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EDITORIAL

The classical development of the dye-stuff industry in Germany which in its later stages acquired control of the chemical industries of the greater part of the world illustrates the role of organized research in maintaining the vitality of modern industries. The success of the German industry spurred other countries to imitate its policy. The phenomenal expansion of the technical industries in Western Europe and America which began in the last quarter of the 19th century initiated in turn a revolutionary change in the pattern of scientific research. The amateur scientist gradually disappeared from the scene and gave place to the professional who became increasingly dependent for support on Governments or organized industrial groups. The growing complexity and volume of scientific knowledge was another important factor which contributed to the emergence of large research laboratories organized by industries. The individual scientist, however gifted, could not hope to keep pace with the volume of new knowledge which rapidly accumulated in the cognate sciences.

The extensive field covered by German industrial research was also a major contributory factor to Germany's pre-eminence in science, though the importance of the spirit of competition among men of unrivalled intellect in the different German Universities cannot be underestimated. The Garung Institute in Berlin organized and maintained by the beer manufacturers of Germany stimulated the study of fermentation processes and led to discoveries of fundamental scientific importance, while the parallel Zucker Institute advanced knowledge in several fields ranging from chemistry to agriculture. Some of the most significant developments perhaps were in the field of electrical technology, where application followed close on the heels of scientific discovery. The establishment of the Reichsanstalt for the promotion of research in the physical sciences was responsible to a good extent for this expansion of the electrical industry in Germany. The application of electrical processes in chemical industries was however, soon to pass to the U. S. A. where the enormous development of cheap electric power and the research laboratories of Weston, Edison, Bell Telephone and the General Electric Co., laid the foundations for a flourishing electrochemical industry.

The changing pattern of research organization has created problems that are of vital concern to all scientific workers. Large research institutes employing a diversity of scientific and technical talents have now come to stay. The creation of new fields of scientific endeavour lying in between the frontiers of the old disciplines is a phenomenon of frequent recurrence throughout the history of science. We may point to the new science of cybernetics as a recent example. It is evident that progress in such fields would depend to a great extent on the co-operation of workers trained in apparently unrelated subjects, and would be seriously hindered if the researches were confined to the individual efforts of scientists trained in one particular field. Elctrochemistry is one of the disciplines covering several regions and aspects of science. It may be recalled that one of the objects of the foundation of the Faraday Society in 1903 was to 'promote the study of sciences lying between chemistry, physics and biology'. This is still a good description of electrochemistry, although it cannot be denied that with the growth of knowledge in chemistry, physics and biology the field covered by electrochemistry has also undergone considerable expansion. Research laboratories in general have been classified into two groups[1], depending on whether all the problems are connected with one common subject or are of many kinds having no connecting link or bond of interest. The first type of laboratory has been named the uni-purpose or convergent type, in which the researches of many scientists specializing in diverse fields of science are concentrated upon certain specific groups of problems, such laboratories being considered likely to be the most powerful agencies for the production of scientific knowledge in the future.

It cannot, however, be said that the problem of individual versus team work has yet found a generally acceptable solution. Most scientists trained in universities with their strong individualistic tradition in research, have an ingrained resistance to the idea of team-work. Many eminent scientists like Kapitza still hold the view that a true scientist should carry out personally all the tasks associated with his research. At the same time it has to be conceded that individual research has certain limitations and weaknesses in the peculiar circumstances obtaining to-day. In research which calls for a great diversity of knowledge and skill, as in the fields we have mentioned earlier, the need for collaboration between specialists in solving the various aspects of the large and complex problems is obvious. In pasteur's famous saying "chance favours the prepared mind", it may be said that it is team-work which is the best means of ensuring that "prepared minds" skilled in specialised branches might seize on a chance observation which might otherwise be missed. Team-work inevitably increases the productivity of a brilliant scientist, because he would not then be limited to work which he could carry out with his own hands, but would be provided with opportunities of utilising the hands of juniors in working out ideas and methods of research of which he is a master.

The principal disadvantages of team-work are that the leader of a team may not actively engage in research himself, and that the work may not be sufficiently co-ordinated for each member of the team fully to appreciate the special aspect of the work entrusted to him and its relation to the problem as a whole. Either circumstance is inimical to real progress; new ideas arise only when the leader who plans the work 'thinks with his fingers' and alertness in recognizing the significance of observations comes only from an appreciation of the problem as a whole. The synthesis of indigo by Baeyer in the eighties of the last century with such simple apparatus as a number of clean test tubes and glass rods, and with his own hands may be quoted as a classical illustration of this. Team-work has, therefore, to be organized in such a way as to overcome these inherent weaknesses and the success that has attended recent researches organized along such lines in certain fields like the vitamins, hormones and antibiotics shows that it can be done. The prospects of future advances in electrochemistry may be said to lie in the collaboration of the chemist, the physicist and electrical engineer. The discoveries made in the field of electronics have opened the way for new adventures in this field. It has been pointed out[2] that improvements in electron tube life and performance would be of direct benefit to electrochemistry. Improvements in these and other types of tubes for industrial applications depend upon a better understanding of the chemistry of electronic processes and of the properties of electron-emitting surfaces. Here has risen a field where progress would seem to depend more and more upon the co-operation of the electrochemist and the electronics engineer.

The establishment of the National Laboratories marks a mile-stone in the organization of scientific research in India. The pattern on which they have been organized is one that adapts itself admirably to team-work on the right lines. The various divisions of the Central Electrochemical Research Institute, for example, represent so many self-contained units specializing in one particular aspect of electrochemistry. These units can work as separate teams on their own speciality, or when the problems embrace two or more specialized aspects, there may be appropriate combinations among themselves for the maximum productive effort. The conditions for creative work and progress are already there, and their fruition depends on the sustained labours and devotion of the scientific workers.

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* SOME VIEWS ON THE PRESENT POSITION AND FUTURE OF ELECTRO-METALLURGY IN INDIA

by

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The employment of electricity is so general in metallurgical operations that if the word electro-metallurgy were taken to include all applications of electricity to metallurgical processes, the field under review would be unmanageably wide. On the other hand it would be wrong to restrict the subject matter of this review to electric smelting, in contradiction to the views of Bray,[1] who states that electro-metallurgy comprises both electric furnace and electrolytic processes for the winning and refining of metals. To the scope as defined by Bray should, moreover, be added the direct production of alloys by either of the types of process. In accepting this definition, the author is deliberately excluding all uses of electricity in electric furnaces for straightforward melting, alloying or heat treatment as well as in ancillary processes such as welding. Within the fields defined, an attempt will be made to review the present scope and standing of electro-metallurgy, with special reference to processes which have already found application in India or which have potential applications in this country and should find use under the stimulus of the increased production of electricity by hydro-electric and efficient thermal stations, brought into being under the First Five Year Plan. Attention will be drawn *inter alia* to some of the subjects of research in this field recently under investigation at the National Metallurgical Laboratory.

On a world-basis, electro-metallurgy has advanced greatly in recent years. Some idea of the recent expansion and present status of electro-metallurgy is given by the figures for World Production of aluminium from 1905 onwards[2]:

1905	...	12,100 Tons (metric)
1910	...	43,000
1915	...	81,700
1920	...	154,300
1925	...	181,200
1930	...	268,100
1935	...	258,000
1940	...	818,000
1945	...	900,000
1950	...	1,342,000
1955 (estimated)		2,800,000

That the 1955 estimate is not in error is borne out by the actual figures for 1951 (1,550,000) and 1952 (1,900,000). The trend figures above omit the war years, when there was a somewhat unnatural expansion e. g. 1943 (1,950,000).

The small present dimensions of the electro-metallurgical industries in India were made clear in 1953 by Rama Char[3] in an article on 'The Development of the Electrochemical Industries of India'. At that date, the total connected load of the electrochemical-metallurgical industries (rather broadly defined) was only 40,000 kW. out of the national power production of nearly 2 million kW. The small load is partly explained by the higher cost of industrial electricity in India than most countries, say 0.5 anna per kWh. of 0.15 anna in Norway, where the electro-metallurgical load is heavy. This in turn is partly attributable to the present small provision of hydro-electric power, only 30 per cent of the total, but

* Paper presented at the Symposium on 'Electrochemical Processes and their Applications to Indian Industry, March, 1954.

the opinion is stated that costs will remain high whatever the means of production until a larger proportion of the generating equipment is locally produced for which 'the day is not far off'.

Rama Char foresees an expansion within ten to fifteen years of total production to 10 or 15 million kW., but apparently no proportionate expansion of the electrochemical-metallurgical industries can yet be envisaged, as will be seen from the modest expansion figures given in a table in his paper and extracted to show his ideas of the likely developments in the next few years:

Grade	Lump Rs.	Powder Rs.	
75/80%	890	845	per ton
70/75%	820	779	
65/70%	663	630	
45/50%	460	443	

These prices are well in line with the costs of ferro-silicon anywhere in the world, though it is true that they would not allow a margin for profitable exportation. When it is borne in mind that Bhadravati production is on quite a small scale there seems to be no doubt that ferro-silicon will be produced in India fully competitively once the advantages of larger scale production and cheaper power are available. Since ferro-silicon is to some extent an 'out price' com-

Name of Product	Present Demand Tons/Year	Existing Production Capacity Tons/Year	Additional Production Target Tons/Year	Requirements of Power kW	Requirements of Energy 10^6 kWh
Calcium Carbide	3,500	...	7,000	4,200	29
Carborundum	600	...	2.000	3,000	21
Ferro-silicon 75 % Si.	4,000	2,000	4,000	5,500	40
Ferro-chrome 60 % Cr	1,000 (est)	3,000	2,000	4,000	30
Aluminium	10,000	7,400	20,000	64,000	480
Special Steels	6,000 (est)	5,000	10,000	10,000	70
Pig Irons (Special)	1,750,000	...	84,000	27,000	236
				117,700	

modity amongst the ferro-alloys, there is no reason to suppose that this capacity for competitive manufacture will not apply to all ferro-alloys and indeed to all other electro-metallurgical products for which India has the necessary ore resources in reasonable proximity to surplus power.

In case it should be felt in any quarter that the present small scale of electro-metallurgy in India and the small expantion predicted by Rama Char are due to inability for electric furnace operations to be carried out efficiently and economically in India, of considerable importance is the recent statement of the Tariff Board[4] that it is no longer necessary to continue protection for the Indian ferro-silicon production industry, because production is regularly being effected at Bhadravati below the landed cost without duty of imported ferro-silicon. The Tarriff Board have fixed the fair prices, with a satisfactory profit to the producer, of the various grades of home-produced ferro-silicon as follows:

Whether Rama Char is right or not in foreseeing an expansion of electricity production to 10 to 15 million kW., it is clear that completion of the power and irrigation schemes under the First Five Year Plan is bound to result in some 2 million kW extra capacity. If we supposed half of this to be available for electro-metallurgy, we should arrive at a fantastic metals production potential, far exceeding anything which could be physically achieved because of limitations in mineral resources and/or facilities to work resources at the indicated rate : e. g. the electric energy would be sufficient to yield over 400,000 tons of aluminium or magnesium, or 2,500,000 tons of zinc or 35,000,000 tons of copper. The extent to which a number of ores are really likely to be available is estimated with considerable guess work, in the following table :

Metal	Ore	Potential Production tons per annum	Metal content Tons
Aluminium	Bauxite	100,000	25,000
Chromium	Chromite	40,000	15,000
Copper	Chalco pyrites	40,000	8,000
Iron	Iron ore	5,000,000	3,000,000
Magnesium	Magnesite (Also sea-water)	1,000,000	200,000
Lead	Lead Zinc ore	...	1,500
Manganese	Manganese ore	2,000,000	600,000
Titanium	Ilmenite	250,000	50,000
Zinc	Lead-Zinc ore	...	1,500

Electro-metallurgy employs electric current both for furnishing heat and for electrolysis of solutions which may be aqueous or igneous. The aqueous solutions may be the direct product of hydrometallurgical leaching of ores or solutions of salts or impure metals formed in one or more stages from the ore.

It should perhaps be pointed out, though it will be no new observation to those familiar with the subject, that electrolysis is not the only means of dealing with metal values which have been taken into solution, whether direct from the ores or from products obtained by deliberate refining steps or as scraps from other production or service. The principal alternatives are (1) sedimentation with added metals which may be carried out in progressive stages where the solution contains ions of several metals, (2) precipitation by reduction with hydrogen, as in the 'Chemico' processes[5] for copper, cobalt, nickel, etc., or by other chemical means, and (3) evaporation to crystallise out salts which can be employed directly or reduced to the metal. Whether electrolysis is cheaper or produces a more saleable product than these alternatives is not a question with one general answer but one which must be considered in relation to the circumstances applying in the particular field. For example, use of iron to precipitate copper is frequently an economic process, while sedimentation by means of added 'grain' of the principal metal present is one of the commonest methods of purifying solutions from other metals ions. The use of hydrogen in this connection is fairly new. In the Chemico processes oxygen is used to assist pressure leaching of sulphide ores to sulphates. The hydrogen used arises from the electrolytic production of oxygen and is in consequence a cheap bye-product. For some metals carbon monoxide reduction suffices. Methods (1) and (2) are sometimes combined e. g. in dealing with a mixed copper, cobalt sulphate liquor at Garfield, the copper is sedimented out with part of the cobalt produced and the cobalt then reduced out with hydrogen; the scale is 2000 tons of cobalt powder per annum.

Some Indian Researches in Electro-Metallurgy

Work undertaken at the National Metallurgical Laboratory which falls directly under the head of Electro-Metallurgy includes the following items:

(a) *Study of the Preparation of Metal Powders*: The conditions were investigated in which brittle cathodes of iron can be electrodeposited, which can then be milled to powder.

(b) *Preparation of Electrolytic Manganese:* Manganese metal of 99.5% average purity was produced by electrolysing a sulphate solution, preferably using cathode starter sheets of stainless steel with a flash deposit of copper. Means have been found of regenerating the solution by digesting ore in the presence of organic reducing agents, preferably saw dust. A pilot-scale plant is being set up.

(c) *Electrolytic Production of High Purity Manganese Dioxide*: 99/100% manganese dioxide was produced electrolytically from a sulphate bath operated at 80°C.

(d) *Production of Beryllia:* As a first step towards the production of beryllium metal, beryllia was deposited in a diaphragm cell from a solution produced via the treatment of beryl with sodium ferric fluoride.

(e) *Recovery of Nickel from Silver Refinery Waste Liquor*: As described in detail in another paper submitted to this symposium nickel and zinc metals and nickel plating salts were produced from simulated silver refinery waste liquor.

(f) *Titanium*: In view of interest in the electrolytic preparation of titanium from titanium trichloride baths, much effort has been devoted to efforts to prepare titanium trichloride.

(g) *High-temperature Electrolysis of Lead Sulphide:* With the idea of simultaneously producing lead and elemental sulphur, trials have been made of several possible containers. So far only one, fireclay fired at 1500°C, has offered promise.

In addition to the above items, several important investigations have been undertaken which represent indirect usage of electro-metallurgy.

(h) *Preparation of Aluminium-Silicon Alloys:* Silica-aluminium mixtures have been reacted in the electric furnace in the presence of cryolite to yield aluminium-silicon alloys of desired compositions. Here the energy involved in producing aluminium is employed at second hand.

(i) *Manufacture of Low Carbon Ferro-Chrome:* Electric furnace ferro-silicon was reacted in a basic-lined electric-furnace with chromite ore in the presence of fluorspar. Partial reduction of the chromite occurred, which was 90% completed by aluminium treatment of the slag. The product contained less than 1% carbon and 6 to 10% silicon.

(j) *Titanium:* The conditions for operation of Kroll's process were worked out on a 1-lb. scale. Here magnesium produced electrolytically is reacted with titanium tetrachloride.

There have also been many investigations into electro-plating processes and problems.

Ferrous Metallurgy: When we omit, as stated earlier, electric-furnace melting as such from our definition of electro-metallurgy a position is left in which what we have to describe is confined to developments in Mysore [6]

The electro-metallurgical developments which have taken place in Mysore are closely allied to the developments of hydro-electric stations in that State. The Sivasamudram power station was one of the earliest in India. This with the Shimshar hydro-electric station serves the needs of the Kolar Gold Fields. Those of the Mysore Iron & Steel Company at Bhadravati are met by the more recently established Mahatma Gandhi Hydro-Electric works at Jog. The combined rated production of these three stations is 142,000 kW., but fresh sources are having to be sought to meet a peak-demand of 183,000 kW. The electro-metallurgical activities at Bhadravati include the two Tyseland-Hole electric low-shaft furnaces each producing some 70 tons of high quality pig iron a day, ferro-alloy furnaces mainly engaged on producing ferro-silicon and equipment for electric-furnace production of duplex steel.

Electric pig iron shaft furnaces first came into use thirty years ago in Scandinavian countries[7] where shortage of metallurgical coke could be made good from cheap hydro-electric power. Since then, there have been notable advances, particularly the introduction of the Soderberg self-baking type of electrodes, but the total tonnage of iron made in such furnaces remains only a small proportion of the world total. On the basis of that content, the electric pig iron furnace becomes theoretically economical only when the price of 1 lb of coal is more than 3.7 times that of I kWh. of electricity, i.e. with the prevailing Indian industrial power cost of about 0.6 anna per unit, coal at up to Rs. 84/-per ton is theoretically more than competitive. If this were the whole story there would be no place for electric pig iron smelting in India, where coking coals are relatively plentiful (reserves of 2,000 million tons) and cheap. It is, however, a fact that Indian coking coals suffer from high general contents of ash and phosphorus which make it impossible to produce the highest grades of pig iron in the blast furnace; moreover, the coking coals are not well distributed through the country and are not reasonably accessible to the central and southern parts of India The electric pig iron furnace needs only about 800 lbs. of coal (which may be of almost any quality, with up to 50% volatiles) per ton of iron produced, its capital cost is smaller per ton of iron since it is not operated on blast and therefore requires no expensive blowing machinery, and the gas generated is of higher quality than from the blast furnace. It is also an advantage from some points of view that the electric pig iron furnace is efficient in relatively small sizes say with a power rating of 3,000 kVA. and a daily yield of 25 to 30 tons iron; there are however, much larger furnaces in operation including those of 12,000 kVA. In sizes up to this the power factor can be kept as high as 0.9. It is found that the maximum power is given at the lowest voltage and smelting conditions are in general best when the electrodes are arranged in a triangle and deeply submerged in the charge.

