

ELECTROLYTIC REFINING OF GOLD.

By EMIL WOHLWILL, PH. D.

At the request of the editor of *ELECTROCHEMICAL INDUSTRY*, I herewith give some notes on the electrolytic method of gold refining, to supplement the article of Dr. Tuttle (Vol. 1, page 157, January, 1903). My electrolytic method of refining gold was introduced by Dr. D. K. Tuttle into the United States Mint of Philadelphia, and I am pleased that, after two years of use, he calls it "a great boon for the patrons of the United States Mint." This method was the result of experiments which were undertaken by me for the single purpose of investigating whether in parting platinum from gold the usual method can be replaced by an electric method. These experiments were made by me as director of the Deutsche Affinerie in Hamburg, and were begun in 1874. I established the following facts, which were unknown up to that date:

(1) In an electrolyte of chloride of gold which contains no other chloride, a pure gold anode, or an anode rich in gold, behaves like an anode of platinum or carbon. Chlorine is developed in gaseous form, while the gold is not dissolved.

(2) This development of chlorine gas can be prevented and gold is dissolved from the anode, if hydrochloric acid or certain other chlorides are added to the electrolyte of chloride of gold.

(3) There exists for a given solution a maximum of current density at which gold is dissolved from the anode without a development of chlorine gas. If the current density is increased beyond this maximum, chlorine gas is developed. However, by increasing the quantity of hydrochloric acid, or chlorides which act in the same way, and by increasing the temperature of the electrolyte, this maximum of the current density is increased.

(4) In a solution of chloride of gold, even with the addition of hydrochloric acid or of such chlorides which have the same effect, and even with increased temperature, pure platinum is not dissolved from the anode, and causes, therefore, the development of chlorine gas. If, however, platinum is contained in an alloy with gold, and such an alloy is used as anode in an electrolyte of chloride of gold with an addition of hydrochloric acid, the platinum goes into the solution in the same manner as the gold, while at the cathode gold is precipitated, completely free from platinum, from the solution containing gold and platinum; the platinum remains in the solution.

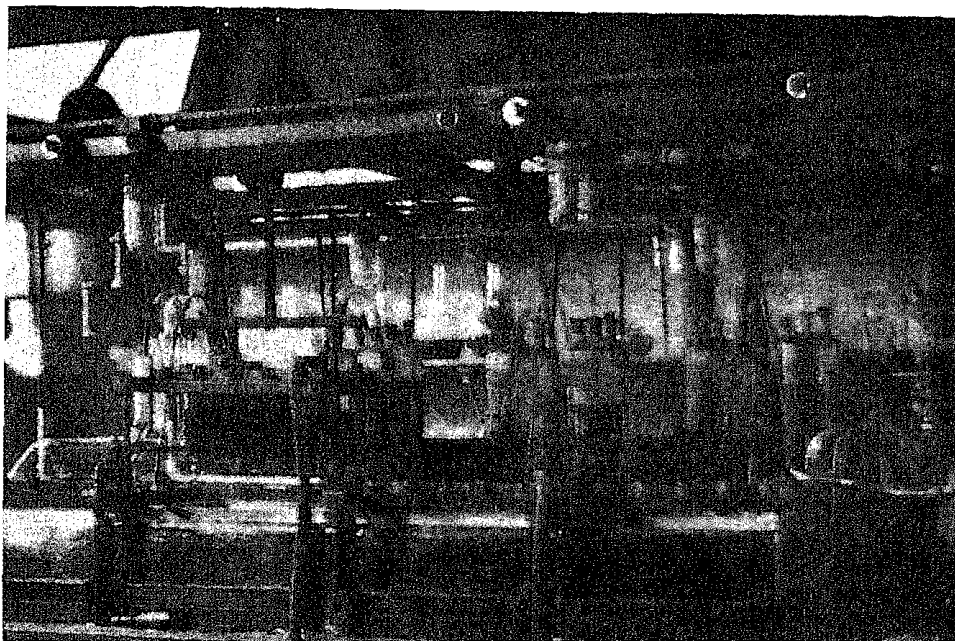
These facts represent the principles upon which the method is based by which, since 1878, the Norddeutsche Affinerie in Hamburg produces chemically pure gold from impure gold, and especially from gold containing platinum. The facts given above also indicate a very simple way by which from gold containing platinum the smallest quantities of platinum can be completely won. Since platinum is dissolved from the gold anode, but is not precipitated from the solution, it is

possible to collect the platinum from a great many impure gold anodes in the same volume of solution and to continue with this process until the concentration of the platinum in the solution is sufficiently high to permit direct precipitation by chloride of ammonium.

