Electrolytic Extraction of Beryllium-oxide from Beryl

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Beryllium has of late come into prominence because of its immense value as an alloying element in some binary and ternary non-ferrous alloys. The most important use of this metal is in atomic reactors where it acts as a moderator for slowing down fast neutrons. It is obtained from the mineral beryl of which India is one of the principal producers. An electrolytic method for the extraction of beryllium-oxide from beryl has been developed at the National Metallurgical Laboratory, which consists in first obtaining the beryllium in solution as a soluble beryllium salt and then electrolyzing this solution between two graphite electrodes in a diaphragm cell. A slurry containing the hydroxide of beryllium is obtained from the cathode compartment, which on washing, drying and ignition, gives the oxide.

BERYLLIUM, till recently regarded as a 'rare metal' and of little practical use, has of late come into prominence in the industrial field. Binary and ternary alloys of beryllium with some non-ferrous metals like magnesium, aluminium, nickel, cobalt and particularly those with copper are unique in some of their properties and hence industrially very useful. In fact, it is claimed that "beryllium is to copper what carbon is to iron".

Beryllium oxide is an important raw material for manufacture of special types of refractory wares. Because of its extra-ordinary resistance to thermal shocks and high electrical resistance even at high temperatures, it may be rightly called a 'super refractory' which can be used with great advantage for making crucibles, muffles, laboratory boats, electrical furnace linings, and vacuum tubes. It is also an important ingredient in 'phosphors' for fluorescent lamps.

By far the most important is its use in the atomic reactor as a moderator along with pure graphite and heavy water. But because of the extreme difficulties encountered and hence high cost involved in the manufacture of the high purity metal, its use there is being gradually supplanted by the other two materials, graphite and heavy water.

Though there are several minerals in nature containing beryllium, the only mineral of commercial importance is beryl, which is aluminium-beryllium silicate, $3\,BeO,\ Al_2O_3,\ 6SiO_2$. India is one of the principal beryl producing countries, others being Russia, Argentine and Brazil. Rich deposits of beryl occur throughout India[1], the most productive localities being Ajmer-Merwara and Mewar in Rajputana, Gaya and Hazaribagh districts of Bihar, Vellore district in Andhra and Kashmir.

In the years preceding the last World War, production of beryl in India was not much, as the following table[1] will show :

Year	Output (in long tons)
1932	281
1933	324
1934	55
1935	139
1936	98
1937	26.6
1938	17.4
1939	9

But this industry received a great incentive during the war and the production rose as high as 1500 tons/annum[2], practically whole of which was exported abroad. After the termination of hostilities, the necessity for conserving this mineral was felt because of its strategic importance and its export was banned. At the same time, investigations were initiated under the auspices of the Council of Scientific & Industrial Research to explore the possibility of processing the mineral in the country for beryllium oxide and beryl.

Two chemical processes are employed at present, for large-scale processing of beryl into beryllia. They are (i) the sulphuric acid process and (ii) the fluoride process. One of the authors[3] worked the fluoride process on semi-pilot-plant scale. He obtained a recovery of 83.2% of beryllia from beryl with 97.7% purity, by the fluoride process. While working on that process, the necessity was felt of finding out an alternative method which would

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enable the final product to be obtained in a much shorter way.

When a beryllium salt solution is electrolysed, a coating of beryllium hydroxide is obtained on the cathode. Price and Thomas[1] made use of this property in making silver corrosion-resistant by coating it with a thin layer of beryllia. They did it by electrolysing a simple salt of beryllium like the nitrate or the chloride between a silver cathode and platinum anode. Carlo Adamoli[5], in 1943, obtained a patent for preparing beryllium hydroxide by electrolysing the leach-liquor obtained from a sinter of beryl, calcium fluoride, nitric acid and sodium nitrate. Recent work of Jolibois and Berges[6] on this problem also deserves mention in as much as it indicates the way in which high purity insoluble oxides like beryllia, magnesia can be prepared, by an electrolytic method, in gram quantity. This gave the authors the idea of adopting the electrolytic method for preparation of beryllium oxide. Adamoli's method was tried first. Though beryllium hydroxide was obtained, the current efficiency of the process was low. The authors investigated the problem thoroughly and effected a marked improvement on Adamoli's process whereby they could obtain beryllium oxide with high current efficiency for the process.