Walde[8] has given the figures for electric pig-iron furnace smelting of a difficultly reducible magnetite which are set out below. The ore contained 53 per cent iron and the fuel was a mixture with coke of a poor anthracite containing 62 per cent carbon and 8 per cent ash. The material balance was:

Input		Output	
Iron Ore	4,180 lbs.	Iron	2,240 lbs.
Manganese Ore	88 ,,	Slag	1,650 ,,
Limestone	616 ,,	Gas (diff.)	2,316 ,,
Anthracite/coke	1,122 ,,		
	6.006 lbs.		6,006 lbs.

The heat balance was:

Input	Thousand kcal	Output	Thousand kcal
Power (2,800 KWh)	2,400	Reduction of iron	1,600
Solid Fuel	2,280	Reduction of Si, Mn, P.	100
		Calorific value of gas	1,600
		Heat content of iron	310
		Heat content of slag	270
		Evap. & dissoc. of water	80
		Calcining limestone	120
		Sensible heat of gases	60
		Electric losses	180
		Conduction and convection losses	360
	4,680		4,680

It will be noted that even in this very efficient electric furnace operation only 34 per cent of the heat input goes to achieve the direct object of the process, reduction of iron. The electrical losses are somewhat exaggerated as they include the power used in baking the electrodes.

The lowest power consumption recorded in practice is 2,000 kWh. per ton of pig when smelting a pre-treated high grade Swedish ore.

As regards the class of iron produced in electric furnaces, it has already been indicated that phosphorus can be kept down, both by the selection of low-phosphorus coal and the smaller total quantity which must be used. The local intense heating in the electric furnace favours desulphurization. The electric furnace cannot easily be used to make the low-silicon iron preferred for steel making, which demands low temperature operation, but is particularly suitable for foundry irons, of which India has need of some 2/300,000 tons per annum. A typical composition is—4.5% C, 1.4% Si, 0.8% Mn, 0.08% P, and 0.01% S. Electric furnace pig iron production in India today is concentrated at the one site and amounts to less than 50,000 tons per annum. Despite what has been said above it seems likely to remain at or near this level, because when all is said and done, the iron produced in this way is quite expensive. There are at least two alternative ways of producing foundry-irons which may be more economical: (1) smelting ores with non-coking coals in the low-shaft furnace, and (2) recarburising steel scrap in a hot-blast cupola.

What has been said above regarding the improvement of quality which can be secured by electric smelting applies with even greater force to the case of ferro-manganese. Here, in the blast furnace some 50 cwt. of coke is used for each ton of product, so that unless hand-picked supplies of metallurgical coke from the best sources are available, a pick-up of some 0.5% or more phosphorus is usual, adding to the 0.2%-0.3% commonly derived from the ores. By specification and common acceptance there is little market for ferro-manganese of this quality on the world markets—though this is clearly a matter more of prejudice than technical merit, as will be seen from the following:

It is very rarely the case that more than 80 pounds of ferro-manganese is added per ton of steel in making ordinary steels and processes can readily be introduced which make 40 pounds adequate: it follows that 0.6% phosphorus in ferro-manganese cannot introduce more than 0.02% phosphorus to the steel and need not introduce more than 0.01% phosphorus. Electric-furnace ferro-manganese is a regular market commodity which commands a much higher price than the blast furnace grade and has the advantage of a low carbon content which allows the production of case-hardening steels and the Hadfield manganese steel.

Khedker[9] has recently referred to the manganese situation. India has exported nearly one million tons of contained manganese during 1952, or about 70% of the total requirements of American and European (excluding Russian) steel works. Since the manganese contents of the ores average well below 50 per cent, over 500,000 tons of shipping space were thus employed to no advantage. India might conceivably produce up to 400,000 tons of manganese as ferro-manganese etc, per annum, but at present she only makes what she needs for her own steel industries, namely 25,000 tons of ferro-manganese. It is strongly urged by Khedker that there be set up in India a plant handling low grade (25 to 30 per cent) manganese ores to produce 80,000 tons of ferro-manganese per annum plus superphosphate and pig iron. Such a plant might use Krupp-Renn kilns followed by electric furnaces. He estimates that the exportable surplus would bring in Rs. 6 crores in foreign exchange. This estimate is probably high but it is quite clear that there would be a very substantial gain, perhaps Rs. 4 crores, over exporting the ore to be consumed.

In the ferro-manganese field, as in that of pig iron production, the low shaft furnace, particularly when supplied with an oxygen enriched blast, is a serious competitor of the electric furnace.

Since reference has already been made to the ferro-silicon position, which is eminently satisfactory, this will not be discussed much further, but attention needs to be given to that of ferro-chrome and other ferro-alloys.

Production of ferro-silicon of the 75% grade is well established at Bhadravati, though the scale is small. There remains a need for the higher grades up to and including 95% ferro-silicon. This can be used for many purposes as an alternative to 'silicon metal' though its price is much lower. In connection with ferro-silicon manufacture, the Australian and European operators attach great importance to the recent development of the Ellefsen furnace[10] with a slowly-rotating hearth. This spreads the reaction and the heat throughout the mass and makes it easier to produce the higher grades.

Ferro-chrome is produced in India at Bhadravati but not as a regular product and the tonnage so far made has been quite small. The grade produced has been the standard high carbon grade with 4/6 per cent carbon. This is serviceable only for introducing chromium into low alloy steels with appreciable contents of carbon. As has already been remarked, the production of a lower carbon grade with less than one per cent carbon seems a practical proposition by employing ferro-silicon (75 per cent or better) to reduce chromite[11]. This does not produce quite such a high quality as the Perrin process but has the advantage of freedon from patent complications. The ferro-chrome produced in this way could be employed, with oxygen-lancing, for almost any metallurgical purpose, including production of stainless steels. In the writer's opinion there is a large future for materials of this class in India and a pressing need to increase the scale of production of ferro-chrome.

Another ferro-alloy of considerable importance in India is the so called ferro-cerium (really ferro-mischmetall) which can be produced from the monazite ocurring in Travancore beach sands. These typically have the composition[12]:

Ilmenite	)	per cent
Zircon	to 6	,,
Sillimanite	3 to 5	,,
Rutile	4 to 6	,,
Garnet	0.5	,,
Monazite	0.5/1.0	,,

The monazite may be concentrated by gravity methods and the mixed rare-earth metals extracted by chemical and electrolytic processes. The treatment of Indian monazite is the responsibility of the Indian Rare Earths Limited[13], a company with a subscribed capital of Rs. 80 lakhs of which 55% was put up by the Central Government, and 45% by Travancore-Cochin, *The Societe des Produits Chimiques des Terres Rares* are the consultants. The factory is designed to treat 1,500 tons of monazite per annum, yielding rare earths chlorides and corbonates and trisodium phosphate. It was built in 1951 and came into production in July 1952. The residual cake, containing thorium and some uranium is to be passed to the Atomic Energy Commission for processing in a factory which will be ready within 15 months. Some thorium will be processed to nitrate but the remainder of the thorium and the uranium are to be converted to metals of 'atomic' purity.

While it does not seem likely that any large-scale manufacture of ferro-titanium need be instituted in India, there may be a case for producing aluminium-titanium as an intermediate stage in making the metal or as a source-material for introducing titanium into alloys. This is however a 'thermit' rather than an electric furnace product.

Valuable deoxidants whose electric furnace manufacture in India should not be overlooked are ferro-silicon-zirconium and calcium silicide.

So far, on the ferrous side, attention has been given only to processes in which electricity is used for heating purposes in reduction processes. Electrolytic processes are also of importance, and it should be borne in mind that expansion of such processes demands special attention from the planners since, in these days, unless there are special requirements to the contrary, current is always generated as a. c., while d. c. is wanted (principally at least) for all electrolytic processes.

An aspect of iron-making which is of more technical than commercial significance, and hence does not always receive the attention which it merits, is the production of special high-quality iron melting-base for the fairly small scale manufacture of high-alloy steels in induction furnaces and for the introduction of iron into non-ferrous alloys. There are many possible methods of manufacture, including elaborate refining processes applied to steel baths, and direct reduction of very pure ores, but the writer believes that the most promising methods are electrolytic. Such processes may have as their starting points either ores or steel scrap. There have been in the past several attempts at the leaching of iron ore fines with ferrous liquors which are subsequently electrolysed but such processes could not be established largely because of lack of sufficiently corrosion resistant materials for the pumps, pipes vessels, and diaphragms. In view of the great progress made in perfecting non-corroding alloys in recent years, such processes could in the writer's opinion be reconsidered to-day with more hope of success. It does not seem by any means improbable that processes of this sort could be profitably introduced later in India. Closely related to this is the 'Research' item of producing iron powder for powder-metallurgical and other applications electrolytically.

In view of the attention which has already been given under the 'Ferrous Metallurgy' head to ferro-manganese and ferro-chrome, it will be appropriate to refer briefly to the extents to which electrolytic manganese metal and chromium metal are attractive as alternatives. The case of manganese has already received some attention under the head of 'Research'. It should, however, be emphasised that the process is applicable to the lowest grade ore rejects and that the overall cost of production excluding ore-costs, which should be very low, need not exceed 10 annas per lb. including plant costs—if U. S. estimates can be transferred to Indian conditions.[14] The metal as produced is practically pure but needs degassing before adding to steel. It should be competitive in price with the manganese contained in ferro-manganese. There is evidently justification for serious consideration of production of this material in India.

Chromium metal can also be produced electrolytically but the processes so far developed are only efficient on a very large scale. The metal is produced in this way at a similar price to 'thermit' metal, but the cost is many times that of the chromium content of ferro-chrome. It may be, however, that efficient processes can be developed which form the electrolyte direct from the ore without much preliminary purification, and which would be financially attractive in India.

Non-ferrous Metallurgy: As already pointed out, non-ferrous electro-metallurgy in India is virtually limited to the fairly small scale production of aluminium, together with some secondary copper production.

Aluminium has established itself as a major non-ferrous metal in less than half a century and its uses are ever-increasing. The Materials Policy Commission appointed by the President of the United States (Paley Commission) have expressed the view[15] that in the next twenty-five years consumption of aluminium will increase in three directions: (1) normal expansion, due to population increase and similar factors, (2) substitution for non-ferrous materials, and (3) substitution for steel and wood. To the last of these three, the Commission attached large quantitative significance. In total, they expected consumption by 1975 in the United States and the rest of the 'free world' to be between four to five times that in 1950 when it was approximately 1¼ million tons.

To quote from an official U. K. source[16] :-

"There is no danger that the expansion of aluminium production will be restricted because of shortage of bauxite" Known reserves of bauxite of good quality in countries of the free world are estimated to be of the order of 1,500 million tons, (350 million tons metal content) and they are widely distributed. Nor is there any reason to think that shortages of other raw materials will be a handicap to expansion. The chief difficulty is the heavy demand on electric power which the extraction processes make. Unless cheap power is already available in large quantities, any major new development of aluminium producing capacity involves at the same time the large scale development of power—normally, as things are, hydro-electric power."

The only large scale developments in prospect at present outside India are in Canada, U. S. A. and the Gold Coast. The Aluminium Company of Canada has increased installed production capacity in Quebec from 450,000 to 500,000 tons per annum since the war and has almost brought into operation its Kitimat project in British Columbia[17] with its initial capacity of 83,000 tons per annum and final capacity of 500,000 tons per annum. In the United States the post-war expansion has approximately doubled the 1950 capacity bringing it to 1·4 million tons per annum. It is not anticipated by informed opinion that the continued expansion of U. S. aluminium production capacity will do more than keep pace with the increased internal demand envisaged by the Paley Commission.

Meanwhile there is clear evidence that the U.K. has an excess of milling capacity over existing production and importation of aluminium of the order of 200,000 tons per annum and that the demand is increasing by at least 5 per cent per annum. An estimate of 1 million tons per annum by 1975 has been made for U.K. consumption satisfied by virgin metal. Since most importation at present is from dollar areas, the U.K. would clearly appreciate the production of increased quantities of aluminium within the sterling area.

Expanding needs for aluminium within the sterling area were carefully reviewed in the White Paper for H.M. Government[16] which recommended the Volta River Aluminium Scheme in November 1952. According to this scheme a hydro-electric power station with a final capacity of 564,000 kW. is to be set up in Agena in the Gold Coast and aluminium works installed at Kpong 12 miles away which will ultimately have a capacity of 210,000 tons of aluminium per annum (80,000 tons at first) and should be operating at full capacity within 20 years. Local bauxite deposits with known reserves of 200 million tons will be utilised, with a consumption of one million tons per annum.

The Volta River Scheme is remarkable for the clarity with which all its phases have been considered. To quote from the White Paper: "It has always been realised that any major development of the Volta Basin would only be economic if an adequate demand could be found for the available power. Existing and estimated future demands for electric power in the Gold Coast are insufficient to justify the hydro-electric power without a heavy power consumer like aluminium production as the main outlet."

Separate estimates are given for the power project, the aluminium smelter and port, rail, road and other public works, at each stage of the development; also for the way in which the required capital requirements are to be shared between the Governments concerned and the Aluminium companies. The figures given reveal that an aluminium smelter of moderate size costs £500 (Rs. 6,500/-) per ton of annual capacity.

The Volta Scheme when complete will cost approximately half of the total cost of all India's power and irrigation works under the First Five Year Plan. The smelter is initially to be of 80,000 tons capacity, later to be increased to 120,000 and finally to 210,000 tons. It is stated 'as a result of the Scheme, United Kingdom consumers should be able to count on at least 60,000 tons a year of additonal sterling area aluminium in the early days of the smelter—on present expectations by 1960 or soon after—and on a minimum of 157,500 tons a year when the full capacity of 210,000 tons is being worked.

The current demand[18] for aluminium in India has been estimated as between 15 and 20,000 tons per annum. The Panel for the Aluminium Industry fixed in 1947 the short-term (5 year) target of production at 15,000 tons per annum, but the long term (15 year) target at 50,000 tons per annum.

Of the present demand, 2,500 tons per annum is for A. C. S. R. cables, the technical requirements of which are not fully met by the quality of aluminium at present produced in India, but only by material which has been refined to a 'super-pure' grade.

The Planning Commission's Report, recognised aluminium as almost the only non-ferrous metal which India can produce in large quantities. India has large resources of bauxite and from the new hydro-electric projects should have power at a reasonable cost. She is unfortunately without cryolite and has little fluorspar (M. P.), with the aid of which synthetic cryolite could be produced, to be used as the solvent for alumina in the igneous electrolytic bath. Vital as one or other of these solvents is, the tonnage used is small (say 0.10 ton per ton of aluminium produced) and can be secured from abroad without undue expenditure; there is however, need for a good sized stock-pile within the country if a large section of industry is to depend on aluminium production. The total of raw materials which goes to make one ton of aluminium is:-

Bauxite	... 4.5	Tons
Caustic soda (for purifying bauxite to alumina)	... 0.16/0.20	,,
Cryolite	... 0.07/0.10	,,
Aluminium Fluoride	... 0.03/0.04	,,
Fluorspar	... 0.007/0.008	,,
Petroleum coke *	... 0.75	,,
Pitch *	... 0.2	,,
Coal *	... 4.0	,,
Electric energy	... 20,000/24,000	kWh

(* for making Soderberg electrodes & furnace blocks)

Mention has already been made of the need for aluminium of above the normal 99·5 per cent grade for certain special purposes. These include ACSR cables, sheathing of strong alloys, and foils and other materials used in food packaging. The high grade material, commercially termed 'super pure', of better than 99·97% is made by a second stage of electrolysis using as a soluble anode commercial aluminium alloyed with copper. The scale on which this type of refining needs to be carried out is estimated at between 5 and 10 per cent of the rate of aluminium production.

It should also be noted that aluminium (as well as magnesium, calcium, silicon and sodium) is required to a considerable extent as 'packaged power' for the reduction of difficultly reducible metals in relatively small quantities. Among the metals which can be produced in this way are titanium and uranium. While for thermit-welding secondary aluminium serves, for most of the reduction processes in mind the aluminium must be of the highest commercial purity. Where the reduction is effected in electric furnaces aluminium ingot suffices, but for other conditions the aluminium must be reduced to powder.

It is generally reckoned that for an aluminium plant to be fully efficient it must have a production of at least 15,000 tons per annum. No plant of this size exists or is really likely to exist in India for a long time to come.

There are at present two companies producing aluminium in India. These are: The Indian Aluminium Co. Ltd., which purifies alumina from Bihar bauxite at Muri (Bihar) and transports this to Alwaye in Travancore-Cochin for smelting using hydro-electric power, and the Aluminium Corporation of India, Ltd., operating at Jaykaynagar near Asansol also on Bihar bauxites, but using thermally generated power with coal from a mine on their ground. The two plants have a combined rated capacity of 4,000 tons per annum but actually produce less. They find a need to import cryolite, aluminium fluoride, carbon blocks and filter cloth.

Both the present producers of aluminium in India have plans to increase the production capacity of their existing smelters (and also their rolling mills etc.) In the case of the thermally powered Aluminium Corporation of India, Ltd., the proposed expansion is fairly small, from 1,500 to 2,000 tons per annum[18]. The approved expansion of the Indian Aluminium Co.'s Alwaye Smelter is from 2,500 to 5,000 tons per annum. The same Company have also proposed to Government the establishment of a third, and larger, aluminium smelter adjacent to the Hirakud Dam, with an annual capacity of 10,000 tons per annum, from 1956. This suggestion seems to have been accepted by Government but the wording of the Planning Commission Report mentions 'any alternative project designed to bring into existence additional capacity for production of 10,000 to 15,000 tons of aluminium per annum.' The Company propose to supply the new smelter by increased bauxite mining at Lohardaga (80,000 tons) and alumina production at Muri (30,000 tons) to be ready by the end of 1958.