Electrolytic gold, produced by this new method from a material rich in platinum, was first exhibited at the Paris Electrical Exposition, in 1881, in form of the original cathodes as well as in form of bars which had been obtained by melting the former. At the request of M. Debray, at that time director of the Mint of Paris, the exhibited gold was subjected to an analysis. The test certificate of the Paris Mint, which I still have, records a purity of 1,000 in 1,000; M. Debray remarked that this is a purity which had not been obtained before.

The method as it was used at that time had an essential disadvantage besides its great advantages. It was the cleanest operation imaginable; any quantity of gold was dissolved in uncovered vessels, without producing any smell of chlorine. Even an evaporation of hydrochloric acid from the hot, but only slightly acidified solutions was scarcely noticeable. A higher price was paid for the precipitated gold on account of its purity. The operation, however, was very slow, much

slower than the usual chemical method (solution by means of aqua regia and precipitation of the gold by protochloride of iron). With the chemical method the total contents of gold could be obtained in twenty-four hours from the largest quantities of gold containing platinum. On the other hand, the electrolytic process required generally three times twenty-four hours to obtain only about 80 per cent of the contents of gold



GOLD REFINING ROOM OF THE DEUTSCHE AFFINERIE IN HAMBURG.

as first product. This was evidently a very distinct disadvantage.

In order to reduce the electrolytic method to a really industrial process, it was therefore absolutely necessary to increase the speed of the operation. To a limited extent the speed could be increased by using anode plates of smaller thickness, but a really satisfactory reduction of the time of operation required a considerable increase of the current density, but this appeared to be impossible beyond a certain limit. When the current density was increased up to a certain limit, any further increase, either by increasing the current with constant anode surface or by diminishing the anode surface with constant current, resulted in the evolution of chlorine gas at the anode, and the quantity of gold dissolved from the anode was therefore smaller than that of the gold precipitated on the cathode.

The remedy was found in a consequent application of the principle indicated above under (3). On the basis of the facts stated there I had given for many years the following rule to my workingman: When you smell chlorine, measure at once the temperature; if the thermometer shows less than 67° C., heat the bath; if this is not sufficient to make the smell of chlorine disappear, add hydrochloric acid in small portions

to the solution. At that time, as long as the increase of speed of operation was not absolutely necessary, I kept the average addition of hydrochloric acid as small as possible, and, as a result, I regarded a relatively low current density as normal. However, when I seriously asked myself the question whether the arbitrarily fixed limit represented really the normal condition (i. e., the limit attainable on account of the principle of the method) I soon discovered that this was by no means the case.

Experiments proved that by continually increasing the amount of hydrochloric acid in the electrolyte, continuous solution of the gold anode without any evolution of chlorine gas could be obtained at current densities which were six times greater than those which I formerly considered as normal; but less than one-half was sufficient for practical purposes, i. e., for an operation in which from any quantity of impure gold, 80 to 90 per cent of the total contents of gold are precipitated in the morning, if the plates had been placed into the baths the afternoon before. Only in this improved form the electrolytic method was able to completely replace the chemical method which up to that time had been used exclusively for the same purpose. That the substitution of the electrolytic for the chemical method was advantageous has been recognized first by the largest German parting plant, the Deutsche Gold und Silber-Scheideanstalt (vormals Roessler), in Frankfort-on-the-Main, many years after the introduction of the electrolytic method by the Norddeutsche Affinerie. In the Frankfurt plant the chemical method had been used for a long time for parting platinum from gold, it had been developed there to great perfectness, and had been employed on the largest scale. Since 1896, however, this chemical method was given up, and the electrolytic method was introduced instead, and the latter has since been used continually for refining of gold won in the plant.

Dr. Tuttle, in his article mentioned before, also calls attention to the very simple method of recovering all platinum contained in the gold as one of the advantages of the electrolytic method.

For the same main purpose, i. e., for refining gold containing platinum, the Royal plant of Freiberg-Halsbrücke has installed in May, 1903, a smaller electrolytic plant, in which four months after erection more than 6 kg. of pure platinum had already been won.

