THE USE OF ELECTROLYSIS IN TECHNICAL CHEMICAL PROCESSES.[1]

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TECHNICAL chemistry covers a very wide field stretching from metallurgy on one side to the production of the most delicate colors and odors on the other, in all of which, possibly, electricity is destined to play a part although up to the present time it has only been used to any important extent in the division including the chemical side of metallurgy. Here by far the most notable examples of its use are in the purification of copper and in the extraction of aluminum.

The electrolytic separation of pure copper from crude copper is substantially only a large expansion of the old processes of electrotyping and electroplating, and therefore does not offer much which is novel, but the production of aluminum from its oxide is a typical example of an electro-metallurgical operation. I propose, therefore, to describe somewhat in detail the method employed as it will serve to indicate the steps and precautions to be observed in the applications of electrolysis to other metallic compounds.

The electrolytic production of aluminum is an industry only five years old, but in that short period it has completely revolutionized the manufacture of this metal; indeed it is to-day the only successful method and will probably remain for a long time without a competitor. In this country the process is carried on only by the Pittsburg Reduction Company, at New Kensington, Penna., which manufactures under broad patents granted to Chas. M. Hall, the discoverer and patentee of what is now generally known as the Hall process.

The very important discovery which is the foundation of this method is the fact that oxide of aluminum is soluble in certain double fluorides in a fused condition, the salt which operates the best for this purpose must be composed of fluoride of aluminum and of a fluoride of a base more electro-positive than aluminum; sodium, potassium, and lithium fulfill this condition, but on account of expense fluoride of sodium is preferred. The

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mineral cryolite $Al_2Na_6F_{12}$, or as it may also be written Al_2F $(NaF)_6$, is a native fluoride coming within the requirements of the class of double fluorides necessary and it forms the principal solvent used. Only, as its melting point is somewhat high, it is an advantage when not operating on a very large scale to add to it small amounts of other fluorides to bring down the fusing point.

Cryolite will dissolve more than twenty-five per cent. of its weight of alumina forming a clear and colorless solution from which the metal can be readily electrolyzed.

There are some features of theoretical interest about this act of solution, for that it is a solution rather than a chemical compound there can be no doubt. Alumina when added to the melted salt dissolves quietly without effervescence or any manifest evolution of heat, resembling in all respects the solution of salt or sugar in water. But alumina is not appreciably soluble in melted sodium fluoride, and aluminum fluoride by itself is infusible except at extremely high temperatures. The presence of both fluorides is absolutely essential. The two fluorides may be taken initially as a double salt or they may be separately mixed with alumina, the final result is the same, *viz.*, the perfect solution of the oxide.

The electrolytic decomposition of the dissolved oxide is carried out on a manufacturing scale by using carbon electrodes. A rectangular vessel made of iron boiler plate is lined with compressed carbon to a thickness of from four to six inches. This constitutes the negative electrode, the positive electrode is formed of carbon rods three inches in diameter by twelve in length, suspended by copper rods from a horizontal copper arm above the iron vessel. The number and disposition of these carbon anodes depends on the scale of the operation. They are hung so that they will terminate about one inch from the carbon lining, and the purpose of suspending them is that they may be easily removable one or two at a time without stopping the whole current going through the apparatus.

The iron vessel is called the pot. The melted cryolite the bath, or when it holds alumina in solution is often termed the electrolyte.

To start the operation some powdered cryolite or the mixture of double fluorides is placed on the carbon lining which is cold. The carbon anodes are then lowered till they make contact with the lining, much local heat being at once produced partly by the resistance of the carbon at the points of contact and partly by numerous short arcs formed where apposition is not perfect. This heat soon melts some of the bath material which flowing between the electrodes adds its own resistance thereby increasing the heat because there is now a larger cross section of conductor and consequently more current carried. In this way the bath material is fused and the pot finally filled. The pot may also be initially charged with melted cryolite ladled into it from a separate melting pot.

During this period while the bath mixture is fusing electrolysis is necessarily going on but it yields only a small quantity of aluminum, probably because of the access of the air and also because any fluorine potentially or actually liberated finds some of the metal in a finely divided and diffused condition with which it reunites.

When a sufficient volume of melted bath is secured the second or permanent stage of manufacture begins, powdered alumina is spread over the top of the bath and periodically stirred down into it. It dissolves almost immediately and normal electrolysis takes place. Aluminum is deposited in a melted condition at the bottom of the bath against the negative electrode, while the oxygen which is transferred to the positive side.burns the anodes escaping as carbon monoxide and carbon dioxide. The anodes are thus consumed and must be from time to time pushed down further into the bath. The melted fluorides are not electrolyzed and may be used over and over again indefinitely, it being only necessary to add enough to supply the small losses principally of a mechanical nature occasioned by the removal of the metal. The operation is strictly continuous, alumina is added on the top of the bath and the metal is ladled out from the bottom.