Although there is much to be said for a high tonnage alumina plant at one site, the author is not sure whether the economic advantages overrule the obvious disadvantages of the long haul of the Muri bauxite to Alwaye. In his opinion serious consideration should be given to limiting the expansion of bauxite treatment at Muri to what can be smelted in the fairly near vicinity (Hirakud) and finding a new source and setting up a new treatment plant for the ore to be smelted at Alwaye. Provided Salem bauxite is equally readily processed as Bihar bauxite, this suggests itself for the purpose.

The Five Year Plan contemplates in total an expansion of production by 1960 to 20,000 tons as against the present capacity of 4,000 tons. This with the related expansion in production of petroleum coke, etc. is going to take a considerable effort to achieve, but in the writer's opinion this should not be the limit of India's aim. As pointed out earlier, there is a great anticipated shortage of sterling-area aluminium production, which present plans will not fully meet, and it is open to India to enter the export markets as well as meeting home needs in this metal, of which she has high quality ores in plenty and which represents one of the best possible uses of any surplus power generated as d. c.

For *magnesium* the situation is superficially similar; but the same expanding use cannot be predicted. India's present need of magnesium is mainly confined to alloying with aluminium for strong light alloys, but she may need some also for reducing such metals as titanium. The methods of production both from magnesite and sea-water are well-known and could be established in India once a sufficient demand was felt.

Copper is generally produced by smelting methods, followed if necessary by electrolytic refining, though there is some direct hydro-metallurgical production in Spain and elsewhere. This is usually non-electrolytic. In Canada, U. S. A. and N. Rhodesia as well as India primary smelting of copper ores is normally in reverberatory furnaces, but in Norway, Sweden and Russia closed-top pig iron type electric furnaces are employed and the sulphur dioxide collected for acid manufacture.

In India there has been some electrolytic production of secondary copper for several years but no corresponding primary production. Whether a large scale secondary refinery would be justified is an open question. Rama Char[3] says 'although there is a scarcity of copper in India, it is a matter for consideration whether a large copper refinery plant is worth establishing. In order to reclaim large quantities of scrap copper available annually in the country. Investigations are being made to ascertain the most economical locations for such a plant.'

In a recent article entitled 'Minerals of the Subarnarekha Basin: Their Industrial Prospects', V. R. Khedker has laid great stress on the need for primary electrolytic copper production in India. He states that the pyritic ore, which is mined at Mosaboni to the extent of 28,000 tons per month has a copper content of 800 tons, valued at Rs. 25,60,000 together with a little nickel — 22 tons, valued at Rs. 1,32,000, and valuable amounts of phosphates, sulphur and ilmenite. He writes ' In view of the Bokaro power station of the D. V. C., it should be possible to introduce the process of electrolytic manufacture of copper to replace the fire refined process at Ghatsila. In addition, it should be possible to increase the annual production of 7,000 tons to about 25,000 tons by incorporation of the ore loades at the Rakha-mines. Electrolytic copper ingot costs us Rs. 3,700/- per ton. If a target of 20,000 tons of electrolytic copper production were to be attained, then Rs. 7·5 crores would be saved for us *prima facie.* Khedker's estimate assumes that ores with much less than 1·5 per cent copper from Rakha mines can be processed efficiently. This analysis also ignores (i) the present value of the current production and (ii) the fact that electrolytic refining is normally supplementary to smelting. There is, of course, much to be said for increasing production to the maximum and where total indigenous production will not meet the full demand. for producing indigenously the more costly variety and transferring importation to the less costly variety.

The need has already been mentioned of other 'reducing metals' such as calcium and sodium.For the latter, there are other possible sizeable uses in India which encourage its production.

The question of refining zinc in India is already before the Government[19]. At present the zinc concentrates from the Zawar mines are shipped to Europe for treatment and only half the product returned to India. This is quite inadequate to meet home consumption. Among the methods available for processing are the St. Joseph's Lead Company and New Jersey Zinc Co. methods with electrical heating for distillation, and electrolytic refining. The *lead* production of these mines is satisfactorily handled along normal smelting lines and it seems unlikely that electrolytic methods of refining will be introduced. Reference may again be made, however, to the interesting possibilities of fusion electrolysis of lead sulphide, with simultaneous recovery of lead and sulphur.

Conclusions:

There is justification for large scale expansion of certain phases of the electro-metallurgical industries of India, and for this the necessary resources of electric power should be available in the next ten years. The projected expansion would not only assist India in her struggle for metal self-sufficiency but should allow her to enter more profitably into the export market, selling valuable ferro-alloys and metals instead of ores. It is emphasized, however, that these industries can much more readily be expanded on paper, as the writer has done, than in practice. Much planning will be needed to provide the required facilities, especially as regards d. c. power supplies, chemicals for electrolytes and other purposes, metals for insoluble anodes and cathode starter sheets, as well as for pumps, lines and vessels to handle corrosive solutions, and non-metallic materials for diaphragms, filters, arc-furnace electrodes and so on. Efforts in this direction will, however, find their complete justification when India becomes able to 'play a large part in making up the rapidly dwindling base metal resources of the older and more exploited countries', a task which A. G. Robiette[7] regards as the natural destiny of the Commonwealth Countries. Towards the achievement of this end a large responsibility will fall on the Central Electrochemical Research Laboratory.

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THE CORROSION CELL

by
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The cells responsible for the corrosion of a metallic specimen exposed to acid or salt solution differ little from the primary cells known to all electrochemists, except that, since the corrosion cell is short-circuited, the strength of the current flowing is determined more by polarization than by the circuit resistance. As in any primary cell, the anodic reaction consists in the passage of metal (as cations) into the solution, but the cathode reaction generally consists, not in the reduction of manganese dioxide (as in the Leclanche cell) or the deposition of copper (as in the Daniell cell), but rather in the reduction of oxygen (to hydrogen peroxide or hydroxyl) or the evolution of hydrogen gas.

If a bi-metallic specimen, consisting of copper and zinc in union, is placed in dilute sulphuric acid, the zinc will be the anode and the copper the cathode, the main cathodic reaction being hydrogen-liberation. If the liquid is a solution of sodium chloride containing dissolved oxygen, there will be little liberation of hydrogen, and the cathodic reaction will be principally oxygen-reduction, so that the rate of anodic attack on the iron will be controlled by the replenishment of oxygen at the copper cathode. If the specimen consists of zinc alone, and is partly immersed in a salt solution, the cathodic region will be the zone near the water-line, where oxygen can readily be replenished, thus maintaining the cathodic reaction.

The driving force for corrosion by a neutral salt solution in presence of air is derived ultimately from the affinity of metal for oxygen; expressed as an E. M. F., it is usually of the order of 1 volt, although the value varies from one metal to another. Since the resistance of a short-circuited cell in which the anodic and cathodic members are in contact may be very low, very strong currents would be anticipated if the current strength were obtainable by dividing the E. M. F. by the resistance; since the corrosion-rate is connected with the current strength in the sense of Faraday's Law, corrosion might be expected to be alarmingly rapid. Fortunately, polarization intervenes to prevent this swift destruction of metal. When the cathodic reduction is the reduction of oxygen, there is a maximum current strength fixed by the rate at which oxygen can cross the "diffusion layer" in the liquid next the metal under a concentration gradient; since the solubility of oxygen is low, the concentration gradient is also low, and the corrosion-rate consequently limited. When hydrogen is being evolved, there is no definite limit set by diffusion; but, except on some materials like platinum, the cathodic reaction (the transformation of hydrogen ions through hydrogen atoms into hydrogen molecules) is a sluggish one.

From the electrochemical point of view, we see that as the current increases, the cathodic and anodic potentials must approach one another owing to polarization and there will clearly be some value of the current which would reduce the available E. M. F. to zero. However high the conductivity of the liquid may be, this value (I on Fig. 1) can never be exceeded. If the conductivity of the liquid is not high (as in a rather dilute salt solution), we need an

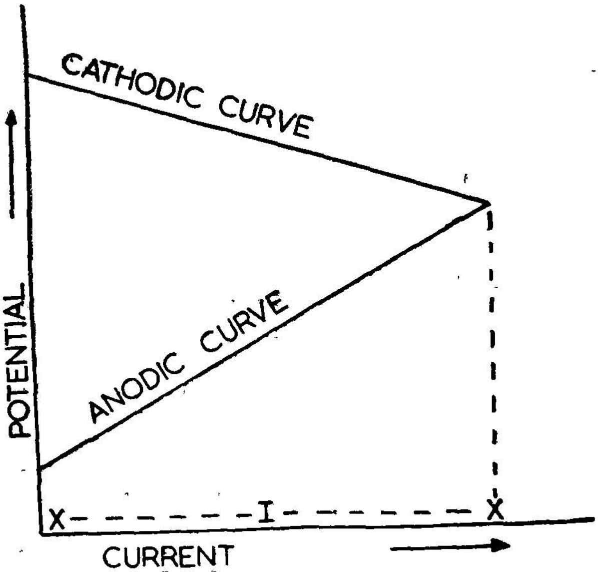

Fig. 1. Factors determining the corrosion current when the resistance is small.

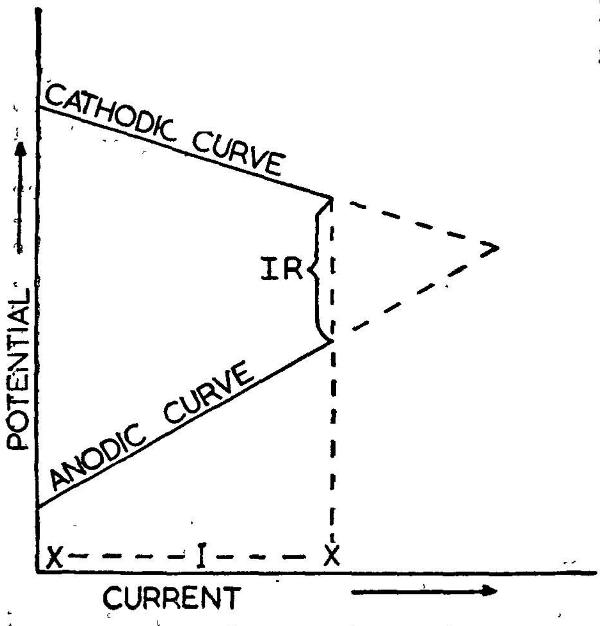

Fig. 2. Factors determining the corrosion current when the resistance is not small.

appreciable E. M. F., and the current flowing will be that value, I, which will make an intercept between the two curves equal to IR, where R is the resistance of the circuit; clearly by Ohm's Law, this residual E. M. F. (IR) will exactly suffice to keep the current I flowing through resistance R (Fig. 2). If I is expressed in amperes, the corrosion rate will then be 1/F gram equivalents per second, where F is Faradays number.

When zinc is placed in dilute sulphuric acid, there will be little hydrogen at first, since zinc itself has a high overpotential. Gradually, however, "noble" impurities in the metal will accumulate at the surface; if they are present in the original zinc as particles of a separate phase, these particles will be gradually uncovered as corrosion proceeds; if the impurities are in solid solution in the zinc, they will enter into the liquid momentarily as cations and will be redeposited as a new metallic phase, often in spongy (surface-rich) form which provides an effective cathodic surface. Thus the rate of hydrogen evolution, which is equivalent to the rate of corrosion, will increase with time. However, the nature of the "impurities" in the zinc will affect the issue. As shown by the curves of Vondráček and Iźak-Križko, reproduced in Fig. 3., the introduction

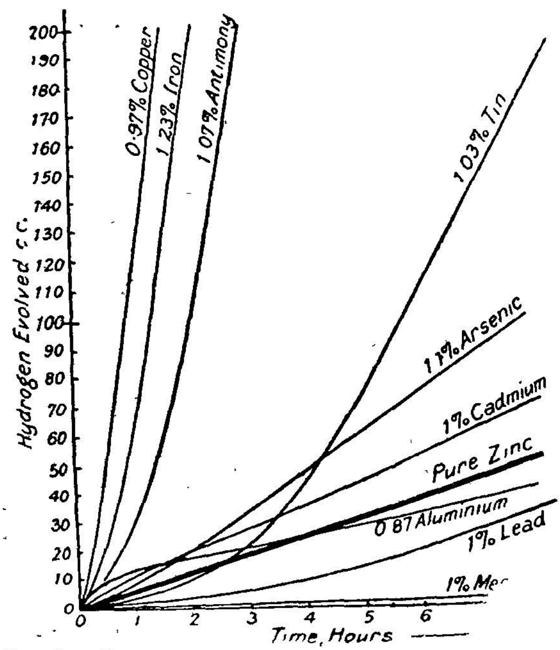

Fig. 3. Corrosion-Time curves for zinc and zinc alloys in N/2 Sulphuric acid (R. Vondráček and J. Iźak-Križko, *Rec. trav. chim.* (1925) **44**, 376)

into the zinc of metals of low overpotential (copper and iron) causes a far more rapid evolution than is obtained from metals of high overpotential such as lead. In almost all cases the corrosion-rate rises with time as the second metal accumulates on the surface. The curve for unalloyed zinc, however, is straight, and the alloy containing aluminium bends down slightly with time, suggesting the formation of a protective film of alumina.

If, however, we consider zinc partly immersed in neutral chloride solution, the oxygen-replenishment which maintains the cathodic reaction is determined by geometry. There is no reason why an alloying constituent should greatly affect the rate of arrival of oxygen; nor is there any obvious reason why the current-flow (and hence the corrosion-rate) should alter with time. The curves of Borgmann and Evans for zinc or zinc alloys partly immersed in potassium chloride are remarkably straight (Fig. 4), and there is only a small difference between the corrosion-rate for pure zinc and that for its alloys. Here again, the effect of aluminium, in diminishing the corrosion-rate of ordinary zinc, should probably be ascribed to film formation.

For thirty years it has been known that there really is a current flowing between the water-line zone as cathode and the lower region as anode. Just before the World War II the current flowing on zinc immersed in sodium chloride was measured by Agar and Evans and found to be equivalent to the corrosion-rate in the sense of Faraday's Law; this established the electrochemical mechanism of corrosion of zinc. In the case of iron, the same equivalence between current and corrosion-rate had been demonstrated some years earlier by Hoar and Evans, using a different method.

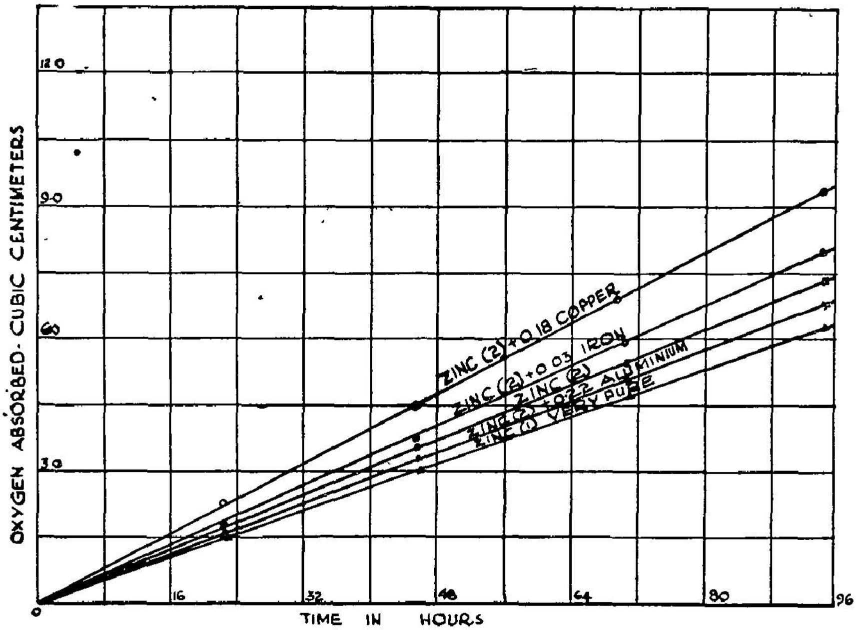

Fig. 4. Corrosion-Time curves af zinc in N/10 Potassium chloride (C. W. Borgmann and U. R. Evans, *Trans. Am. Electrochem. Soc.* (1934), 65, 249)

THE ELECTRODEPOSITION OF SOME OF THE TRANSITION METALS AND THEIR ALLOYS FROM AQUEOUS SOLUTION

by
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The one hundred chemical elements now known can be classified on the basis of the electronic structure of their atoms into the following four different types: (a) the inert elements having all electron shells of their atoms completely filled, (b) the representative elements with the outermost shell incomplete (c) the regular transition elements with the two outermost electron shells incomplete, and (d) the inner transition elements with the three outermost electron shells incomplete. The inert elements are the noble gases of group zero of the periodic table (see Fig. 1), the representative elements are the Ia, IIa, IIb, and IIIa to VIIa groups of elements, the transition elements are the IIIb to VIIIb, and

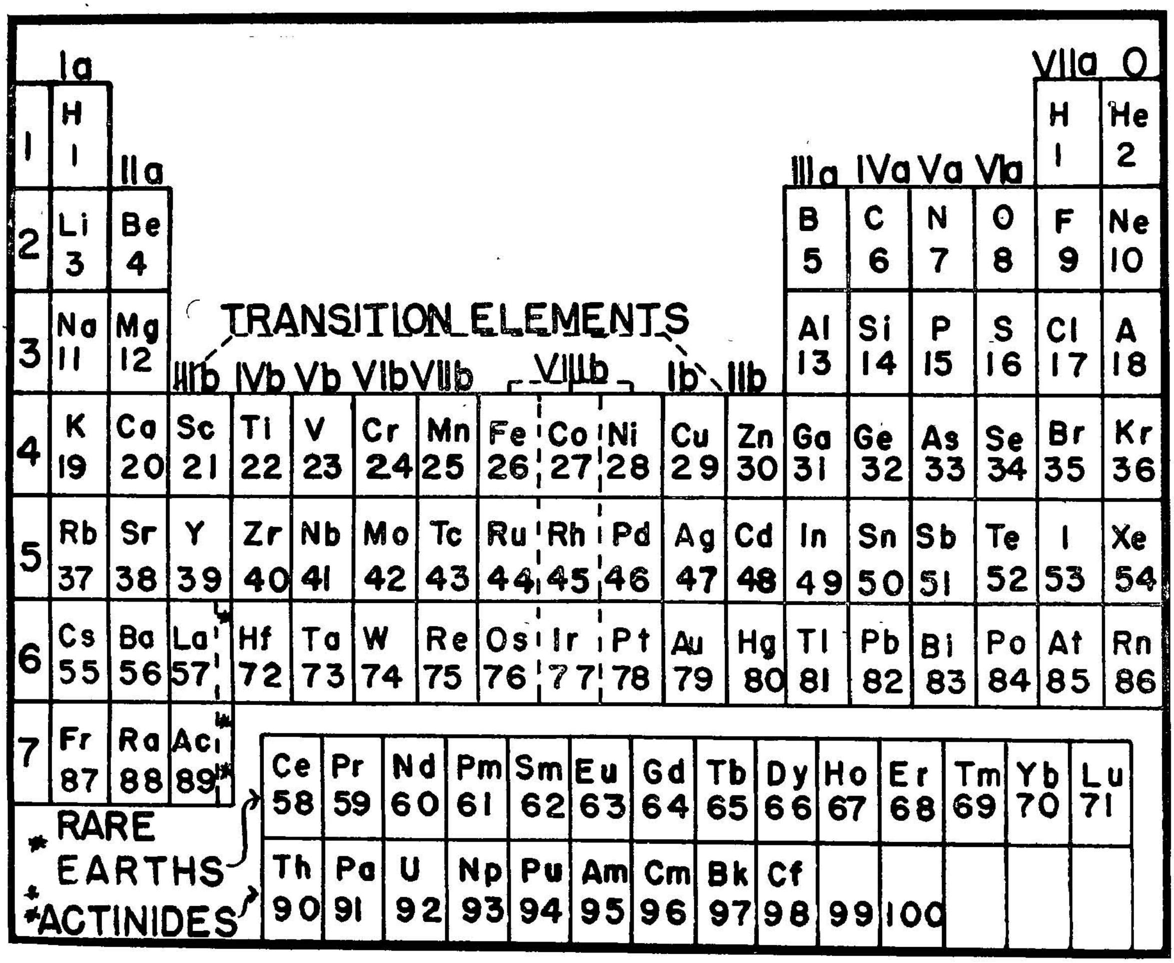

Fig. 1. An extended form of the periodic table.

