater at a platinum cathode than at a nickel cathode, on account of the over-voltage effect. It might be said, therefore, that with a platinum cathode, a low efficiency would be expected, since the tendency to liberate hydrogen is greater than when a nickel cathode is used. In the former case, some time is required to build up a surface of nickel, while in the case of a nickel cathode, the nickel film is present from the beginning. Having the nickel surface from the beginning, the over-voltage effect would operate over a longer time than in the case of a platinum cathode, and the tendency to deposit hydrogen would be less in the case of a nickel cathode. If the above were true, the efficiency would be lower with platinum than with copper or nickel cathodes. When these were tried practically no difference could be shown to exist, as is shown in Table I. The cells were run in series for 17 minutes.

TABLE I
Effect of cathodes on efficiency of deposition

Cathode material	Copper	Nickel	Platinum
Efficiency percent	95.5	96.0	95.3

These differences are well within the limit of experimental error and show that the cathode over-voltage has nothing to do with the efficiency.

If the increase in efficiency with time is due to the accumulation of ammonium hydroxide at the cathode, this condition could be realized synthetically throughout the whole solution, by adding to the solution some ammonium hydroxide. It ought to be possible to start the electrolysis with a high efficiency by adding the alkali to neutralize the acid present. Runs were therefore made with solutions (190 cc each) to which 2, 5, and 10 cc of 1 : 10 ammonium hydroxide (sp. gr. 0.89) were added. With 2 cc of material as is shown in Fig. 3, the efficiency is increased slightly over the neutral solution, the amount of increase being very great

in the cases with 5 and 10 cc. The solution containing 5 cc of ammonium hydroxide always gave a more adherent and a better deposit. These runs are with stationary electrodes, the anodes being 0.5 percent iron, the cathode being copper, held stationary. The current density was about 1.5 amperes

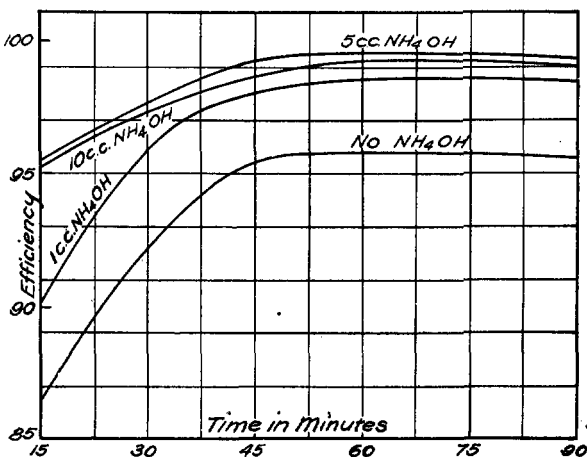


Fig. 3

per square decimeter, and the cells were run in series with a coulometer as in other cases. It seems that the efficiency can be begun and maintained at almost any desired point within limits by adding ammonium hydroxide. The same effect is obtained with anodes containing 7.5 percent iron as is shown in Fig. 4. It is interesting to note the fact that iron

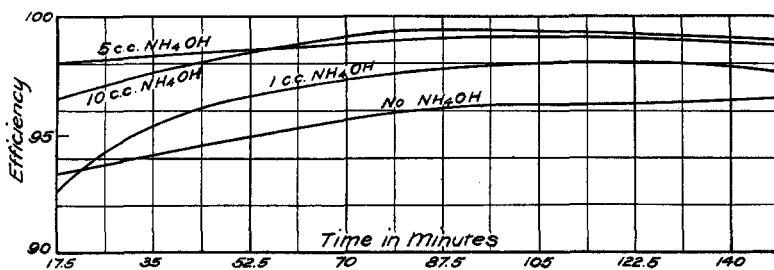


Fig. 4

is found in the cells after electrolysis as shown in Table II.

TABLE II
Iron in cells with ammonium hydroxide

Amt. of ammonia cc	None	2	5	10
Iron in deposit at bottom of beaker, grams	0.0225	0.0300	0.0685	0.0442
Iron in solution, grams	0.0144	0.0092	Trace	Nil

The amount of iron in the precipitate on the bottom of the beaker increases as the concentration of alkali increases, while the amount in the solution decreases just as it should.

The explanation of the decrease in efficiency with the rotating cathode over the stationary one, becomes apparent at once. The rotation of the cathode stirs the solution and gives a very effective means of breaking up this alkaline film over the rotating part. This broken up, the efficiency is low by amounts depending on the efficiency of the removal of the ammonium hydroxide from the film. The stirring may just as well be considered as preventing impoverishment of hydrogen which of course amounts to the same thing, *viz.*, prevents the formation of an alkaline film over the cathode. The efficiency should begin lower than the stationary one and should increase as the electrolysis proceeds, since some ammonium hydroxide is piling up in the solution.

The efficiency of removal of a surface film will depend on the speed of rotation. It may be seen, therefore, that the efficiency should decrease as the speed of rotation is increased.