The novel feature of the process consists in using a partition membrane in the electrolytic cell for separating the anodic and cathodic products. Manifold advantages accrue by the use of the diaphragm; firstly, an increase in current efficiency; secondly, a spent catholyte is obtained which, after being relieved of its sodium fluoride content can be used again in the process. Sodium fluoride thus recovered would be an important raw material for the flux for decomposition of the ore, and thirdly, chlorine is evolved at the anode during electrolysis, which is also an important by-product.

MATERIALS AND METHODS

Catholyte.—A catholyte stock solution containing sodium beryllium fluoride was prepared as described below.

Requisite quantities of beryl and sodium silicofluoride or sodium ferric fluoride were mixed together and sintered in an electric furnace at 700°C till there was no evolution of gases. The sintered mass was finely ground and extracted with water when beryllium went into solution as sodium beryllium fluoride, aluminium and silica remaining behind in the residue. After filtration the extract was treated with hydrogen peroxide and left overnight. The precipitate of ferric hydroxide was filtered off and the clear and colourless liquor was stored in a glass reservoir lined inside with paraffin wax. The strength of the solution with respect to beryllium oxide content determined at different intervals was found to remain constant.

Anolyte.—Ten per cent sodium chloride solution was employed as the anolyte.

The electrolytic cell.—This consisted of a paraffin wax-coated pyrex container (1l) with a porous pot (from a Leclanche cell) diaphragm (height, 11 cm; dia. 5 cm. and wall thickness, 3 mm) placed in the centre. A carbon rod (length, 24.5 cm and dia. 2.2 cm) served as the anode. The anode was dipped to a depth of 5.5 cm. in the anolyte. Two graphite rods (length, 23 cm. and dia. 1 cm) served as cathodes. The cathodes were dipped to a depth of 4.3 cm. in the catholyte. A 12V storage battery was used as the source of current. For the recovery of chlorine, the diaphragm was fitted with a three-holed, tight-fitting, paraffin-coated cork. The central hole was for the anode, and of the two side holes, one was kept open and the other fitted with a bent tube and connected to a water suction pump via a gas washer containing caustic soda solution was meant for removing chlorine from the anode chamber (Fig. 1).

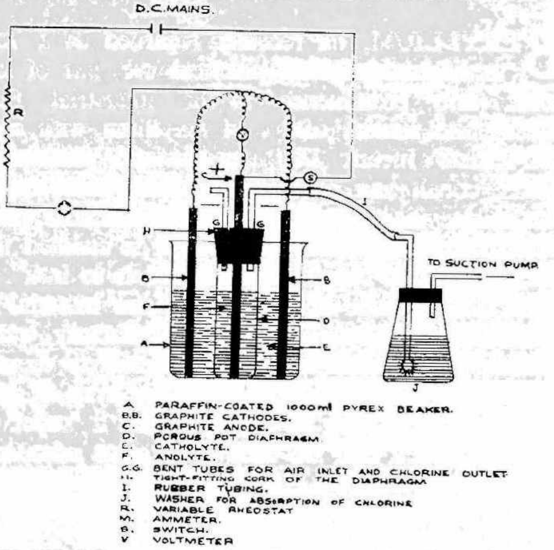

FIG. 1

Electrolysis.—Electrolysis was carried out with 250 cc. of catholyte in the beaker and 70 cc. of anolyte in the porous pot. The chlorine exit tube was connected to the suction pump and slight suction applied to remove chlorine.

The strength of the current passing through the cell was adjusted by means of a variable rheostat. In certain experiments, the total current passed was checked by a copper coulometer.