Ib groups of elements except the rare earths (numbers 57-71) and the actinides (numbers 89-100) of group IIIb which are the inner transition elements. It should be mentioned that according to some definitions the group Ib elements are not considered to be transition elements.

Most of the regular transition elements and a number of other elements have been electrodeposited from aqueous solutions according to the literature reports which are summarized in Fig. 2. Some of the reported results are rather questionable and in Fig. 2 such results are indicated by a question mark following the symbol of the element. An excellent summary of the published results describing the electrodeposition of many of the uncommon metals is given in the new edition of "Modern Electroplating" (1). Without doubt some of the rare earths and actinides have been electrodeposited from aqueous solution but these metals are omitted from Fig. 2 and are not iucluded in this discussion. The purpose of this article is to summarize and evaluate the available information dealing with the electrodeposition of some of the transition elements and their alloys.

Only fifteen or so of the elements that can be electrodeposited from aqueous solution are of real interest and importance in the electroplating field at the present time and these are summarized in Fig. 3. Manganese is included in this group but with a question because, although it is of little importance in

IVb	Vb	VIb	VIIb	VIII			Ib	IIb	IIIa	IVa	Va	VIa
Ti?	V?	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Zr?	Nb?	Mo?	Tc?	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
Hf?	Ta?	W?	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po

Fig 2. Elements which are reported to be electrodeposited from aqueous solution. (Rare earths and actinides are not included.)

VIb	VIIb	VIII			Ib	IIb	IIIb	IVb
Cr	Mn?	Fe	Co	Ni	Cu	Zn		
			Rh	Pd	Ag	Cd	In	Sn
				Pt	Au			Pb

Fig. 3. Metals electro-deposited from aqueous solution which are important in practical electroplating.

electroplating, the electrolysis of manganese (II) solutions has application in the electrowinning of manganese.

The present discussion will be limited to the electrodeposition of the transition elements of periodic table groups IVb to VIIb inclusive and will also be limited to aqueous solutions. These transition metals have incomplete *d* electron subshells which are being filled as the atomic number increases. In each case the total number of electrons in the outer *d* and *s* sub-shells gives the maximum oxidation number of the element in its compounds. Variable oxidation number is of course a characteristic of these elements and of the rest of the transition elements. These metals also have other common characteristics of the transition elements such as the property of forming numerous colored ions and compounds, of forming complexes with many other compounds and ions, and of serving as catalysts for a number of reactions.

It is very doubtful that any of the group IVb metals (Ti, Zr and Hf) have been electrodeposited from aqueous solution although reports in the literature indicate some degree of success. Numerous attempts to electrodeposit titanium and particularly zirconium (2) have been carried out in this laboratory without success. Since the calculated potential, E_0, of zirconium (3) is close to the potentials of aluminium and beryllium, neither of which has been electrodeposited from aqueous solution, these failures are not surprising. Not much is known as yet about the electrochemistry of hafnium but it can be assumed that its properites are about the same as those of zirconium.

The reports of the successful electrodeposition of the group Vb metals (V, Nb and Ta) from aqueous solution are in some cases rather definite but again with this group as with the group IVb metals it is extremely doubtful that electrodeposition from aqueous solution has been accomplished. Work in this laboratory with vanadium (4) and with tantalum (5)(6) indicates that a successful process for the electrodeposition of these metals from aqueous solution has not yet been developed.

Information about the electrodeposition of the group VIb metals (Cr, Mo and W) is more definite than for either of the two preceding groups. The plating of chromium is of course a common commercial process but it should be noted that the cathode current eficiency of the chromium plating bath is quite low, approximately 15% An aqueous solution for the electrodepositon of molybdenum has been described (7) and work in this laboratory indicates that this plating bath gives a cathode deposit containing molybdenum but that the current efficiency of the process is not more than 1% and probably less. Although the electrodeposition of pure tungsten from aqueous solution has been reported (8) (9), it is now generally recognized that the cathode deposits obtained from these solutions are alloys of tungsten rather than pure tungsten (10) (11). If pure tungsten has been electrodeposited from aqueous solution, the cathode current efficiency of the process is certainly much less than 1%.

Electrodeposition of the group VIIb metals, particularly manganese and rhenium, is well established although little if any use is made of these metals as electrodeposited. Whereas the cathode current efficiency for the electrodeposition of manganese is about 75%, the current efficiency for rhenium deposition is not more than 15%. Technetium can be electrodeposited from aqueous solution but there is no information available about current efficiency since the solutions used were necessarily extremely dilute; however, it might be guessed that the current efficiency would be in the order of 50%.

It is interesting to speculate about the reasons for the lack of success in attempts to electrodeposit some of the transition metals. Usually it is suggested that the activity of the metal, the hydrolysis of simple compounds, and the absence of M^{+n} cations in solution are among the causes for the failures. There are however interesting differences within periodic table groups and periods that should be considered. For example, why is it possible to electrodeposit chromium from aqueous solution but not tungsten which is in the same group, and why is it possible to electrodeposit manganese but not titanium which is in the same period? Perhaps these different results can be correlated with the variation in the size of the atoms of these elements. Information about the percentage cathode current efficiency of deposition of the transition metals of groups IVb to VIIb and the covalent radii of their atoms is summarized in Table I. It can be seen from this table that in each period with increasing atomic number there is of course a decrease in the covalent radius of the atom and at the same time a tendency toward an increase in the current efficiency of metal deposition. Again referring to Table I it can be seen that for groups VIb and VIIb with increasing atomic number and consequent increasing covalent radius the current efficiency of metal deposition decreases. Thus it can be suggested that cathode current efficiency of metal deposition tends to increase as the size of the atom being deposited decreases, since within groups as well as periods the smallest atom is deposited with the greatest current efficiency.

Table I. Correlation of the cathode current efficiency (C. C. E.) of deposition of some of the transition metals with the covalent radius of their atoms.

	IVb	Vb	VIb	VIIb
	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn
C. C. E. %	0	0	15	75
Radius, A°	1.324	1.224	1.172	1.168
	$_{40}$Zr	$_{41}$Nb	$_{42}$Mo	$_{43}$Tc
C. C. E. %	0	0	1 ?	50 ?
Radius, A°	1.454	1.342	1.291	—
	$_{72}$Hf	$_{73}$Ta	$_{74}$W	$_{75}$Re
C. C. E. %	0	0	0	15
Radius, A°	1.442	1.343	1.299	1.278

In the past few years there has been considerable interest in the electrodeposition of alloys of some of the transition metals, particularly alloys of tungsten, of molybdenum, and of rhenium. Alloys of these metals with iron, with nickel, and with cobalt have been studied most completely (12) (13) (14). Three types of alloy-plating baths have been reported: (a) regular iron, nickel, or cobalt plating baths to which has been added an anion of the alloying metal ($MoO_4^{=}$, $WO_4^{=}$ or ReO_4^{-}), (b) a solution which is supposed to be a tungsten, a molybdenum, or a rhenium plating bath to which has been added small amounts of Fe^{+++}, Co^{++}, or Ni^{++} and, (c) a solution containing an anion ($WO_4^{=}$, $MoO_4^{=}$ or ReO_4^{-}), a cation (Fe^{+++}, Ni^{++}, or Co^{++}), a complexing agent such as citrate or tartrate, and ammonium hydroxide to adjust the pH of the solution. In all cases reported the current efficiency for alloy plating is considerably greater than the efficiency of deposition of the single metal (W, Mo or Re). A comparison of these efficiencies is given in Table II.

Table II. A comparison of the cathode current efficiency (C.C.E) of the tungsten, molybdenum and rhenium plating baths with the efficiency of the plating of alloys of these metals with iron, nickel or cobalt.

	Tungsten	Molybdenum	Rhenium
C. C. E., metal deposition	less than 1%	about 1%	about 15%
C. C. E., alloy deposition	about 75%	about 75%	about 90%

The composition of these electrodeposited alloys may be varied considerably. Recent work with molybdenum alloys indicates that alloys containing about 20% of molybdenum are readily deposited from a citrate type of bath. Some of the tungsten alloys, also from a citrate bath, contained about 40% of tungsten. Alloys of rhenium obtained from similar baths often contain as much as 80% of rhenium.

The question of why it is possible to electrodeposit alloys of tungsten and of molybdenum and not the metals alone is as yet unanswered. It would seem that the codepositing metal iron, nickel, or cobalt must have a marked effect on the process which is taking place at the cathode. The electrodeposited tungsten-cobalt and tungsten-iron alloys appear to have a laminar structure (15) and this fact suggests that the cathode deposit may not be a true alloy but may instead be made up of a series of very thin layers of the two metals being deposited. A catalytic reduction theory to explain this reduction process has been proposed (16). If this theory is used to explain the electrodeposition of tungsten-nickel alloys, the first process taking place at the cathode is the deposition of metallic nickel according to equation A.

$$\text{(A)} \quad Ni^{++} + 2e \rightarrow Ni$$

The thin layer of nickel deposited on the cathode surface then acts as a catalyst for the reduction of tungstate anion according to equation B

$$\text{(B)} \quad WO_4^{=} + 8H^{+} + 6e \xrightarrow{(Ni)} W + 4H_2O$$

Then, when the nickel catalyst is covered with a thin layer of tungsten reaction B stops and reaction A again proceeds to give a new catalyst surface. This is again followed by reaction B and thus alternate layers of nickel and tungsten are deposited on the cathode surface.

Other explanations have been proposed for the mechanism of alloy deposition (17) but it is doubtful that as yet a completely satisfactory explanation has been offered. There is need for extensive research on various cathode processes which result in the deposition of single metals and of alloys. Perhaps when more is known about cathode reactions during metal deposition a way will be found to electrodeposit some of the transition metals which have not as yet been successfully electrodeposited from aqueous solution.

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* THE SULPHAMATE BATH FOR CADMIUM-ZINC ALLOY PLATING

by

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The electrodeposition of cadmium-zinc alloys is of importance in the decorative and protective finishing of metals. They are commonly plated from cyanide solutions. In view of the poisonous nature and comparative instability of the latter, it is desirable to have a cyanide-free bath. The other baths studied are the acid sulphate [1, 2] and sulphamate by Piontelli and Canonica [3] who have, however, not given the details. The present investigation was restricted to the possibility of obtaining alloys of different composition.

Prëvions work carried out in this laboratory [4, 5, 6] has shown that cadmium and zinc can be electrodeposited on steel at high current density and current efficiencies close to 100% from a bath prepared by adding the metal carbonate to sulphamic acid. The cadmium and zinc contents were analysed according to standard methods [7] and sulphamate by conversion to sulphate with nitrite and estimation as barium sulphate. I - *N* solutions of cadmium and zinc sulphamate contain 56 gm/l cadmium and 32.5 gm/l zinc respectively. The cathode potentials, during deposition, of cadmium in cadmium sulphamate (containing 2. 5, 5, 10, 15 and 20 gm/l cadmium) and zinc in zinc sulphamate (containing 65 gm/l zinc) were measured against a saturated calomel electrode, with a steel cathode and platinum anode. Fig. 1 shows the current density-cathode potential curves; the potential values are given with reference to the calomel electrode. The cadmium curves (2. 5. to 15 gm/l cadmium) intersect the zinc curve at certain points indicating the possibility of co-depositing the two metals from sulphamate solutions. A low concentration of the nobler metal (cadmium) or a high current density makes the deposition potential of cadmium more cathodic and brings it close to the potential of zinc.

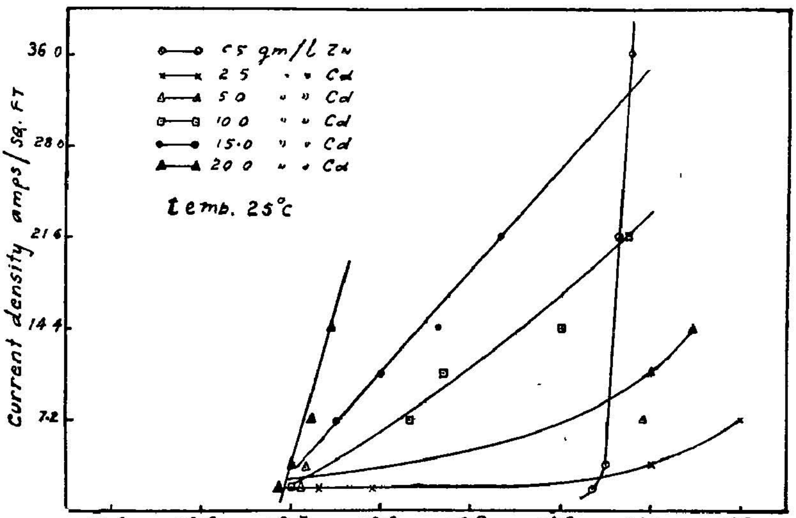

FIG 1 SINGLE METAL DEPOSITION POTENTIALS

In order to obtain an idea of the limiting concentration of cadmium in the alloy plating bath, i. e., the concentration at which only cadmium plates out [2, 8] the cathode potentials during alloy deposition were measured against a

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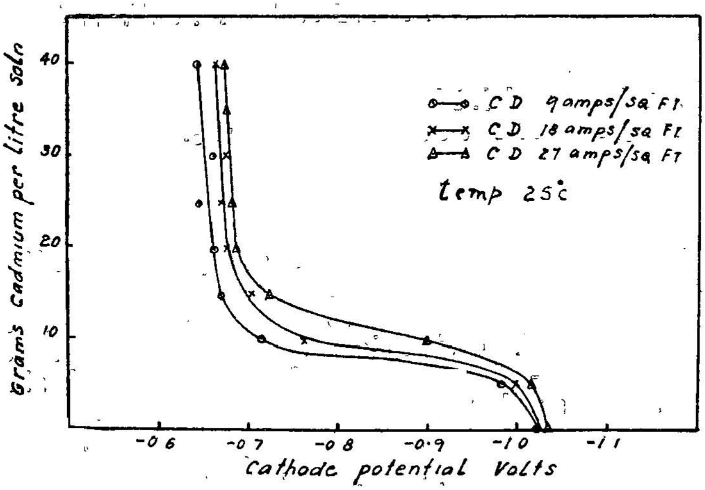

FIG 2 ALLOY DEPOSITION POTENTIALS

saturated calomel electrode for solutions containing 65 gm/l zinc and varying amounts of cadmium from 0 to 40 gm/l, with vigorous stirring. The cadmium concentration - potential curves given in Fig. 2 show that with increasing cadmium content in the electrolyte the alloy deposition potential becomes less cathodic and the curve straightens out ultimately. At this point the potential value approaches that of cadmium and only cadmium is expected to plate out from the bath. For a solution containing 65 gm/l zinc the limiting cadmium content for co-deposition, as obtained from the curves, is about 15-25 gm/l for the current density range 9-27 amps/sq. ft. This checks closely with the values obtained by analysis of the deposit in plating experiments. (Fig. 3)

As a result of potential measurements, the zinc content of the alloy plating bath was fixed at 65 gm/l and the cadmium at 13 gm/l. The pH was adjusted to 2 with free sulphamic acid, the total sulphamate content (as acid) being 220 gm/l. The electrodeposition was carried out with a steel cathode and 2 cadmium anodes placed on either side of the cathode, the inter-electrode distance being 1 in. and the immersed cathode area (4 sq. in) equal to

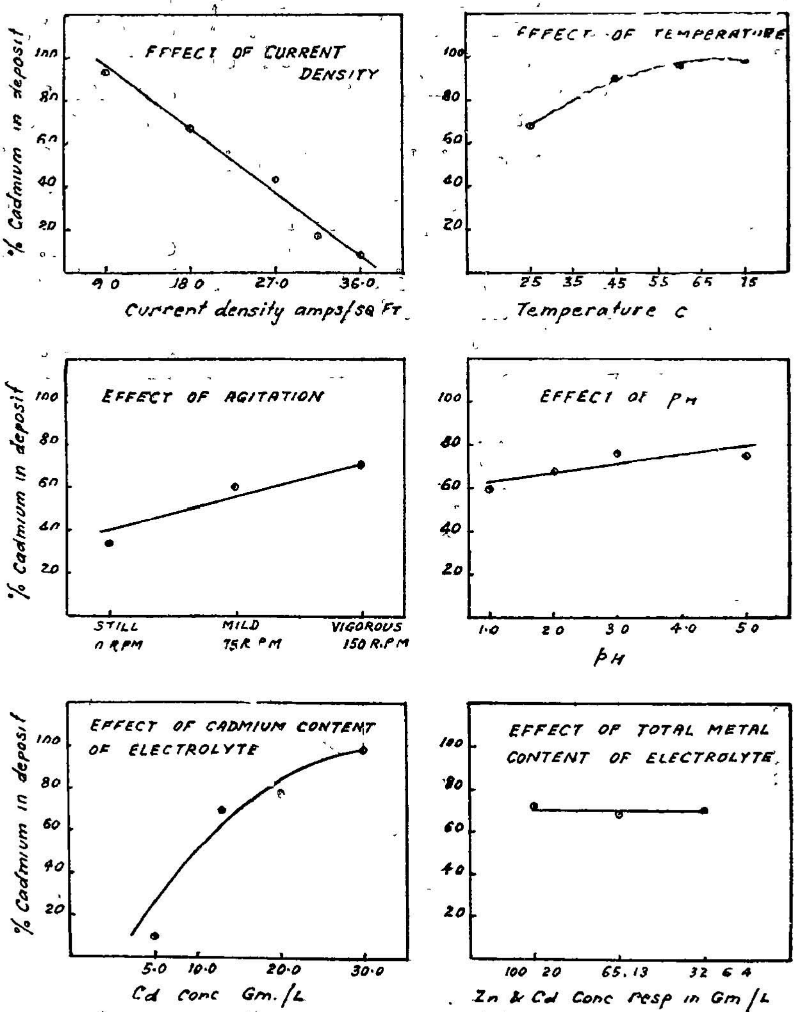

FIG. 3 EFFECT OF VARIOUS FACTORS ON ALLOY COMPOSITION

half the anode area. The temperature was 25°C., the time of plating 20 minutes and the solution was vigorously stirred. After electrolysis the deposit was stripped[1] and the cadmium content determined by electroanalysis under controlled cathode potential. The zinc content was obtained by difference.