There is quite a complicated adjustment of chemical and electrical forces concerned in the successful electrolysis of alumina which are interesting from the stand point of pure science.

The current employed by the Pittsburg Reduction Company is 7000 amperes. In order to send this through a bath of melted fluorides only, with the usual current density requires fifteen volts, but as soon as alumina is added the pressure promptly falls to from six to seven volts which is that necessary for the normal working of the process. This E. M. F. is obviously consumed in two ways: First, by the force of polarization necessary to break up a molecule of Al_2O_3; second, by the fall of potential due to the resistance of the anodes and of the bath. It is possible to calculate this work both in chemical and in electrical measures.

The heats of formation of one molecule each of the bath constituents is as follows:

Sodium fluoride	109,700 calories
Aluminum fluoride	550,000 ''
Aluminum oxide	388,920 ''

The electromotive force of decomposition depends, as is well known, on the equivalent and not on the molecular weight and these will be $Al_2O_3 = Al_2F_6 = 6\ (NaF)$.

The energy of 22,900 calories is proportional to one volt, according to Sir William Thomson, therefore the E. M. F. of decomposition will be:

Sodium fluoride..	$\frac{109700}{22900}$ = 4.8 volts
Aluminum fluoride	$\frac{550000}{22900 \times 6}$ = 4.0 volts
Aluminum oxide............	$\frac{388920}{22900 \times 6}$ = 2.8 volts

Thus the oxide of aluminum is the weakest body present and the only one to be decomposed provided the current density is not permitted to become too great.

The fact that no appreciable quantity of fluorine is given off, but only oxygen, when the pots are working at normal voltage and current is perfectly explained by the above theoretical values of the electromotive force of decomposition. The direct measurement of this force presents considerable difficulty on account of the variation of the resistance of the bath with its temperature, but the best estimates from actual measures show that the breaking stress of one-sixth of a molecule of alumina is certainly less than 3.5 volts. Thus the theoretical number is fairly well sustained by practical observation.

The fundamental conditions for the successful electrolysis of any metallic compound are then these: First, the metallic salt must be in the fluid state; second, if it is rendered fluid by a solvent then the electromotive force of decomposition of the salt must be less than that of the solvent; third, the current density must be carefully regulated. These statements apply equally to aqueous solutions and to baths rendered fluid by fusion. The double fluorides would seem to be the only substances which can fulfill these conditions on a commercial scale for aluminum.

The theoretical equation of the decomposition of alumina by carbon is

$$Al_2O_3 + 3C = 2Al + 3CO$$

which would require about two-thirds of a pound of carbon for each pound of metal produced. Now, in the electrolytic process one pound of carbon anodes is lost for each pound of metal, the slight excess over theory being due to some combustion of the carbon by the air above the surface of the bath. The yield of metal is one pound of aluminum for 18.1 electrical horse power hours. This energy, it must be remembered, is spent both in causing decomposition and in maintaining the temperature of the bath, which is about that of the melting point of copper.

Taking the voltage of the baths as 7, then 18.1 electrical horse power hours represent a continuous flow of 1,926 amperes for one hour. This would theoretically deposit 1.43 pounds of aluminum, so that the actual yield is seventy per cent. of the theoretical ampere production. This must be considered fairly satisfactory. Of course the yield calculated on the total energy consumed is considerably less than this, owing to the large fraction which is turned into heat; but this loss must be set over against the consumption of fuel in ordinary metallurgical work where it is burned solely to produce heat.

Another example of the application of electrolysis to an important industry is the refining of gold and silver, but more particularly silver. The practical details as carried out by the Pennsylvania Lead Company, of Pittsburg, Pa., under the Moebius process are as follows:

Tanks are made and divided into compartments so that they may be connected up in series. The unit compartment is 18"x 24"x 17" deep, and seventy of these are in the circuit at one time. Each compartment has three anodes, 10"x 20"x ⅛", and four cathodes of about the same area as the anodes. The anodes are composed of the metal to be refined which will average 990 fine in silver, the rest being mainly copper, lead, bismuth with a little gold. The cathodes are thin sheets of pure silver. The surface exposed in each compartment, reckoning both sides of the plates, is twenty square feet, or 1,400 feet for all the tanks. The anodes are hung in a bag to catch the insoluble material which drops from them. The electrolyte is a dilute nitric acid as free as possible from sulphuric acid or chlorine. A current of 180 amperes is used and the voltage required by each compartment is 1⅓ volts. The consumption of nitric acid (36° B.) is about two pounds per day for each compartment. The amount of silver deposited is, in practice, about 470 ounces per twenty-four hours in each compartment, which is equal to 1.35 pounds avoirdupois per hour. This includes all interruptions of current for all reasons. The total amount of silver refined per day is 32,900 ounces, or practically one ton. This is eighty-four per cent. of the theoretical yield for 180 amperes working the same length of time without any interruption whatever. The product is practically silver 1000 fine.