It seems not superfluous to discuss somewhat more in detail the question how far a method for completely parting platinum and gold can be of practical importance.

Wherever exists an industry of noble metals the scrap from such industries represents an important object for the work of the parting plants. In this scrap a certain, not negligible, content of platinum will be present, for the reason that the manufacture of vessels which consist entirely or partly of platinum, or which are covered with platinum, takes place often at the same places as the manufacture of gold and silver articles. As a result, scrap will contain the three metals in various quantities. In view of the high price of platinum every well-conducted parting plant must endeavor to win the total content of platinum, besides gold and silver from the mixed scrap. This will be especially necessary if the parting plant has to pay for the platinum.

But this more incidental and irregular occurrence of platinum does not represent the richest of the sources from which platinum comes into the plants devoted to the parting of gold and silver. It is well known that in nature at many places gold and platinum occur together. In this way platinum contained in gold, together with its kindred metals, iridium, palladium, rhodium, etc., is supplied from the gold mines to the parting plant. Less attention appears to have been paid to the fact that even at places where platinum, iridium, etc., are not found separately, the gold and silver found in nature have been found to contain platinum.

More than fifty years ago Max Pettenkofer discovered the

content of platinum in the noble metals, and stated that "all silver which is found in trade and which does not come directly from a parting plant, contains platinum, so that this metal, which has been considered as extraordinarily rare, can be obtained in larger and profitable quantities if the silver is subjected to a process in which the platinum remains in the residue, that is, on a large scale in the treatment with sulphuric acid and in amalgamation." Pettenkofer would add to-day, "and in the electrolytic method of parting silver containing gold."

As far as I know quantitative determinations of this contents of platinum in silver, or in gold, won from silver, have never been published, and in the literature I cannot even find notes which would confirm the statement of Pettenkofer that all silver which occurs in nature contains platinum. It should, therefore, be of interest to give here some data for which I am obliged to Mr. Ludwig Opificius, chief chemist of the Deutsche Gold-und-Silber-Scheideanstalt in Frankfurt.

At the time when a uniform system of money was introduced in Germany the largest part of the old German coins were melted and the melted metal was subjected to a parting operation. At that time Mr. Opificius tested the various kinds of silver coins and also several sorts of silver obtained from metallurgical plants, and determined the content of platinum in quantities of silver between 5 and 10 kg. The results obtained by him are given in Table I. (I add for the greater convenience of comparison figures for the content of gold which was determined simultaneously from smaller quantities, as far as they have been placed at my disposal by Mr. Opificius):

TABLE I.

		Gr. gold.	Gr. platinum.	Gr. platinum per 1 Gr. Gold.
10 kilogram	French Laubthaler.....	...	0.016
5 "	French Laubthaler.....	...	0.009
5 "	Spanish Säulthaler.....	2.8	0.011	0.0039
10 "	Coins, each 1/6 thaler.....	4.5	0.025	0.0055
10 "	Coins, each 1/6 thaler.....	4.5	0.0225	0.0050
10 "	Coins, each 1/3 thaler.....	2 to 3	0.0275	0.0110
10 "	Thaler	0.0145
10 "	Thaler	0.0245
10 "	Prussian Thaler.....	6.2	0.016	0.0026
	(from 1820 to 22)			
10 "	Conventionsthaler	6.5	0.0165	0.0025
10 "	Conventionsthaler	6.5	0.0180	0.0028
10 "	Kronthaler	7.6	0.0250	0.0033
10 "	Kronthaler	7.6	0.0245	0.0032
10 "	Coins, each 20 kr. (Austria).....	1.5	0.0135	0.0050
10 "	Coins, each 20 kr. (Austria).....	4.8	0.0220	0.0046
10 "	Iambos	2.2 to 4.7	0.0300	0.0136—0.0073
10 "	Iambos	0.0365
10 "	Emser Silber	4 to 6	0.029	0.0058
10 "	Emser Silber	0.029
10 "	Eschweiler Silber.....	5 to 10	0.0482	0.0096—0.0048
10 "	Eschweiler Silber	0.0477

The average of sixteen determinations in Table I. shows, therefore, that gold parted from silver by means of sulphuric acid or electrolysis contains 6 milligrams of platinum per one gram of gold. This corresponds to a value of about \$1.00 for each 10 ounces of gold.