The effect of the variables on alloy deposition is shown graphically in Fig. 3. The influence of temperature, agitation, pH and metal content was studied at a current density of 18 amp./sq. ft. The cadmium content of the deposit decreased with increasing current density. At constant current density it increased with increase of temperature, agitation, pH (upto 3) and cadmium content of electrolyte. The deposit composition depended only on the ratio of cadmium to zinc in the electrolyte and was unaffected by the total metal content if this ratio was maintained constant (1 : 5 in the graph).

The sulphamate bath gave cadmium-zinc alloy deposits of any desired composition from 8 to 98% cadmium (92 to 2% zinc) by varying the operating conditions. The throwing power of the bath was fairly good. The deposits were generally of a coarse crystalline character and not of presentable appearance, having a tendency to darken in colour. At the outset this bath has some advantages over a complex salt bath like the cyanide from the viewpoint of simplicity, stability and ease of control and maintenance. If the quality of the alloy deposit can be improved by further investigation—use of addition agents etc.—the sulphamate bath will be useful in cadmium-zinc alloy plating.

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HARD CHROMIUM PLATING OF PISTON RINGS

by

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INTRODUCTION :

The type of chromium planting known as 'decorative plating' was introduced in 1925 and has become well established as an important process for imparting a pleasing finish and increasing corrosion resistance in the metal finishing trade. [1,2] About the time of world war II a different type of chromium plating known as 'hard chromium plating' came into vogue for the building up of worn-out parts and for increasing wear-resistance. This type of plating has greater thickness and is without any under-coat; the conditions of plating also vary slightly. It has been stated that the thin decorative plates have random distribution while thick hard chromium deposits are oriented.[3] Hard chromium plating is of great value in engineering for increasing the life of cutting tools, gauges, drills, reamers etc., and has important applications in defence.

ADVANTAGES OF HARD CHROMIUM PLATING :

Great improvement in the life of bearing surfaces has been achieved in recent years by hard chromium plating and porous chromium plating. The useful service life of Internal Combustion Engines (I. C. E.) depends upon the cylinder and piston ring. The cylinder bore or piston ring is hard chromium plated for increasing the life of the engines.

In this laboratory work was taken up on hard chromium plating of the compression or top piston rings. It has been shown by actual service tests that the use of plated top piston rings reduces the wear of the cylinder bore to one half while the life of the piston rings is increased by 3 to 4 times their normal life.[4] Hard chromium plating of small cylinder bores has been reported to be not only difficult, but also uneconomical.

Chromium has got many desirable properties which make it the most suitable metal for minimizing abrasion, and increasing the life of bearing surfaces. Among the properties which enhance its usefulness are[5,6]

1. Its resistance to corrosive combustion products.
2. Its low coefficient of friction.
3. Its high melting point which prevents scuffing (i. e. microwelding of the piston ring sliding surface to the cylinder wall)
4. Its hardness(700-1000 B.H.N.), an asset in so far as it minimizes the wear of the ring, digests abrasive materials, and therefore increases the life of the bearing surface.

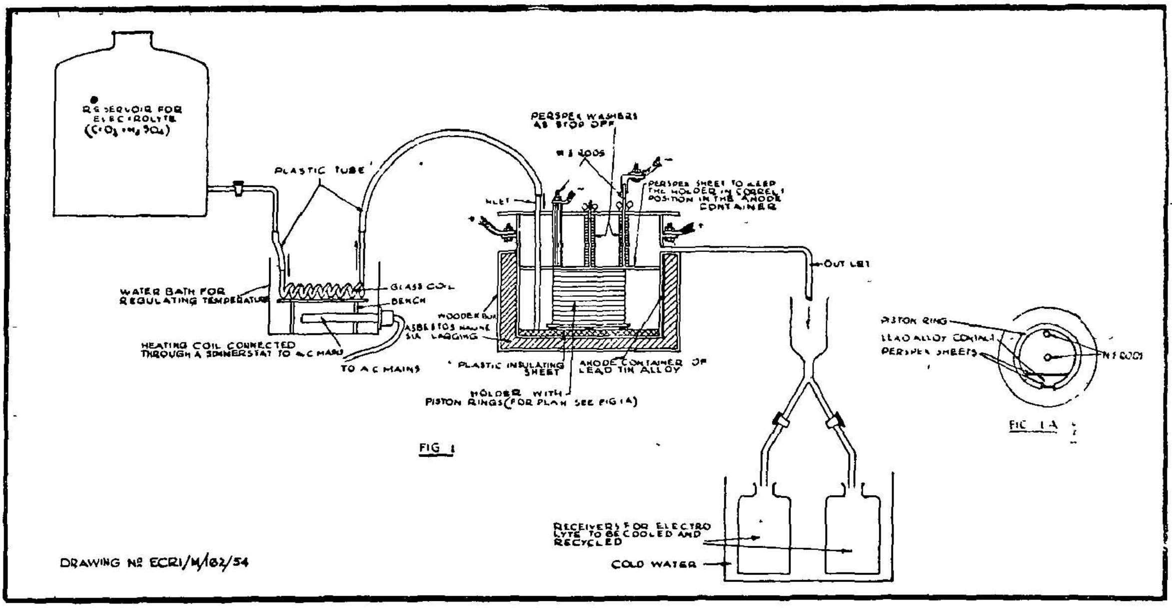
Piston rings are generally made of cast iron in which the graphite is distributed in a fine 'lamellar form' in a pearlitic matrix[6] and some of them are heat treated. The wear of both piston rings and cylinder bore is greater in high speed diesel engines than petrol engines[5]. Of the rings, the top piston ring suffers the greatest wear. The most widely used high speed diesel engine in India is the 5 H. P. engine and this engine is manufactured in India by Messrs. Petter-Kirloskar. Hence the top ring used for this engine was used in the experiments reported here.

Not much work appears to have been done on the plating of cast iron surfaces. In order to standardize plating conditions experiments were done using cast iron discs (used for the manufacture of piston rings) held in specially designed jigs. Piston ring pieces were plated first, and in the light of the experience gained, jigs were designed and tested for plating an entire piston ring, and later a dozen rings at a time.

PLATING ASSEMBLY:

The assembly for plating a dozen rings at a time consisted of a glass aspirator of six litres capacity acting as a reservoir for the electrolyte, and placed at a higher level than the pre-heater and plating bath. A spiral glass tube kept in an electrically heated water bath was attached to the reservoir by means of a plastic tube, the temperature being maintained within limits with the help of a simmerstat. The electrolyte from the reservoir got heated during its flow throug the glass spiral and was then led into the bottom of the anode container—a thin-walled hollow cylinder of lead-tin alloy (92:8); the electrolyte was allowed to flow out of the plating vat through an outlet tube welded on near its top, collected in receivers surrounded by cold water, and transferred to the reservoir for recycling by manual labour. The anode container was kept in a wooden box packed on the inside with heat insulating magnesia-asbestos mixture for minimizing heat loss by radiation. There was a circular perspex insulating sheet completely covering the bottom of the container and thus cutting down the anode area, while a circular perspex sheet of larger diameter than the container was used as a lid and effectively minimized the escape of chromic acid as spray.

Perspex was chosen as the insulating material since laboratory tests indicated that it would resist the corrosive action of the chromium plating solution at a temperature of 50-60°C.



Figs. 1 and 1 A. Plating assembly (diagrammatic)

PISTON RING HOLDER:

A perspex sheet of slightly larger diameter than that of the piston ring formed the bottom sheet on which the rings rested. Screwed on to this sheet was a small block of lead-tin alloy shaped to hold a maximum of twelve piston rings. These are in a slightly stretched state when in position (Figs. 1 and 1A). The lead alloy structure acted as cathode lead which was in contact with the non-sliding surface of the rings. Diametrically oppsite to this lead alloy block was a mild steel rod pressing against the inner surface of the rings and thus preventing their lateral slip. In addition it also served as an auxiliary lead for the current. The rings were covered on the top by a perspex sheet acting as a stop-off. Over this sheet was another circular sheet of the same material of a size which would slide freely into the anode container. This sheet effectively maintained an uniform inter-electrode distance which was constant in all the experiments. The perspex sheets were kept in position by the threaded central rod and wing-nut. These sheets when screwed tight helped also to maintain the rings in position. The nuts, rods and exposed portions of the lead-alloy contact were all stopped off by sleeves or sheets of perspex.

PRE-PLATING TREATMENT :

Degreasing :- The piston rings were first cleaned with benzene and then degreased with hot trichlorethylene. The degreasing was repeated thrice. The degreased piston rings were allowed to cool to room temperature.

Electrocleaning : They were then jigged and electro-cleaned cathodically and anodically in alkaline solution (37.5 G. P. L. sodium hydroxide and 25 G. P. L. sodium carbonate at 70-80°C and a current density of 2 amp/sq.in.) During the two minutes of cathodic treatment large amounts of hydrogen were evolved which removed any greasy matter and foreign bodies present on the surface. An anodic treatment of the same duration was given mainly to eliminate the hydrogen embrittlement and effect some further cleaning. The electrolytically cleaned piston rings were spray cleaned with rapidly flowing water and then subjected to anodic etch.

ANODIC ETCH :

In order to increase the adhesion by providing a better 'keying' surface and to remove to some extent the 'Beilby layer' consisting of broken-down crystals, metal fragments etc., produced during the machining operation, the piston rings were given an anodic etch.

Chromic acid was chosen as the etchant in preference to sulphuric acid (sp. gr. 1. 706) as test experiments showed that chromic acid etch led to a more continuous plate. The piston rings were etched anodically in chromic acid (450 G. P. L.) for half a minute at a current density of 2 amp/sq.in. at room temperature and immediately transferred to the plating cell.

PLATING :

The electrolyte was contained in a lead-tin alloy vessel of 600 c. c. capacity which also served as the anode. During plating the electrolyte was kept circulated. After transferring the work to the plating bath an initial strike was given at a high current density of 5 amp/sq.in. for 5 minutes. The plating was then continued for six hours at a current density of 4 amp/sq.in. at a temperature of 51°C.

The first lot of the electrolyte was preheated. The transfer of the jig containing the rings led to a temporary lowering of the temperature. The passage of current raised the bath temperature rapidly and the rate of circulation of the electrolyte was so adjusted that the temperature remained stationary at 51°C. The circulation was maintained at this rate throughout the run. At the start of the experiments, the water-bath was kept at a temperature of about 55°C. As the temperature of chromic acid in the reservoir increased, the temperature of the water-bath was suitably adjusted between 55°C and 51°C so as to keep the plating temperature at 51°C.

After plating for six hours the rings were taken out and washed in a rapid stream of cold water and then hot water. They were then stress relieved immediately by heating at 150°-180°C in an air oven or oil bath.[8]

Several experiments were conducted to determine the optimum composition of the electrolyte. The effects of varying the concentration of chromic anhydride as well as the chromic anhydride to sulphate ratio were studied. The following plating conditions were found to give the most satisfactory results as judged by the current efficiency achieved and the hardness of the deposit:-

Electrolyte:

Chromic Anhydride	300 G. P. L.
Sulphate	4.286 G. P. L.
Ratio of chromic anhydride to sulphate	70 : 1
Current density	4 amp/sq.in.
Applied voltage	5.5
Temperature	51°C
Inter-electrode distance	0.85 in.

The following table gives the results of a typical experiment in which a set of 12 rings were plated for 6 hours.

TABLE

Weight of unplated ring (gms)	Weight of plated ring (gms)	Weight of chromium plate (gms)	Thickness as calculated (in.)	Average thickness as measured (in.)	Hardness (Rockwell 'A' scale)
13.0336	14.1838	1.1502	0.01097	0.009842	......
13.2578	14.3152	1.0574	0.01009	0.008268	63-65
13.0660	14.6734	1 0074	0.009607	0.01181	......
13.2420	14.2240	0.9820	0.009371	0.009055	64-66
12.9052	13.8230	0.9178	0.008760	0.01221	......
13.3168	14.3076	0.9908	0.009454	0.007874	65-67
12.8664	13.8340	0.9676	0.009234	0.01143	......
13.1248	14.1372	1.0064	0 009598	......	64-66

Current Efficiency-13.23%

bore also and is then replaced afresh from the piston rings. The transfer, dislodgement and replacement of chromium may occur continuously under strenuous conditions of service. and appear to be influenced by temperature or pressure or both[5]. The chromium plate must therefore have a minimum thickness in order to give good service. The minimum thickness of chromium plate needed for an economical service life is closely related to the type of engine and the service it is put to.

Service tests have shown that petrol engines fitted with piston rings having a chromium plate of .003 in. thickness give upto 1,00,000 miles with low cylinder bore wear. On the other hand, a compression ignition engine of the diesel type gives only one fourth of this mileage when rings are plated to the same thickness[5]. This apart, the dusty condition of Indian roads and the climate may lead to a greater wear[7]. Therefore the thickness rquired under Indian con-

THICKNESS OF THE CHROMIUM PLATE:

The chromium plate on a piston ring wears away during service. The cause of the disappearance of the chromium is not quite clear. Experiments with a radio-chromium plate have shown the actual transfer of the chromium from the piston ring to the cylinder, especially near the top portion[9]. The chromium seems to get dislodged from the

ditions has to be standardized by actual service tests. The standard European practice is to have a thickness of 0.003 to 0.006 in. for I. C. E. piston rings. In the course of the work reported here it has been possible to build up thicknesses of upto 0.01 in. The results of service tests are awaited for deciding the thickness of the plate actually required.

As the railways are interesting themselves in hard chromium plating of piston rings and valves used in steam locomotives, the problem of plating these is also under investigation.

It is desirable to have a certain amount of roughness on the sliding surfaces of cylinder or piston rings in order to facilitate 'running in' and ensure the retention of oil, abrasive particles, dust etc.[7] The right degree of roughness is present in a porous chromium plate, which is essentially a hard chromium plate interspersed in all directions by multiple cracks.

The porosity is induced by etching the plated article anodically in chromic acid for a short while. Such an etch produces two types of porosity (1) pin-point porosity—where the porosity is isolated and (2) channel-type porosity—where the plate has been traversed by numerous branched cracks. Pin-point porous plates are used in diesel engines, gas engines, pumps, compressors etc., while a channeltype porous plate is applied to air craft engine components[10]. Another method of inducing porosity is to present a knurled surface for plating[11].

Preliminary experiments on the post-plating etch to induce porosity indicate that the duration and other conditions of etching decide the nature of the porosity.

According to Hepworth it is not absolutely essential to provide a porous chromium plate for I.C.E. piston rings[5]. Porous chromium plating of piston rings has however been found to be advantageous in heavy duty engines for aircraft etc[12]. Porous chromium plating of piston rings is likely to find extensive application in India because of the dusty roads and the possibility of obtaining good service life with a relatively thinner plate.

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ANODIC OXIDATION OF ALUMINIUM

by

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Anodic oxidation of aluminium is an electrolytic process for increasing the thickness of the oxide film normally present on all aluminium surfaces. The phenomena associated with the modern process of anodising were first observed in 1857 and the early patents were taken on the use of the film in electrolytic rectifiers and condensers. The resistance to corrosion, hardness and other useful properties of anodic films have led in recent years to important practical application of the process in diverse fields e.g., in decorative finishes, photographic reproductions on metal, electrical insulators, heat radiators etc.

Though these oxide films can be produced by chemical processes (e.g. the M.B.V. process, Jirotka Process, Protal process etc.) the oxide film formed by these processes is of limited thickness.

THEORY OF ANODIC OXIDATION:

The reaction underlying anodic oxidation is the electrolysis of water which has been rendered conductive by the addition of suitable electrolytes e.g., sulphuric acid, chromic acid, sulphamic acid, oxalic acid. etc. A wide range of electrolytes have been tried successfully. According to Piontelli any electrolyte satisfying the following two conditions can be used.

(1) The electrolyte must possess an oxygen-containing anion.