Although the method of removal of this film by stirring the solution is an inefficient one, it ought to be possible to decrease the efficiency by stirring the solution without rotating the cathode. This is a necessary conclusion from the theory given above. On the other hand, Calhane and Gammage have shown that when a stirrer is rotated 130 revolutions per minute the efficiency is not greatly different from the stationary one. They have carefully avoided stirring more vigorously even though it might easily be guessed that stir-

ring vigorously out in the center of the solution would probably disturb the cathode film only as much as that occasioned when the cathode itself is revolved very slowly. It seemed safe to say, therefore, that if the stirring were more vigorous, the efficiency would be decreased. At any rate, since the theory requires this, the experiment had to be made. The results for two rates of stirring will be shown. The conditions were practically the same as before: nickel anodes, 0.14 percent iron, perforated platinum sheet cathodes, solution as before (80 grams nickel ammonium sulphate, and 10 grams

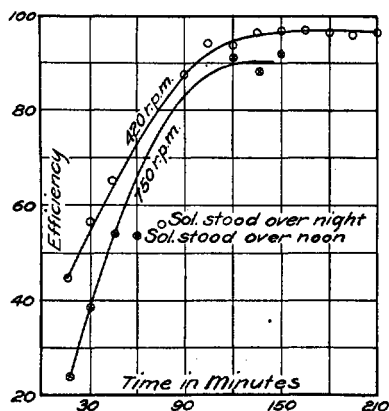


Fig. 5

nickel chloride per liter). The current density was about 1.5 amperes per square decimeter and the cathodes were weighed every 15 minutes. No coulometer was used, it being desired to see the difference between a stationary solution and one which was well stirred. The containers were crystallizing dishes 12.5 cm in diameter, the anode being placed on one side and the cathode on the opposite side. Situated about 2 cm from the cathode in one cell, was a cylindrical, perforated, sheet, platinum electrode about 3 cm in diameter and 5 cm long, fastened to a shank or shaft, which was held in a chuck and rotated. This gave very good stirring at the surface of the cathode sheet. The rotating piece, of course,

was not electrically connected, it being used only for stirring. One run was made with stirrer rotated at 420, and another at 750 revolutions per minute. The former rate of stirring gives curve A, and the latter one, curve B, Fig. 5. These curves show relative efficiencies of the cells with a still solution and that with a stirred solution. In other words, they give the efficiencies of the stirred solution as compared with the still solution which is assumed one hundred percent. From these curves the conclusion may be drawn that the efficiency of deposition decreases, as the rate of stirring is increased, as it should according to the theory just advanced.

With this, a number of facts become intelligible which otherwise are weird. The curve at the top of Fig. 1, which was run at a higher current density than the other stationary curve, shows a higher efficiency because the rate of carrying in the ammonium ion is relatively greater as compared with its diffusion backward, the current density being higher. This gives conditions for the formation of a more alkaline film where the current density is higher, and therefore the higher efficiency.

As to the behavior of iron, it may be said that if it is deposited at a lower voltage than nickel,¹ it will be deposited first if it can get to the cathode. Where an ammoniacal film exists over the cathode the iron cannot get in, since it is deposited as hydrated oxide. But when the film is broken by rotation, iron may enter and be deposited. In other words, just as was found, the amount of iron in the deposit is greater with a rotating than with a stationary electrode. If iron is deposited after nickel,² it would be deposited when nickel is impoverished. When the electrode is rotated, this impoverishment is prevented. The increase of the iron content with increasing rotation would seem to indicate that Küster's conclusion is due to some specific effect other than the voltage relations. On the other hand, it was noted that the solution

¹ Toepffer: *Zeit. Elektrochemie*, **6**, 342 (1899).

² Küster: *Ibid.*, **7**, 690 (1901).

became clouded in the cell with a rotating electrode. It is possible, therefore, that some of the increase could be due to mechanical deposition of the hydrated oxide which presumably causes the clouding effect.

The best deposits are obtained when the solution is alkaline at the surface of the cathode. This would mean that at the time the best deposit of nickel is being obtained, it should be impossible to get iron deposited at the cathode unless it be by mechanical occlusion or deposition.

When the solution, which has been electrolyzed, has stood, the ammonium hydroxide necessary for good efficiency will diffuse away from the electrode and the efficiency will be less after standing, less than that obtained if the solution were worked continuously. This is shown very well in Fig. 5 where the solutions stood as noted, and it is seen from the curve that the efficiencies are very much lower than if run continuously. From the measurements as taken from the work of Calhane and Gammage, 12 percent efficiency was obtained with a rotation of 130 R. P. M. Then with 260 R. P. M., 69 percent was obtained. It appears that both must have been made in the same solution. If so, it is unfortunate that they did not try to duplicate the 130 R. P. M. run in the same solution after running the 260 R. P. M. one. The efficiency would probably have been about 70 percent instead of 12 percent.

It may be concluded that:

A good deposit of nickel may be obtained from the double sulphate if the solution at the surface of the cathode is kept alkaline.

The efficiency is dependent upon the degree of alkalinity of the cathode film.

The efficiency can be started high and maintained high by adding a definite amount of ammonium hydroxide to the solution.

The alkaline solution film at the cathode may be disturbed and the efficiency of deposition decreased, by stirring the solution vigorously.

Since alkalinity is necessary for good efficiency, it is very probable that in acid solutions, nickel is deposited only when impoverishment of the hydrogen ions has caused the solution to become alkaline and given the conditions where nickel may deposit.

The iron content of a deposit formed on a rotating cathode, is greater than that formed on a stationary electrode. This may be due to mechanical occlusions.

The iron content of the anode does not materially affect the efficiency.

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