Mr. Opificius has not published these figures, because in dissolving the silver in his experiments, concentrated sulphuric acid was used. According to investigations made at a later date this acid can never be considered as free from platinum if it was concentrated in platinum vessels. It is, therefore, possible that a part of the platinum which was found came from the acids; its amount cannot be estimated; the same suspicion might also be raised against the observations of Pettenkofer. No investigation has as yet been made whether in parting silver by means of sulphuric acid containing platinum, platinum is really precipitated.

I do not think it is probable that the quantity of platinum which in this way is added to the original content of platinum in the noble metals is an appreciable amount. In the Norddeutsche Affinerie, in Hamburg, gold and silver were parted exclusively by means of sulphuric acid up to 1894; in the next years this method was replaced by the electrolytic process with the use of a nitrate solution, first only to a small degree, later on nearly completely. The material of the parting operation was essentially the same before and after 1894; all

gold which was obtained was afterwards treated to win the platinum from it. If a considerable amount of the platinum obtained in this way had come from the use of sulphuric acid the total quantity of platinum recovered should have decreased in considerable degree as a consequence of the introduction of the electrolytic process. From the record books of the Norddeutsche Affinerie, however, such an influence has not been found at all. The figures of Mr. Opificius may, therefore, be considered as not completely certain for the circumstances mentioned, but there is no reason why they should not be considered as approximate figures for the real content of platinum in the tested sorts of silver.

These figures relate, as can be easily seen, to silver with a relatively small content of gold, which was not parted at that time since the small quantity of gold would not have paid for the cost of the operation of parting by the method in use at that time. The investigations of Pettenkofer also appear to refer mainly to silver poor in gold. From the experience of the German parting plants, however, there is no doubt that the content of platinum is not limited to such sorts of silver poor in gold. It seems very probable that American silver is no exception from this general rule. Up to the present I have tested only a few products of American silver parting plants, but have found in them platinum without any exception, and in some a relatively high content of platinum.

Considering the large quantities of noble metals in various mixtures which are produced every year in the United States, we may conclude from the facts mentioned that very considerable quantities of platinum are supplied to the works which part gold containing silver or silver containing gold. In view of the present market price of platinum we must assume that the income of the producer and refiner would be increased by a considerable amount if the platinum would be extracted from the gold in which it is contained. One more reason why this extraction should be carried out is that while for his main purpose the refiner may not need to undertake the recovery of platinum, yet he cannot avoid to separate this substance if it is present in his gold. Even before it was known that platinum exists in pure gold, refiners used to remove the unknown impurity by repeatedly melting with potassium nitrate, and the same method is to-day used by those who want to get as pure gold as possible without parting the platinum from it by a special process.

The presence of platinum in any considerable quantity results in a certain quantity of silver being retained in the gold in such a way that it cannot be removed by the ordinary methods of parting. Moreover, where there is platinum there is very often also a certain addition of iridium, which, even in very small quantities, renders the gold brittle. These disadvantages can, indeed, be overcome by melting with potassium nitrate. One obtains by this method nearly pure gold, since platinum and iridium with a small quantity of gold pass into the slag, from which the platinum may then be obtained in a somewhat roundabout way, which has already been described by Pettenkofer. It may be doubted that this method is used to any extent in the United States, either by the producers of gold or by the parting plants to which the slag is sold. It is at least certain that scrap of various kind is exported every year abroad containing, besides gold, very considerable quantities of platinum.

It seems superfluous to remark that in comparison with a process by which, as described, an obnoxious although valuable impurity is simply removed, another process is preferable by which the valuable impurity is not merely removed, but recovered in a simple way. If we apply this general remark to the refining of gold it means that the rational solution of the parting problem must consist in a process by which the gold is obtained in an entirely pure condition, while the total platinum which was present in it is also recovered.

For this purpose, since Pettenkofer's discovery, the repeatedly mentioned chemical method has been in use which

had also been suggested by Pettenkofer. The impure gold is dissolved in aqua regia, and from the dilute solution the gold is precipitated by protochloride of iron, free from platinum, etc. The solution from which the gold has thus been removed, is treated with metallic iron, and all platinum is thereby precipitated, first mixed with most of the other impurities of the gold. The advantages of the electric process, in comparison with this method, are of a manifold nature.