(2) The electrolyte must have a definite but neither too strong nor too weak solvent action on Al and on the oxide coating.

On applying a suitable voltage water reversibly breaks up into positively charged hydrogen (H^+) ions and negatively charged hydroxyl (OH) ions. The hydrogen ions are discharged at the cathode and the hydroxyl ions at the anode. Two of the hydroxyls discharged at the anode combine to form a coating of oxide on the aluminium anode while the hydrogen escapes into the atmosphere. The ionic reactions at the electrodes are probably as follows:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Cathode	Anode
$H^+ + \theta = H$	$OH^- - \theta = OH$
$\downarrow$	$2OH = H_2O + O$
Escapes in the atmosphere	Combines with Aluminium to form Al_2O_3

COMMERCIAL PROCESSES:

Of the numerous commercial processes the following three are of great importance though several new modifications have come into practice.

(1) The sulphuric acid process patented by Gower and Stafford O' Brein and Partners Ltd., in 1927.

(2) Chromic acid process or Bengough Stuart process patented by Bengough and Stuart in 1923.

(3) The oxalic acid process patented by Hojin, Rikagaku & Kenkyujo in 1924.

The operating details of these processes are tabulated below:—

Process.	Meterial	C. D. (amps/sq. ft.)	Film thickness (mm)
I. **Sulphuric Acid:** 15V. D. C. for 30 min at 20°C.	Pure Al	11.0	0.007
II. **Chromic Acid:** 0-40V. D. C. over 15 min., held for 35 min.; 40-50V. over 5 min., held for 5 min.; and at 40°C $\pm$ 2°C.	Pure Al.	5.0	0 005
III. **Oxalic Acid:** 56V. D. C. or A. C. for 60 min at 25°C $\pm$ 1°C (D. C.); 35°C $\pm$ 1°C (A. C.)	Pure Al	20	0.030

I. *Sulphuric acid process:* Of all the processes this is the one most widely employed, especially for producing decorative articles. A wide range of Al alloys can also be anodised by this process. The electrolyte used can vary from 3% to fuming sulphuric acid. But to get films of high corrosion resistance and sufficient hardness, acid of 18% to 21% by volume is used and a voltage of about 10—15 V is applied The temperature is maintained at 15°C.

Some of the solutions mentioned in the literature were employed in experiments on the production of anodised films carried out by the author in these laboratories. The effect of addition of sodium, magnesium, ammonium and ferric sulphates to the bath has been studied in detail. Aluminium strips of 99.2% purity were used in these experiments. A current of 14 amp. per sq. ft. was applied and the temperature was 25°C. In general, it was found that addition of sulphates improved the oxide ratio i.e., the ratio of the weight of aluminium oxide formed to the total weight of aluminium used up in the process. Magnesium sulphate gave the highest oxide ratio, as compared to the other sulphates tried. More satisfactory oxide ratios could be obtained by adding oxalic acid. Addition of oxalic acid also made it possible to get harder films at higher temperatures.

The practical applications of these processes were also successfully tested in the laboratory. By adsorbing different dyes on the anodised films multi-colour effects could be produced on aluminium articles, and photographs could be reproduced by adsorbing light-sensitive chemicals on the anodised films. Optimum conditions for these special purposes have been worked out. It has been found that a 10% (V/V) sulphuric acid solution at a current density of 17 amp./sq.ft. and a temperature of 25-30°C gives films suitable for photographic reproduction.

II. *Chromic acid process:* The electrolyte used in this process is chromic acid of 1 to 5% strength. The water used should be soft and free from sulphates and chlorides, the maximum limits allowed being 0 05% sulphate (calculated as H_2SO_4) and 0.02% chloride (calculated as NaCl). The anode voltage is raised in steps; initially it is raised from zero to 40 V during the first 15 minutes. After 35 minutes at 40 V, the voltage is again raised over a period of 5 minutes to 50 V. After 5 minutes' treatment at 50 V. the current is switched off and the articles removed.

Films produced by this process are opaque, and range in colour from a light grey on pure Al to dark purple grey on silicon rich alloys The film thickness is of the order of .005 to 0.006 mm. The film obtained has high corrosion resistance, but dye-penetration is not good.

Much of the fundamental work on this process was carried out by Tarr, MacDarrings and Tubbs.[1] They have studied the effect of current density, concentration, pH, temperature and time of treatment on the corrosion resistance and thickness of the anode film, the current efficiency, chromic acid economy and loss of alumina.

As the chromic acid process gives opaque films, it has been suggested that the process can be utilised for producing opaque enamel-like finishes on aluminium. It is possible to get opaque enamel like finishes by adding a mixture of zinc and manganese chromates to the chromic acid bath[2]. In the present work opaque films have been obtained by adding other opacifying agents like ferric hydroxide. The chromic acid strength used was above 10%. The films formed have been found to be excellent for photographic reproduction.

III. *Oxalic acid process*: The electrolyte for this process is a 3–8% (W/V) solution of oxalic acid in which articles are immersed for sixty minutes at a temperature of about 25-36°C and at a steady voltage between 50 and 60. Films produced by A. C. are brass yellow to gold (in the case of pure Al) whereas those produced by D. C. are silver grey in colour. The films are semi-transparent, and have good wear resistance. The addition of sulphates of metals giving complex salts with oxalic acid seems to lower the operating voltages and give perfectly white films. Preliminary experiments by the author in this direction have proved successful.

SULPHAMIC ACID PROCESS:

Recently sulphamic acid has engaged the attention of several workers in this field. Tajima, Kimura and Fukushima of the Electrochemical Laboratories, Tokyo, have carried out investigations on the sulphamic acid process. They have reported the optimum conditions for obtaining suitable films from a sulphamic acid bath[3]. These films were found to possess greater abrasion and corrosion resistance than films produced by the sulphuric acid or oxalic acid processes.

REFERENCES:

(1) Tarr, O. F., Mac Darrings, & Tubbs, G. L., *Ind. Eng. Chem.* **33**, 1575 (1941)

(2) *B. P. 652,743* (December 23, 1947)

(3) Tajima, S., Kimura, Y., and Fukushima, T., *Metal Finishing,* **50**, 65 (1952)

CALCIUM CARBIDE

by

A. Sreenivas

(Central Electrochemical Research Institute, Karaikudi)

INTRODUCTION: Although calcium carbide was discovered by Robert Hare and Wohler as far back as the year 1839, commercial production started only in 1892 when Moissan in France and Thomas Wilson in America independently developed the electric furnace process for its manufacture. The industry grew mainly on the demand for acetylene for welding and cutting operations and for the production of calcium cyanamide used as a fertilizer. Both acetylene and cyanamide are also the starting materials for the synthesis of a variety of organic chemicals. During World War II, the German production went up to 3 million tons, mostly on account of the large demand from the German Chemical Industry.

Calcium carbide in a pure state is stated to be colourless and transparent. It can be produced, though with great difficulty, by thermal decomposition of pure calcium cyanamide in the presence of carbon. The commercial variety is dark in colour since it invariably contains impurities such as calcium oxide, carbon etc. A typical analysis of commercial carbide shows that it contains 82.3% CaC_2; 1.2% C; 14.72% CaO; 0.06% CaSi; 0.07% Ca_3P_2; 0 13% CaS; 0.72% FeSi; 0.8% other impurities. Calcium carbide is reacted with N_2 at 1000-1200°C in stationary or rotary furnaces in order to produce calcium cyanamide.

RAW MATERIALS: The raw materials required for the manufacture of calcium carbide are lime, coke and electrodes. These should be pure, as no refining is done in the furnace. The coke should contain the minimum of ash. Phosphorus is the most deleterious impurity as it forms calcium phosphide under the strongly reducing conditions in the furnace, and goes into the carbide. This reacts with water to give phosphine which ignites spontaneously. Sulphur usually volatilises in the furnace but sometimes it goes into the carbide and thence into the acetylene and plugs up the burners. Presence of more than 0.5% of MgO reduces the fluidity. Silica is partly volatilised and partly reduced to combine with iron to form ferrosilicon, but a large part of it combines with lime to form low-fusion calcium silicate which dissolves in calcium carbide. Oxides of iron and aluminium also undergo similar reactions.

The coke used should be of low ash-content and high resistivity. Hence metallurgical coke is mostly used. As the coking coals are fast getting into short supply, there is a great need to find out suitable substitutes which will be satisfactory for use in the carbide industry. The extensive deposits of lignite located at Neiveli in the Madras State appear to constitute a most worthwhile source for the supply of carbon. With this idea, extensive laboratory investigations have been planned and are in progress in this Institute. Details of the results obtained will be published in a separate communication.

The limits of impurities allowed in the raw materials are as given in the following table:

Material	%Ash	%P	%S	%SiO_2	%MgO
Anthracite.	4	0.04	0.5	...	...
Coke.	7.5	0 04	0.5	...	...
Limestone.	96% pure	0.02	...	1.5	2

The electrodes used in the carbide furnaces and in fact for all electrothermal work should have high electrical conductivity, a slow rate of oxidation, good mechanical strength and the correct shape and dimensions. The electrical resistance of a carbon electrode varies inversely as the carbon content and the density, and directly as the ash and volatile contents. Graphite electrodes have a quarter of the resistance of carbon electrodes of identical dimensions and their density is 2 to 3 points higher. For electrothermal work, however, carbon electrodes are preferable since they are mechanically stronger (tensile strength is 50% greater than that of graphite) and for the same current density a bigger electrode could be used covering a larger area in the furnace. The advent of Soderberg electrodes in recent times has very much facilitated the continuous operation of the carbide furnace without interruption.

FURNACE: Although the carbide furnace has been developed from the familiar arc furnace like that used in electric smelting, it is not a true arc furnace. It is operated keeping the ends of the electrodes below the charge. It is a submerged arc and a major part of the heat comes from the resistance of the charge to the passage of the current. It may be either the single phase or the 3 phase type. Single phase operation has the drawback of unbalancing the three phase net-work unless three units or other methods are adopted and hence 3 phase operation is usually preferred. The three electrodes of a three phase unit can either be placed in a line or in a triangular form. Three electrodes in a line create a dead phase, and the power input is not uniformly distributed between the electrodes. Electrodes arranged in a triangular form will eliminate this difficulty. The power input to a furnace cannot be raised by increasing the voltage, since it is more or less set by the electrical resistance of the charge. The electrodes will rise out of the charge if excessive voltage is applied and will produce an open arc. The load increase is achieved by increasing the amperage. But the increase in amperage brings about increased inductance losses with consequent lowering of the power factor. It is therefore of the utmost importance in large furnaces that the secondary current leads and interlacing busbars are designed with care in such a way that the P. F. can be maintained high. Capacitors are mounted in the circuit for high loads, to decrease the phase-angle of the outside net-work.

FURNACE OPERATION: The electrodes are guided and attached to water cooled bronze headers by means of water cooled bolts. An automatic mechanism operating a cable drawn over the furnace adjusts the height of the electrodes to maintain a constant resistance through the reaction bed. If the resistance of the bed increases, the electrodes are lowered. If the resistance decreases usually because of excessive carbon, the electrodes are raised. The level of the charge is maintained by adding fresh charge. Satisfactory operation of the furnace will depend upon maintaining an optimum heat-concentration. This determines the voltage and amperage. These in turn depend on the electrode-spacing and the tapping system.

A recent development in the field of furnace technique is the rotating furnace nowadays being tried for phosphate-smelting. Its use can perhaps be extended to the production of calcium carbide also. In stationary furnaces craters are formed usually around the electrodes. The crater walls have a tendency of increasing in thickness, causing a gradual narrowing of the channels through which the gases can escape only with difficulty. This causes the furnace to blow and operate unevenly. In the rotating furnaces, the crucible is mounted on a turn-table, supported from a circular rail by wheels. It is rotated at speeds of 1 revolution in 18 to 144 hours. The electrodes are fed through the top of the crucible, which is stationary. The problem of providing a gas-tight stationary roof is solved by a molten lead seal kept at about 360°F by submerged electric heating controlled thermostatically. By this method the electrodes continuously work on fresh charge and any crusts formed will melt away. The rotation will prevent the charge from clogging and will allow the furnace gases to escape even when fines are charged. The advantages claimed for such a furnace are (1) lower power consumption (2) higher capacity (3) elimination of rodding of the charge (4) The possibility of charging fines also.

USES OF CARBIDE: Synthetic organic preparations such as acetaldehyde, acetic anhydride, acetic acid, acetone, polyvinyl compounds, butanol, chlorinated derivatives etc. can be produced from acetylene. Acetylene can be thermally decomposed to acetylene-black possessing high electrical conductivity and high absorption properties. This is extensively used in the rubber industry and in dry cells manufacture. Cyanamide produced from calcium carbide is used both as a fertilizer and for the production of melamine resins.

FUTURE PROSPECTS: Before the second World War, calcium carbide was the only material available for the commercial production of acetylene. Several processes based on petroleum have since been put forward for acetylene-manufacture. A process of cracking of lower hydrocarbons to acetylene by the electric arc has been tested on a pilot plant scale in America. Upto the present time, none of these processes has proved to be of much commercial importance.

The author wishes to thank Dr. A. Joga Rao for his valuable help in preparing this article.

NOTES AND NEWS

COMMITTEES AND CONFERENCES :

Dr.B.B.Dey, Director, C.E.C.R.I. has been appointed Chairman of the Commission constituted by the West Bengal Government to examine the working of the recognised Secondary Schools in West Bengal.

ADDRESSES AND LECTURES :

Shri C. Rajagopalachari visited the C. E. C. R. I. on 11 - 7 - 1954. He was shown round the various departments and the problems under investigation were explained to him. Addressing a gathering of the members of the staff, he laid stress on the real spirit of science which tends to be lost nowadays by the very abundance of scientific equipment which often leads to helplessness on the part of the scientist, and also by an undue craving for publicity. He exhorted scientific workers to make precision and accuracy the hall-mark of laboratory work in India.

The Hon'ble C. D. Deshmukh, Finance Minister of the Government of India and Shrimathi Durgabai Deshmukh, Member of the Planning Commission, visited the C. E. C. R. I. on 21-7-54. After seeing the research work going on in the various departments they addressed a meeting of the members of the staff. Shri Deshmukh made appreciative reference to the existing scientific talent in India and said that no worthwhile scheme of research would be held up for lack of the necessary finance. Shrimathi Deshmukh spoke about the provisions which the Goverment of India have made for promoting youth welfare activities in the country.

STAFF :

Shri O. P. Khanna joined the Institute as Administrative Officer on 24-6-1954. We welcome him, as well as the following members who joined this Institute during the last quarter.

1.	Shri D. L. Roy	Junior Scientific Assistant	24-5-54
2.	Shri K. Sundararajan	Junior Laboratory Assistant	21-6-54
3.	Shri Gangadhar Tilak	Clerk	17-6-54

The following members of the staff have left us and we convey our good wishes to them.

1.	Shri T. D. Prasada Rao	Senior Laboratory Assistant.
2.	Shri VR. Veerappan	Clerk.

SOCIAL AND PERSONAL :

The annual General Election of the C. E. C. R. I. Staff Club was held on 26-6-1954 and the following members have been elected to serve on the Executive Committee.

1.	Shri S. Ramaseshan	General Secretary.
2.	Shri P. S. Desikan	Joint Secretary.
3.	Shri M. V. R. Rau	Member in charge of Reading Room and Library.
4.	Shri B. S. R. Sastri	Member in charge of Excursion and Transport.
5.	Shri G. Soundararajan	Member in charge of Reception.
6.	Shri S. M. Sundaram	Member in charge of Games.

7. Shri R. Ramakrishnan Treasurer (Ex-Officio).

8. Shri G. Rama Rao Auditor (Ex-Officio).

VISITORS :

	Name	Date of visit
1.	Dr. D. Padmanabhan Deputy Director (Technical), Council of Scientific & Industrial Research.	1-6-54
2.	Shri R. P. Bahadur, Secretary, Council of Scientific & Industrial Research.	27-6-54
3.	Shri C. R. Narasimhan, M. P.	10-7-54
4.	Shri C. Rajagopalachari.	11-7-54
5.	The Hon'ble C. D. Deshmukh, Finance Minister, Government of India.	21-7-54
6.	Shrimathi Durgabai Deshmukh, Member, Planning Commission.	21-7-54

BOOK REVIEWS

Physico-Chemical Methods

by Joseph Reilly & William Norman Rae, Volume I & II, Fifth edition, 1954 (Methuen & Co., Ltd., London. £ 7. 10 S.)

Physico-chemical Methods was first published in a single volume about a quarter of a century ago. The third edition which appeared in 1940 was in two volumes and now the fifth edition has come in three volumes. During this period there have been extensive developments of the borderline techniques of common interest to chemists and physicists, and concomitantly with these developments this excellent book has also grown in size. Students, teachers, and research workers will all profit by going through these two volumes. Students will find the study of physical chemistry made pleasant, teachers will get the 'pattern' to follow, and research workers will find some long-felt needs amply met in the precise descriptions of apparatus and the numerous references to original literature.

The earlier part of volume I covers the general lay-out of the laboratory devoted to the study of problems in physical chemistry, general laboratory technique, fundamental units and their measurement, and the methods used in high pressure and vacuum work. The latter part deals with thermometry, temperature control, and thermal measurements and concludes with an excellent chapter on low temperature technique. This chapter gives in a nut-shell the methods of producing and measuring low temperatures, and reviews the applications and results of low temperature work.

Volume II commences with chapters on the separation processes such as the different types of distillation, sublimation, flcatation, crystallization etc. Then follow chapters on photography, optical measuements and spectrometry. Electrochemistry claims four chapters and at the end there is a chapter on radiochemistry. The work bears the impress of the personality of the authors; the various topics included in it are presented systematically, stressing the history and development of the methods under discussion. The suggestions for further reading given at the end of each of the two volumes enhance the value of the book. These volumes should find a place in the chemical library of all teaching and research institutions.