The success of this operation depends evidently on the difference of the electromotive force of silver against nitric acid, and of copper, bismuth, and lead against nitric acid, silver being the lowest. But the difference between silver and copper is not great, and a very careful regulation of current density is necessary, which, however, can be attained, making this method one of the neatest applications of electro-metallurgy and one which replaces the tedious cupellations necessary by the older process which has come down from the middle ages.

Another application, which is wholly chemical, has recently been made to the purification of sewage near New York.

Many attempts have been made to produce caustic soda and chlorine, or bleaching compounds, from common salt by electrolysis; but thus far they have not advanced to the stage of industrial success. One of the chief reasons for this is because no insoluble anode has been discovered, for in strong solutions platinum is dissolved and carbon is oxidized and corroded; but when the liquid is weak this trouble with the anode is considerably lessened. A report by Dr. Cyrus Edson, of the Health Office, New York City, partly reprinted by the *Electrical Engineer*, gives an account of a successful experiment recently made to disinfect the sewage of the village of Brewsters which was finding its way into the city water supply. Mr. Albert E. Wolf proposed to accomplish the purification of the sewage by treating it with electrolyzed sea water. A current of 700 amperes by five volts is delivered to the water as it flows slowly past seven electrodes. Of these, four are carbon, 12"x12"x1" thick, while the anodes are copper coated with platinum. The flow of the solution is so limited that the salt water is electrolyzed to the proper degree and then overflows from the tank directly into the sewer. The disinfection is practically perfect. Tests show that this electrolyzed sea water equals in strength a one per cent. solution of chloride of lime. In the matter of cost the treated sea water costs 0.01 cent a gallon, while a one per cent. solution of chloride of lime costs 1.4 cents per gallon, or the sea water costs only $\frac{1}{140}$ of the lime. Compared with the cost of corrosive sublimate, the latter is one hundred times as expensive for an equal efficiency, while carbolic acid costs from two to three hundred times as much.

Other applications which have been tried and are now on their way to commercial development are: Bleaching fabrics without chlorine by means of electrolyzed acidulated water only, and the tanning of hides.

Seeing that in electrolysis we have a powerful analytic force at work heaping up products of decomposition at each pole, it would be natural to look for some means to utilize the powerful oxidizing and reducing actions of which the electrodes are the foci. This would be to save and turn to useful account the secondary reactions of the cell. A careful study of the conditions under which these secondary actions are a maximum and a minimum can scarcely fail to lead to many applications of the current in technical chemical work where electricity will be used primarily as an oxidizing or a reducing agent and only secondarily as an agent for electrolytic decompositions.

There is one great desideratum, and that is a cheap insoluble anode. Platinum is too expensive, and carbon will not long withstand oxidation. It is this lack which to-day, among other conditions, prevents electricity from being a rival to the ammonia process of making soda and to the Leblanc process for producing bleaching powder as a by-product, and to its utilization as an oxidizing agent. When the cheap insoluble anode is found it will open a wide door to the applications of electricity to the chemical arts.

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THE IODINE FIGURE OF ROSIN.

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IN the analyses of oils, and especially drying oils, one of the most useful tests is a determination of the Hübl number. The iodine figure of rosin, which is a common adulterant of oils, is stated by Benedikt (Analyse der Fette und Wachsarten, 171) to be 115.7; Williams (*Chem. News*, **58,** 224) gives 115.31 and 114.80 for refined rosin and 112.01 and 113.28 for ordinary. Mills (Destructive Distillation, 13) has determined the bromine absorption to be 112.7 per cent., which would correspond to an iodine absorption of about 179. In order to throw some light on the causes of this disagreement, experiments were made to ascertain the effect of different amounts of iodine in excess, different times of absorption and different qualities of rosin.

Five samples were used representing different grades from "W.W." (water-white) rosin to "A" (black).

In the tests made to ascertain the influence of time and of excess of iodine the rosin used was that known as W.W., which is the best grade in the market. The iodine solution used contained twenty-five grams of iodine and thirty grams of mercuric chloride per liter, and the thiosulphate solution 24.8