Whoever has been accustomed to dissolve larger quantities of gold every day in a mixture of hydrochloric and nitric acid, making use of more or less good ventilation, will scarcely consider it a disadvantage that in this process it is impossible to avoid the enormous development of gases and vapors of horrible smell and detrimental to health. Nevertheless, I have not yet found anybody who was accustomed to this disadvantage and who was not pleasantly surprised when entering the working room of a gold electrolytic refining plant and found that here a continuous solution of gold took place under the action of the current in open baths without the slightest development of smelling gas. It may be claimed that in our days the possibility of replacing an industrial process by another one which is better in hygienic respects, and has no other disadvantages, represents a serious consideration in favor of the latter. Of greater importance, however, will be the proof that the new method is also superior in diminishing the cost. I believe that the electric method of gold refining fulfills this condition.

The consumption of acid is more than fifty times greater with the chemical method, and against this main item of cost there is, on the side of the electrolytic process, only the cost of electric energy, of which a very small amount (about 300 watt-hours per kg. gold) is sufficient. For wages an amount is to be charged which is certainly not higher than for the work with aqua regia, especially since in accordance with the nature of the process, the work is not interrupted during the night, but is so arranged that that part of the electrolytic action which needs no attendance whatever, goes on during the night hours; for the manual work which is to be done during the day hours not more than one workingman is required for the treatment of 50 kg. (of rather pure gold). An estimate of the wages will, therefore, give a result in favor of the electric process even if a proper interest is charged for the continual stock of gold which is required for the electrolytic process, and if an extra charge is made for melting the scrap of the anodes and of fine gold serving for the cathodes.

Of the other advantages of the electrolytic process I briefly mention the greater chemical purity of the obtained gold, the essentially greater simplicity of recovering the platinum, and the complete separation of platinum from iridium and other platinum metals.

Platinum can be obtained directly by the chemical process only if the content of platinum in the gold is very high; it is the more complicated the smaller the quantity of the platinum in the gold. In the electrolytic process very small or very large quantities of platinum in the gold anodes pass into the electrolyte with equal facility, and the production of platinum from the electrolyte is always direct.

By the treatment with aqua regia a part of the iridium is dissolved together with platinum, iridium being nearly always present where there is platinum. From such a solution containing iridium, the platinum is then precipitated mixed with iridium if one does not use a specially complicated method for parting the two metals. On the other hand, platinum which has accumulated in the electrolyte, and which is obtained from it by precipitation, is absolutely free from iridium, because the latter is not dissolved from the anode by the action of the current. Iridium and osmium-iridium, which are present in gold, accumulate therefore completely and free from platinum in the anode sludge and may easily be obtained from the latter.

After all that has been said, the electrolytic process of refining gold appears to be especially suitable for overcoming a deficiency in the chemical and electrochemical industries of the United States; this deficiency is the non-winning of platinum present in gold. The production of platinum, as recorded by American statistics, certainly does not differ very much from a complete lack of production of platinum.

According to the statistics in Rothwell's *Mineral Industry*, the total production of platinum in the United States during eight years was as follows:

1895.....	150 ounces.
1896.....	162 "
1897.....	200 "
1898.....	300 "
1899.....	0 "
1900.....	173 "
1901.....	1408 "
1902.....	94 "

If we neglect the exceptionally high output of 1901, the average production was 154 ounces per year. The output of the year 1902 is the lowest on record since the statistical data on the production of platinum in the United States were undertaken. That the above quantities of platinum are parted from gold is said on page 569 of volume 7 of *Mineral Industry*. But the relatively high quantities of iridium which are mentioned side by side with platinum, justify the supposition that the produced platinum was not the result of a real refining process of gold, but came from the treatment of a mixture of gold with platinum ore. On the other hand, there cannot be any doubt that such refining processes are carried out in the United States on a very large scale, and cannot be carried out, or, at least, will not be complete without the separation of platinum. It would be interesting to find out what has become even only of those quantities of platinum which were won together with gold in the anode sludge, since the introduction of the electrolytic treatment of silver, and which were parted from the gold during the treatment of the sludge.

What has happened to platinum during this time has also happened to the corresponding quantity of iridium, since in gold containing platinum, iridium is nearly always present.