S. R.

Zirconium and Zirconium Alloys

A symposium on Zirconium and Zirconium Alloys presented to members of the ASM during the 8th Western Metal Congress and Exposition, Los Angeles, March 1953 (American Society for Metals, Cleveland, Ohio, 1953)

The American Society for Metals must be congratulated for publishing this collection of papers on zirconium and zirconium alloys. The first paper deals with the methods of concentration of zircon and baddeleyite which are the principal commercal minerals of zirconium. In the second paper the preparation of zirconium powder by different methods is clearly described and flow sheets are given. The hydride method is described in detail and also the methods for the safe handling of zirconium powder. The third paper is of immense value as it describes a practical method for obtaining high purity zirconium employing readily available materials and equipment. A simplified fused salt bath containing 25-35% K_2ZrF_6 in NaCl has been proved to be superior to other electrolytes for producing zirconium. In paper 4, the rate limiting factors and the optimum conditions for the refining of zirconium by the iodide process are described. The major steps in the production of zirconium sponge by the magnesium reduction process, namely chemical purification, chlorination, reduction, vacuum distillation, sponge handling, and melting are covered in detail in the fifth paper. A description of a simple, effective and economic process for producing large ingots of zirconium metal and alloys in a production-model, inert-atmosphere arc melting furnace is given in the 6th paper; the power requirement is stated to be 0.5 kWh. and initial recovery of machined ingot is from 75 to 85% of input metal. The next paper deals with fabrication technology and supplies useful information on cold rolling, drawing, swaging, forming and machining. The effects of impurities, the melting practice and the effects of surface contamination during hot working and annealing on fabricability is discussed. The 8th paper describes the main causes for the embrittlement of the metal. It has been stated that as little as 10 ppm of hydrogen in zirconium can cause a noticeable embrittlement in the quenched and aged condition, and to develop embrittlement it is necessary to heat first to a temperature above 600°F and then to cool at a rate slower than the critical rate to a temperature below 500°F. In the next paper a glass vacuum apparatus suitable for rapid and precise hydrogen determination is described. The tenth chapter describes a rapid and simple technique for preparing any zirconium or zirconium alloy specimen for bright field or polarised light metallographic examination by chemical polishing. The physical metallurgy of zirconium and its alloys, its corrosion resistance and the structural use of zirconium in nuclear reactors are also fully described and occupy the rest of the book.

All aspects of the work on zirconium from the time it was considered a metallurgical curiosity to the present day when it shows considerable promise of becoming an important engineering material are very well brought out. The volume is bound to become a standard book of reference.

V. A.

Leybold Polarographische Berichte, edited by Willi Hans and Hans Ulrich Bergmeyer, Band I, Heft 1/2, 1952 to Band II, Heft 1, 1954 (Staufen-Verlag Koln; Yearly subscription 18.50 DM)

This is a quarterly journal devoted to polarography, a subject of growing importance now. The issues of the journal contain comprehensive abstracts of current polarographic literature, original articles, book-reviews, questions and answers on important topics and general notes. The publication satisfies a long-felt need by providing easy access to the rapid advances being made in polarographic analysis and is a venture worthy of admiration.

The references are classified under the heads apparatus, methods, inorganic section, organic section, theory, general, and bibliographic work. They are further subdivided according to the subject matter. This procedure makes the abstract section easy to read and facilitates reference work.

An extension of the applicability of rotating platinum electrodes and the two types of maxima observed with organic solutions are the subjects of two original contributions in the October, 1952 issue (Band I, Heft 1/2) The use of vibrating platinum electrodes in polarogaphy and the method of obtaining current-voltage curves and calculating the diffusion current from a fundamental equation are discussed in the issue for January 1953 (Band I, Heft 3). The use of silicones for improving the dropping electrodes is described in the April, 1953 issue (Band I, Heft 4). A masterly treatment of the theoretical phenomena connected with the Heyrovsky-Forejt oscillographic polarograph is given in the issue for January, 1954 (Band II, Heft 1).

A good author and subjet index is issued separately and adds much to the usefulness of the journal. The get-up and printing leave nothing to be desired.

M. S.

Chemische Industrie

English Edition, No. 1, 1954.
(Published on behalf of the Verband Der Chemischen Industrie E. V. by Verlag Handelsblatt G. M. B. H., Dusseldorf. Annual Subscription $ 3.00)

The journal under review is the first number of the English edition of "Chemische Industrie" which the publishers of the orginal German edition are bringing out twice a year in April and October. Besides containing a selection of the most important articles appearing in the monthly German edition, the journal incorporates many features of special interest to all those connected with the chemical and allied industries in Europe, including the Eastern sector. The journal contains detailed statistical information about the post-war industrial potential of the European countries besides surveys of the production and consumption of the more important industrial chemicals. The aim of the publishers in bringing out this edition is to cater to the increasing needs of the younger generations of chemists, technologists and businessmen who can read German publications only in translation. Backed as it is by the established reputation of the parent journal, this new venture is sure to find a ready welcome from scientific and technical men all over the world. It is a worthwhile addition to any technical and scientific library.

G. S. K.

ABSTRACTS

A simple method for the calculation of electrode potentials in polarography :- Markus, G., *Science*, **119**, 324-5 (1954)

Frequent conversion of applied voltage to electrode potential is necessary in polarographi work It involves separate experimental determination of current and total resistance of the circuit for the IR factor. To eliminate this, a method is proposed for the direct determination of IR factor from the polarograms of the same substance recorded at different concentrations. A gradual shift of the half wave potential is observed with increasing concentration which is due entirely to the increase of the IR factor, and for constant resistance the shift is a linear function of current. A calibration curve of IR versus I is prepared from which the evaluation of the desired voltage is made.

Application of cathode ray polarography to rotating platinum electrodes: Shain, I., and Crittenden, A L., *Anal. Chem*, **26**, 281-4 (1954).

An instrument has been built for observing current - voltage curves at rotated platinum microelectrodes during periods of time comparable to the drop-time of the mercury electrode. The commercial cathode ray oscillograph is modified and a mechanically driven sweep generator used. This set-up has good stability and versatility with regard to zero drift, sensitivity, and rate and range of variation of polarizing potential. With very little alteration it can be applied for studies with the dropping mercury electrode.

The polarographic determination of fluoride: Basic Principles of the method. Application to the cathode ray polarograph: Macnulty B. J.. Reynolds, G. F , and Terry, E. A., *Analyst*, **79**, 190-8 (1954).

A sensitive method for the polarographic determination of fluoride is described. It is based on the depression by fluoride of the polarographic step given by the reduction of the aluminium-Solochrome Violet R. S. complex. The step depression is found to be linearly related to fluoride concentration down to 0.001 μg per ml. The use of this method with the cathode ray polarograph is described.

The Application of Polarogrphic analysis in Leather Research, Ramaswamy, D., and Nayudamma, Y., *Science and Culture* **19**, 475-8 (1954).

Polarographic problems for investigation with special reference to their application in leather research are described under sections—proteins, vegetable tanning materials, mineral tanning and mechanism of tanning. In the beginning, a general resum'e of polarographic theory is given.

The Silver-Silver Halide Electrodes : Janz, G. J., and Tannıguchi, H., *Chem. Rev.*, **53**, 397, (1954)

The preparation and properties of silver-silver halide electrodes in aqueous and non-aqueous solutions are reviewed with 113 references.

Glow-discharge electrolysis: Oxidation reactions in glow-discharge electrolysis: Klemenc, A , and Kohl, W. *Monatsh. Chem.* **84**, 498-511 (1953) *C. A.*, **48**, 3165 (1954)

Around the cathode water was decomposed into H atoms and OH radicals, and these were scattered in all directions with a part of them entering the liquid surface. Oxidizable salts were used to detect scattered OH radicals. The rate of oxidation in the solution could then be measured by the volume of O liberated. With 60 ma. at 500 V and a pressure of 12 mm. Hg 10^{18} OH radicals entered the surface/sec.

Oxidation and reduction in glow-discharge electrolysis : Kohl, W., and Klemenc, A., *Monatsh Chem.*, **84**, 1053-60 (1953); *C. A.* **48**, 3818 (1954)

Oxidation of inorganic solutions proceeded according to :

$$\text{(a) } Fe^{++} + OH \rightarrow Fe^{3+} + OH^{-} \text{ or}$$

$$\text{(b) } 4\, r\, OH \rightarrow 2\, r\, H_2O + r\, O_2$$

Values of r for the compounds studied were H_3Po_3, $NaHSO_3$, 2; K_2CrO_4, 3; NaH_2PO_3, 4. The behaviour of $K_4Fe(CN)_6$ and $MnSO_4$ was complex. Both oxidation processes are represented by curves of S/O_c Vs. C°; where S was the volume of 0 in cc taken up by the system, 0_c was the number of couloumbs used, also expressed in cc. 0; and C° was the solute concentration at the gas solution surface. In these curves the slope at the origin equalled the value of r for process (b); r=1 for process (a). No reduction was observed for H_3AsO_4, $K_2Cr_2O_7$, CrO_3, $Fe_2(SO_4)_3$, or $K_3Fe(Cn)_6$.

Electrochemical conversion of hydrocarbons: Reeves, W. B., (to Phillip Petroleum Co.) U. S. 26,64,394, Dec. 29, 1953; *C. A*, **48**, 4340 (1954).

Hydrocarbon conversions are energised by superimposed electrostatic and magnetic fields. The feed gas is pretreated to 400-2000° F and then passed through the combined fields. The electrostatic potential is 40-300 K. V. d. c., and the magnetic field frequency 40-300 cycles/sec. The effluent gases are cooled and deionised When C_3H_8 is used as a feed gas, approximately 5% is converted, largely to isoparaffins of higher mol. wt. than C_3H_8.

Treatment of hydro carbon gas with electric arc: Inoue, T, and Kauda, Y. (To Bureau of Industrial Technics) Japan 1973, May 1953; *C. A.*, **48**, 4340 (1954).

CH_4 is treated with an electric arc (11 amp. and 2.6 kW.) at the rate of 1.2 cu m./hr while passing in H_2 at the rate of o.ol/cu. m./hr between the electrodes. The yield is 9% C_2H_2.

The evolution of the Sodium Industry: Hardie, D. W. F., *Ind. Chemist*, **30**, 161-66 (1954).

The evolution of the sodium electrolytic cells, including the Down's cell which is widely employed, is discussed. Large amounts of metallic sodium are required for the manufacture of lead-sodium alloy which is used in the production of tetra ethyl lead (TEL). About 60% of the sodium metal produced in the United States is utilized for the manufacture of TEL.

The Chemical analysis of Titanium and its alloys: Payne, S. P., *Light Metals*, **17**, 195 (1954.)

Processes for the estimation of Al and Si in Ti alloys are described.

Continuous feeding of aluminium oxide to the electrolytic cell: I. N. A Industria Nazionale Alumino, Ital. 465,932, Oct. 1951; *C. A.*, **48**, 1181, (1954)

Alumina is continuously fed under mechanical pressure to the fused electrolyte for the efficient manufacture of aluminium, anode-effect being thus eliminated.

Beryllium: *Metal Progress*, **65**, 81-97 (1954).

Contributions to a Symposium on beryllium held recently in the U. S. A. are summarized in three articles The sources, supplies and uses of beryllium are described in the first one and the difficulties encountered in the recovery of beryllium indicated. The applications of beryllium as a neutron moderator and reflector are reviewed in the second article and powder metallurgical techniques adopted in the fabrication of beryllium are described in the third.

Electrolytic chromium from Ferrochrome: Lloyd, R. R., Rosenbaum, J. B, and Homme V. E., U S. 2,663,686, Dec. 22, 1953(*C. A.*, **48**, 3172, (1954).

Low grade chromite ores can be used to make chromium electrolytically by using an electrolyte made by dissolving ferrochrome in a sulphuric acid solution containing ammonium sulphate, removing C and Si by filtration, and iron by cooling to precipitate as ferrous. ammonium sulphate, and getting chrome-alum from the mother liquor for making the cell-feed solution. The depleted mother-liquor, anolyte and catholyte overflows, and also the chrome liquor after removal of iron are all recycled in the process to improve its economy.

Chromium-Manganese stainless steels: Everhart, T L., *Materials and Methods*, **39**, 92-94 (1954).

In view of the world-wide shortage of nickel Cr-Mn steel is suggested as a suitable substitute for conventional stainless steels. Cr-Mn steels have found commercial application in Europe, particularly Germany.

Leaching and electrolysis of low-grade copper-lead-zinc ores: Hilliard, R. V., and Baroch, C. T., U. S. 2,655,472, Oct. 13, 1953; *C. A.*, **48**, 1227, (1954).

The roasted ore is leached in an alkaline solution containing NaCN if Ag and Au are present and then treated with lime. The precipitated silicates or carbonates are filtered off and the solution is treated with zinc added in instalments to remove the metals precipitated by H_2S. Alternatively, copper powder may be added to remove Au and Ag, followed by Pb powder to remove Cu and finally Zn powder to remove Pb The zinc is recovered by electrolysis of the alkaline solution at high current densities. The spent electrolyte can be recycled to the leaching stage.

Electro-deposition of copper powder: Modi, H. J., and Tendolkar, G. S., *J. Sci. Ind. Research (India)* **12B**, 431-8 (1953)

Conditions for obtaining Cu powder suitable for metallurgical use have been investigated. The effects of current density, concentration of Cu and H_2SO_4, temperature, rate of circulation and addition agents like glucose, glycerol, glue and gelatine on the electrolysis of acid $CUSO_4$ were studied using 2 cathodes and 3 anodes of rolled electrolytic Cu. Addition of glue and gelatine increased the apparent density; glucose and glycerol had no appreciable effect.

Germanium: Jones, N. C., *Ind. Chemist*, **30**, 229-39 (1954)

Methods of producing germanium from ashes, flue dust and germaniferous ores are reviewed. The applications of germanium in the electronic industry are described.

Recovery of Manganese from low-grade ores: Allen, L. N., *Chem Eng. Progress*, **50**, 9-13 (1954).

A new method of leaching low grade manganese ores is described with a flow diagram. A slurry of the ore is leached with sulphur dioxide in packed towers, and then oxidised in stainless steel autoclaves. The solution thus obtained is filtered and the

$MnSO_4$ crystallised out and sintered to produce manganese oxide. The SO_2 produced is recycled. Operating costs are given.

Continuous electrolytic preparation of magnesium by means of a magnesia electrode: Ichiro Egami, Japan 305, Jan. 27, 1953; *C. A.*, **48**, 1181 (1954)

A mixture of MgO 50, artificial graphite 30, pitch 10 and tar 10% is moulded to make an anode. An electrolyte containing $MgCl_2$ and KCl is electrolysed with this anode and a C cathode to give Mg on the C cathode. The Cl evolved at the anode reacts with the MgO of the cathode to form $MgCl_2$ which keeps the concentration of $MgCl_2$ in the electrolyte unchanged during the electrolysis.

The Electrolytic Preparation of Molybdenum: Electrolytic Studies: Senderoff, S., and Brenner, A. *J. Electrochem. Soc.*, **101**, 16, 1954.

A study of the operating conditions on the nature of molybdenum deposited by the electrolysis of potassium hexachloromolybdate dissolved in fused alkali halides is described.

Preparation of reduced Molybdenum halides: *ibid*, **101**, 28, (1954):

Methods for the preparation of potassium hexachloromolybdate by the electrolysis of a solution of potassium molybdate in hydrochloric acid in a divided cell and for the preparation of molybdenum dichloride by reduction with molybdenum powder followed by thermal decomposition are described.

Studies of Electrode Potentials: *ibid* **101**, 31 (1954)

Polarization and equilibrium potential studies in molten halides using the new reference cell Ag, AgCl are reported.

Rhenium: Kates, L W., *Materials and Methods*, **39**, 88-91 (1954)

The industrial importance of rhenium as a refractory metal is indicated. It has potential application in the manufacture of thermocouple alloys, pen-points and electrical contacts. The properties, fabrication and industrial applications of ductile rhenium are described.

Electrolytic detinning: Lowenheim, F. **A.**, U. S. 2,665,473, Oct. 13, 1953; *C. A.* **48**, 4339 (1954):

Using a large sized app, high quality, non-spongy Sn is recovered from a rotating, bipolar drum electrode packed loosely with Sn scrap submerged in an alkaline aqueous solution (5% NaOH or KOH) at 70-87°, for 1-5 hours, at 2.7 - 3.9 V. and 2.5 amp. The rotating drum is suspended between the anode and the cathode, above but not touching the anode. Anodic O passing up through the scrap aids in the detinning.

Production of Rare Earth Metals in quantity: Spedding, F. H., and Daane, A. H., J. **Metals**, **6**, 504 (1954)

The production of rare earth metals by the metallothermic reduction of the halides with Ca metal is reported. Kilogram quantities of La, Ce, Pr and Nd have been produced by the reduction of their chlorides with pure calcium metal powder at 700°C. Iodine was used as a booster. Metallic yttrium was obtained in small quantities by reducing its fluoride with calcium at 1550°C in a tantalum crucible. Europium, samarium and ytterbium were obtained by reduction of their oxides with lanthanum turnings. Some of the physical properties of these metals are described. The authors suggest that the range of volatilities of these metals could be used as a basis for their separation from crude rare earth mixtures.

New Titanium Process: *Chem. Eng. News*, **32**, 1998 (1954).

Production of 99% Ti metal by the electrolysis of TiO in a fused $CaCl_2$ bath between Fe electrodes has been reported. TiO is prepared by reaction between Ti carbide and Zn or Mg oxide, yielding metallic Zn or Mg and TiO. The metal is removed by distillation.

Electrolysis of K_2TiF_6 in molten NaCl is reported to give Ti metal comparable in purity to the present commercial metal. Reagent grade salts are essential and are further purified by pre-electrolysis.

An electrolytic process for refining crude Ti has also been reported.

Thorium and rare earths from monazite Bearse, A. E., Calkins, G. D., Clegg, J. W., and Filbert, R. B., (Jr.) *Chem. Eng. Progr.*, **50**, 235 (1954).

Finely ground monazite (−325 mesh) is heated with a 45% solution of sodium hydroxide to 200°F for 2.3 hours. The slurry thus obtained is dilutedand digested at 220°F for an hour. The hydroxides of Th and the rare earths are filtered off, leaving tri-sodium phosphate in solution. The hydroxides are dissolved in HCl and the thorium separated by partial neutralization of the acid solution to a pH of 5 8. 99.7% of the thorium is removed by this method, and the thorium hydroxide precipitate contains only 2-3% of the rare earths. The paper describes the various chemical engineering techniques used in the process for the decomposition of 10 lb. of sand at a time.