Much greater is probably the amount of palladium which was obtained at the silver anode of the Moebius refineries, but was not won from the sludge. It is known that in the Sudbury district in Ontario copper ores containing nickel are won and treated which also contain platinum and palladium in no small quantities, and that in these ores the content of palladium is very near to that of platinum. It was probably raw copper produced from these ores which was treated more than twenty years ago in large quantities in Hamburg under my direction. By electrolytic treatment of the copper, an anode sludge was obtained which was surprisingly rich in palladium. Together with the platinum which was also present, it was collected by a metallurgical process in silver containing gold; it was separated from the silver together with gold; as part of the gold anodes it passed into solution during electrolysis and from the solution it was completely recovered in pure form.

There is good reason to believe that the Sudbury ores are not the only ones in America in which the quantity of palladium present together with platinum is considerable. I do not know the price of palladium in the United States, but I know that one of the most prominent platinum factories of Germany pays at present 2,000 marks (\$476) for one kilogram of palladium. It is therefore possible that if palladium is present, the value of the material thrown away with the ordinary parting method is very considerable. This amount could be easily recovered by the use of the electrolytic method.

In a second article the electrolytic separation of gold from gold alloys will be dealt with.

Hamburg, Germany, May 5, 1904.

ANALYSIS OF REFINED COPPER.

In our March issue, pages 87 to 95, we published a paper on "a laboratory study of the stages in the refining of copper," presented by Messrs. H. O. HOFMAN, C. F. GREEN and R. B. YERXA to the American Institute of Mining Engineers. With reference to this paper, Mr. LAWRENCE ADDICKS has communicated to the secretary of the Institute some interesting critical notes which have just been published. Mr. Addicks starts with the statement that the excellent series of photomicrographs given in the paper referred to (pages 89 and 93 of our March issue) shows clearly the relation between micro-structure and cuprous oxide in refined copper. The authors suggest that this method of examination might be substituted for the "button" method now used to control the refining of copper and that, with the aid of a planimeter, it might displace the present tedious methods of analysis for oxygen-content.

Mr. Addicks points out, however, that the photographs of the button-fractures (page 91 of our March issue) show that the fracture at various stages is quite as characteristic as the micro-structure—which is to be expected, as one depends upon the other—and to a practiced eye enables the process to be followed as closely as would be possible with micro-samples, except toward the very end of the poling operation. But at that stage we have the surface or set of full-size castings to guide us. He emphasizes the fact that it is not a certain percentage of cuprous oxide in the casting which is sought, but such a quantity as will give a mechanically perfect product. This quantity varies through a very small range depending upon the size and shape of the casting. The pitch is easily brought close to the proper point with the guidance of the buttons, and any final adjustment made by judging the surface of a larger casting. The pitch is easily brought close to the proper point with the guidance of the buttons, and any final adjustment made by judging the surface of a larger casting. Personally, Mr. Addicks says he cannot see that the use of micro-samples would give any better guidance, and with anode copper in which are varying quantities of numerous impurities, the micro-structure would not be so readily interpreted.

As to the tediousness of the analysis for oxygen, Mr. Addicks says the simplest way to avoid this is to omit it altogether. The buyer of refined copper wants two things—satisfactory electrical conductivity and a mechanically perfect casting. The conductivity is specified because so much copper finds its way into electrical uses. The purchaser relies on the conductivity requirement to give him a copper so pure that it has satisfactory physical properties, and any analysis of refined copper is rarely necessary. Small variations in pitch are noticeable in the set of the castings long before the conductivity is appreciably affected. In regard to the development of the structure of samples of copper, he has had good results by treating the specimens for about 30 seconds in boiling aqua regia diluted with an equal volume of water. Under this condition comparatively little preliminary polishing is required.

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS.—The report of the Board of Directors at the recent annual meeting shows that the Institute is in a flourishing condition. With the present month the membership has reached the remarkable figure of 3,000, while it promises to run up very soon to 3,300. The rate of increase in membership is now between 800 and 900 new members per year, which is a very high figure. The building fund for the Institute's share in the Union Engineering Building project has already passed the mark of \$60,000, due to the splendid response of members to the request for contributions. The new president is Mr. John W. Lieb, who has been connected with Mr. Edison in his first electrical undertakings; he is at present third vice-president and associate general manager of the New York Edison Co. Like the American Electrochemical Society, the Institute will take a prominent part in the International Electrical Congress in St. Louis in September.