Zirconium Production by Fused Salt Electrolysis: *Metal Industry*, **84**, 468 (1954)

Requirements for the successful operation of Kroll's process for Zr & Ti are discussed and the advantages of the electrolytic process indicated. Considerable success is reported in the fused electrolysis of K_2ZrF_6 and NaCl, in an atmosphere of purified argon. The molten salt mixture is contained in a graphite crucible which forms the anode and is heated by a carbon resistance element fed by alternating current from water cooled leads. A steel cathode mounted on a chlorine-resistant nickel shaft is used and electrolysis carried out at 800-850°C with a current density of 250-400 amps/dm². The bath life is limited only by the build-up of NaF and KF in the salt. Six runs are likely te bo practicable before discarding the bath. The reduction is said to be definitely electrolytic and is not the result of a secondary reaction with sodium liberated at the cathode.

Ductile Zirconium : Chemical Age, 70, 1195 (1954)

Methods of production., properties and applications are reviewed.

Heavy Water—A review of processes and plants for large scale production : Selak, P. J., and Finke, J. *Chem. Eng. Progr.* **50**, 221-29 (1954).

Methods used for large scale production of heavy water are reviewed. The processes generally employed for commercial production, namely distillation of water, electrolysis, hydrogen-water exchange and distillation of liquid hydrogen are discussed. The operating cost, and brief details of the construction and operation of the different plants are given.

International developments in Heavy Water Reactor Technology ;Goedkoop, J. A., *Nucleonics,* Vol.11, No. 12, p. 10 (1953) :

Discussions on the progress of heavy water reactor technology and the prospects for heavy water power reactors which took place at the world's first open international meeting on nuclear energy held in Kjellar and Oslo, Norway in August 1953 are summarized. In spite of the heavy cost of production the use of heavy water is warranted because of the scarcity of enriched uranium and plutonium. Specific reactors and the general merits of heavy water as a moderator in atomic fission, namely good neutron economy, higher power output and higher burn up are briefly described.

The Effect of nitrate ion and ammonia in the electrolytic separation of hydrogen-deuterium isotopes: Hojman, J. M., *Bull. Inst. Nuclear Sci.* "Boris Kidrich" (Belgrade) **3** No 46 121-6 (1953) *C. A.* **48**, 1852 (1954)

The effect which NO_3^- and NH_3 might have as depolarizers on the electrolytic separation factor for obtaining D_2O was investigated. The presence of NO_3-ion in the electrolyte did not change the separation factor whereas it was increased by the electrochemical oxidation of NH_3. A high current density of 1 04-1.22 amp/sq.cm. was used. The anode and the cathode chambers in the apparatus were not separated. Normal water with 0.019% D_2O was used as the starting solution. Experiments were carried out in electrolytic cells with working capacities of 100 and 400 cc of 0.4*N* KOH. The separation factor decreased if the passage of H through the electrolyte was prolonged.

The Cathodic Reduction of Anions and the Anodic oxidation of Cations: Wagner, C., *J. Electrochem. Soc.*, **101**, 181, (1954) :

From theoretical considerations it is found that the cathodic reduction of anions and the anodic oxidation of cations will be affected only if the potential across the diffusion boundary layer is increased, since then the migration of the anions towards the cathode or that of the cations towards the anode is checked by the adverse potential gradient. It is shown that the cathodic reduction of hypochlorite ions in alkaline solution may virtually be prevented at high current densities. However the effect is insignificant when high electrolyte concentrations are involved as in the electrolytic production of hypochlorite.

Diaphragm Type Amalgam Caustic Chlorine Cell, Potter, C., and Bisio, A. L., *J. Electrochem. Soc.* **101**, 158 (1954)

An amalgam type caustic cell consisting of an anode compartment containing brine and graphite anode and a cathode compartment containing a mercury cathode, denuder water and graphite chips was studied. The compartments were separated by a horizontal nylon cloth diaphragm. Optimum operating characteristics of the cell were: denuder liquor velocity 8.0 gal./hr./ft² Hg, brine velocity 1.0 gal./hr./ft² Hg, brine temperature 50°C, current density 1 amp./sq.in. Hg and a voltage drop of 3.7 volts. The cell produced 0.8 lb. caustic soda/kWh. at a current efficiency of 90-91% which is slightly higher than the efficiencies in present commercial operations.

Electrolysis of alkali metal halide brines : Mathieson Chemical Corp., Brit. 695,877, Aug. 19, 1953, *C. A.*, **48**, 1864, (1954) :

A brine containing Fe <0.0001, Mg 0-006 and Ca as $CaSO_4$ 0.8 - 1.45 g per litre is subjected to Hg cell electrolysis at a pH of 1.7-3.0, maintained by the addition of HCl. When the Ca is 0.8 g/l and the pH is> 3.0, H formation is increased. When the Ca is<0.8 g/l the pH may be>3.0 without any H in the Cl of>0.75%.

Electrolysis of an aqueous solution of calcium chloride : I Tatsu Yokoyama (Toyama University) *J. Chem. Soc. Japan. Ind. Chem Sect.,* **55**, 321-2 (1952) : *C. A.* **48**, 470 (1954).

$CaCl_2$ solution was electrolysed without deposition of Ca $(OH)_2$ on the cathode using a diaphragm and a catholyte containing sucrose. The voltage of electrolysis was low. H and Cl were obtained with high current efficiency. The applicability of this process to industry is discussed.

Electrolytic preparation of cuprous oxide: Hira Lal, *J. Sci. Ind. Research (India)*; **12** B, 424-30 (1953)

A systematic study was made of the electrolytic preparation of Cu_2O from a slightly alk. solution of NaCl with electrolytic Cu-foil electrodes in (a) an undivided cell and (b) in an H shaped divided cell with or without a device for continuous circulation and filtration of the electrolyte. The Cu_2O formed was contaminated with $Cu(OH)_2$ and free Cu; the current density, temperature and concentration of electrolyte affected the purity of the product. The colour of the Cu_2O varied from red through orange and yellow to greenish yellow as temperature and concentration of the electrolyte were decreased. X-ray photographs indicated an expansion of the cubic lattice from a= 4.24 kX to a = 4.33kX and a progressive broadening of the diffraction bands. The variation in colour was a crystallite size phenomenon, but the presence of $Cu(OH)_2$ also affected the colour of the product. There was no evidence of Cu(OH).

High grade MnO_2 from low-grade ores: Schrier, E. and Hoffmann, R. W., *Chem. Eng.*, **61**, 152-5, 372-5 (1954) *C. A.*, **48**, 2334, (1954):

Battery active MnO_2 is made from crushed and calcined low-grade ores by leaching with sulphuric acid and electrolysing the purified $MnSO_4$ solution. A flow sheet is given.

Graphite Electrodes: Hader, R N., Gamson, B. W., and Bailey B. D., *Ind. Eng. Chem.* **46**, 2-11 (1954), *C. A.*, **48**, 3821, (1954)

A review of the properties, methods of manufacture and applications is given.

The electrolytic reduction of aromatic carboxylic acids to the corresponding alcohols: Benzoic acid reduction under pressure: Ono, S., and Yamauchi, T., (Naniwa University, Osaka, Japan) *Bull. Chem. Soc. Japan*, **25**, 404-7 (1952)

Studies on thn reduction of benzoic acid under pressure are reported. With a lead cathode and at higher pressures of both H_2 and CO_2, benzoic acid gave higher yields of benzyl alcohol. The yield was 81.3% at 30 atm. of H_2 and 62 1% at 30 atm. of CO_2. In the presence of sodium sulphate and sodium benzoate, mercury cathodes gave the same yields of product at 1 atm. of H_2 and of CO_2. Higher pressure of H_2 increased the yield whereas with CO_2 the opposite effect was observed. At 30 atm. of H_2 the yield was 43% whereas CO_2 at the same pressure gave only traces of the product. At a platinised platinum cathode the ethyl ester of the acid was formed in preference to the alcohol.

Preparation of phenyl hydrazine by the electrolytic reduction of diazonium compounds.

Rultschi, P., and Trumpler, G., (Eidg. Tech, Hochschule, Zurich) *Helv. Chim. Acta*, **36**, 1649-58 (1953)

The optimal conditions for the formation of phenyl hydrazine by the reduction of benzene diazonium chloride in high acid solutions are reported. Reduction cells for working the process both continuously as well as batch-wise have been described. Condensation of the diazonium chloride with the product decreases the yield. This can be prevented by hastening the separation of the product by the addition of KCl to the electrolyte. Optimal conditions for a batch process are:-

Catholyte: benzene diazonium chloride 0.25 parts, KCl 2.0 parts, HCl 0.5 *N*; anolyte: 3.0 *N* HCl; cathode of mercury; c. d. 65 ma/cm^2; temp. −5°C. Yield 70.5%

The process could be continuously worked with a yield of 90% under the following conditions :-

Catholyte benzene diazonium chloride 0.166 parts, HCl 0.233 *N*; anolyte: 6 *N* H_2SO_4; temp. —15°C.

Slight variations in temperature have very little influence on the yield Mild agitation produced little or no effect while vigorous agitation tended to produce phenyl mercury chloride. The concentrations of the depolariser and acid have a pronounced, effect. Wetting agents were detrimental. Mercury as the cathode gave the best results.

The electrolytic reduction of nitriles:

Reduction of benzyl cyanide to phenyl ethyl amine: Kawamura, F , and Suzuki, S , (Yokohama University) *J. Chem. Soc. Japan, Ind Chem. Sectn.*, **55**, 476-8 (1952)

The reduction of benzyl cyanide to phenyl ethyl amine without the formation of the secondary amine is described. The cathode was of palladised nickel and the catholyte a solution of benzyl cyanide in acetic and hydrochloric acids. Other conditions were c. d. of 2 amp/dm^2 and temperture 15-20°C.

P-methyl amino phenol sulphate: Sumio, J., and Koguchi, M., (Konishi Photographic Industries Co. of Japan) Patent **No.** 5128 of **December** 1952; *C. A.*, **48**, 63, (1954)

85 kg of nitrobenzene was reduced in 210 kg of concentrated sulphuric acid and 37 l of water with lead and nickel electrodes at 100°C to produce p-aminophenol sulphate. This was dissolved in 550 l of water aud electrolysed in a cell with a lead anode and copper cathode in the presence of the following.- (1) (p-OH CH_4 N $CH_2)_x$, (2) mono methyl p-aminophenol sulphate and (3) dimethyl p-aminophenol

sulphate. Neutralising the mixture with alkali (NaOH) separates 2 from 3. The filtrate containing 2 is treated with 40 kg of acetic anhydride to precipitate the acetyl derivative of 2 which on hydrolysis with dil. H_2SO_4 regenerates 2,

Anodic oxidation treatment of aluminium and its alloys: Lacombe, P, *Metal Ind.* **84**, 394 (1954)

The sulphuric acid, chromic acid and oxalic acid processes are considered. The effect of alloying constituents on the thickness and hardness of films is discussed. The pore-dimensions of a given alloy increase with increasing temperature and current density, and the hardness of the films is lowered. With refined aluminium (99.99% pure) the oxide film is transparent only when the surface has been electrochemically or chemically polished. Compositions which give high reflective surface are -

99.99%Al: Sulphuric acid (66°Be) 60%, phosphoric acid (60°Be) 10%, nitric acid (36°Be) 1% (by volume); temp. 95°C, C. D, 15-20 amp/dm², time of treatment 20 min.

99.5% Al: Sulphuric acid 600-300 ml, phosphoric acid 300-600 ml, nitric acid 50-100 ml, temperature 95-120°C.

Commercial grade of Al: Sulphuric acid 250-50 ml, phosphoric acid 700-900 ml, nitric acid 30-80 ml, temperature 85-110°C.

Anodic behaviour of aluminium and its alloys in sulpuric acid electrolytes: Mason, R. B., and Fowle, P. E., *J. Electrochem Soc.*, **101**, 53-59 (1954)

This paper deals with the factors affecting the rate of solution of anodic oxide coatings on aluminium as they are being formed in sulpuric acid electrolytes; coating ratios for aluminium and wrought alloys in sulphuric acid under different operating conditions have been determined. High current densities, low temp and addition of 0 5-20% of oxalic acid are found to favour higher coating ratios.

Electro-deposition of brass from a non-cyanide bath I Ray, S. K., and Banerjee, T., *J. Sci. Ind. Research (India)*. **12B**, 438-43 (1953):

Cathode potential-current density measurements were made for the two metals copper and zinc in their respective solutions, viz., sodium cupric tartrate and sodium zincate of different concentrations. The curves indicated the possibility of brass deposition from a mixture of the two electrolytes. This inference has been confirmed by a series of experimental observations on the influence of current density on the composition of the brass deposits from electrolytes containing different concentrations of copper and zinc. A solid cylinder of stainless steet was used as a rotating cathode and an annular brass cylinder as anode. The composition of the brass deposits was almost constant when the current density exceeded a certain critical value. The utilisation of the bath for industrial brass plating is suggested.

Chromium plating of die-cast aluminium engine cylinders: Burt, F. M., *Metal Finishing*, **51**, 65-9 (1953)

The lay-out of the plating department of Mc. Culloch Motor Corporation (Los Angeles) where aluminium engine cylinders, power-saw accessories, steel gauges, and centre-main-bearing cages are hard chromium plated is described. The sequence of operations for chromiun plating of aluminium engine cylinders is alkaline cleaning, chrome-pickling in chromic acid-sulphuric acid mixture, nitric acid etch, fifty per cent nitric acid dip, and zinc immersion, each step being followed by a water rinse. The cylinders are mounted on aluminium jigs and plated in standard (250 G. P. L) chromium plating solution. The thickness of the coating applied ranges from 0 0015" to 0.0035" depending upon the type of engine. The plant uses ion exchangers for removing aluminium from the plating solution.

Metallising of non-metals: Nickel Sulphate-Pyridine bath Chakraborty, K., and Banerjee, T. *J. Sci. Ind. Research (India)*, **13B**, 433 (1954); Ind. Pat. 45579 (1951) (to Council of Scientific & Industrial Research).

Nickel is deposited on the non-metal (soda glass) employing a bath containing nickel sulphate, pyridine and sodium hydrosulphite. Optimum bath composition and temperature have been worked out. An adherent nickel film which can be plated with any desired metal is obtained.

Unplasticized PVC in electroplating plants: Thomas, L. N, *Plating*, **41**, 269 (1954).

The good chemical resistance and fabricating possibilities of unplasticized PVC are made use of in the plating room, e.g, duct work for both acid and alkali tank equipment. The resistance of the material to nearly 300 different chemicals at 72°F and 140°F is listed. The actual service life of the material in several German plants is given. Possible applications for the material in the plating room are suggested.

Electrophoretic rubber deposits for electrical insulation: Inuma, Y., *J. Electrochem. Soc. Japan*, **21**, 129-32; *Electroplating*, **7**, 114 (1954).

The current efficiency decreased with time and with increase in current density. The moisture content of the deposits increased with increase in rubber content, electrolytes in the bath, current density and decrease in pH and duration of electrolysis.

Coating by electrophoresis: Bristol Aeroplane Co. Ltd., Brit. 691,809 (1953); *Electroplating*, **7**, 33 (1954)

The bath (pH 9.5-11.5) contains 5-20% silica or silicic acid in colloidal solution and a neutral filler such as silica, alumina, talc, zircon, graphite, etc. The metal to be coated is made anodic in the above slurry after a preliminary treatment consisting of shotblasting, degreasing and etching.

Electrically insulated conductor: Dorst, S. O. (to Sprague Electric Co.) U. S. 2,650,975 (1953); *C. A.*, **48**, 1864 (1954).

The plating bath consists of a fine suspension of a refractory insulating material (China clay) in an aq. soln. of an inorganic electrolyte (Na silicate). The conductor (Cu, Cu alloy, or nichrome wire) is made the anode on which an adherent and flexible coating is finally obtained. A modified form of this process employs a fine suspension of ZnO and includes treatment of the coating with phosphoric acid before heat treatment.

Sun-Powered Battery: *Science News Letter*, **65**, 278 (1954)

Very pure metallic silicon is grown into single crystals, then one thousandth of an inch under the surface of the wafer of the silicon, impurities are diffused. This produces positive and negative layers of controlled thickness, these positive and negative junctions being the heart of the Solar Battery. The wafer-thin strips of silicon, about the size of razor blades, are extremely sensitive to light. It has been claimed that these can be linked together electrically to deliver power from the sun at 50 watts per square yard of the surface. The new semi-conductor device is claimed to have 6% efficiency in converting sunlight directly into electricity. The Bell Telephone Laboratories scientists G. L. Pearson, C. S. Fuller, and D. M. Chaplin are responsible for the development of these types of batteries. The batteries will be mainly used for mobile power eqipment such as small radio transmitters, battery chargers for rural telephones of newer design, etc.

Separator for storage batteries: Clark, E., U. S. 2,669,599 Feb 16, 1954; *C. A.* **48**, 4338 (1954).

A coating (2 oz./sq. ft) of vinyl chloride-acetate copolymer is given to a wooden core by spraying at 90 lb. air pressure.

Battery separators: Dague, H. F., Collins, W. B., and Caldwell, L. M., U. S. 2,662,929, (1953); *C. A.*, **48**, 3171 (1954).

Polystyrene beads wetted with organic solvents (toluene, CCl_4, acetone, etc.) by spraying are pressed against the battery electrode and the excess solvent is evaporated. The separator thus formed is homogeneous and acid resistant.

Phenol-formaldehyde resin-impregnated battery separators: Uhlig, E. C., and Murray, Jr., L. A., (to United States Rubber Co.) U. S. 2,662,106-7, (1953) *C. A*, **48**, 2498 (1954).

Cellulose sheets are impregnated with a solution of A-stage resin in aq. acetone or alc. and treated to convert the resin to C-stage.

Publication of the proceedings of the Symposium on 'Electrochemical Processes and their Applications to Indian Industry' has been postponed to the next issue.

Ed.

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