After running the experiment for a specified time, the catholyte, which was in the form of a slurry, was removed from the beaker, filtered and the precipitate washed with water until it was free from the catholyte. Washing was continued till the precipitate showed a tendency to pass through the filter paper, when it was given a wash with 2 per cent ammonium nitrate solution (made slightly alkaline with ammonia). This treatment freed the precipitate from free beryllium ions. The precipitated hydroxide thus obtained was dried and calcined.

RESULTS

Stirring on apparent current efficiency.—The results of experiments on the effect of stirring on current efficiency (Table I) show that stirring has an adverse effect on current efficiency.

Varying current density.—The results of studies on the effect of varying current density on current efficiency are shown in Table II and Fig. 2. It will be observed that the current efficiency gradually rises in the initial stages and after attaining the maximum value remains constant over a wide range of current density as long as the concentration of sodium beryllium fluoride in the electrolyte remains high. The current efficiency drops rapidly as the concentration of sodium beryllium fluoride falls.

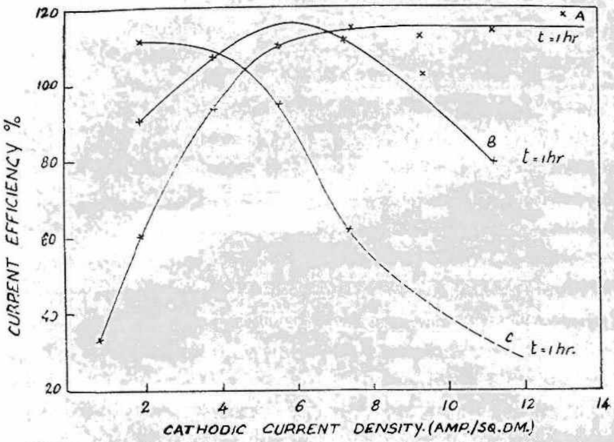

FIG. 2—*Influence of cathodic current density on apparent current efficiency at different concentrations.*

TABLE I—EFFECT OF STIRRING ON APPARENT CURRENT EFFICIENCY

(Temp. 32°-34°C ; anolyte, 70 cc. of 10% sodium chloride solution beryllium oxide in 250 cc. of catholyte, 0.5563 g., duration of electrolysis, 1 hr. ; cathodic current density 1.85 amp./sq. dm.)

Expt. No.	Rate of stirring r. p. m	Qty. of BeO obtainable theoretically. g.	Qty. of deposit obtained g	Apparent current efficiency %
1.	No. stirring	0.2333	0.2580	110.6
2.	95-100	0.2333	0.2430	104.1
3.	260 270	0.2333	0.2400	102.8
4.	450-460	0.2333	0.2070	88.7

Varying the duration of electrolysis.—The results of studies on the effect of varying the duration of electrolysis on apparent current efficiency at different concentrations of electrolyte and at different cathodic current densities are given in Table III and presented graphically in Fig. 3. The results show that when the concentration of sodium beryllium fluoride in the electrolyte is high, there is an "introduction period" during which the current efficiency rapidly rises and attains a maximum value, after which it remains constant. When the concentration of sodium beryllium fluoride is low, a rapid fall in current efficiency is observed.

Adding sodium chloride to the catholyte.—The results of studies on the effect of adding sodium chloride to the catholyte on the apparent current efficiency are given in Table IV. The results show that the current efficiency is more or less independent of the amount of sodium chloride added to the catholyte. The bath voltage required for the passage of the same amount of current, however, decreases when the concentration of sodium chloride increases.

EXPLANATION OF ABNORMALLY HIGH CURRENT EFFICIENCIES

The abnormally high current efficiencies observed in many of the experiments may be due to any of the causes noted here. The hydrolysis of beryllium fluoride stops at an intermediate stage and produces an insoluble basic salt as shown below:

$$BeF_2 + OH^1 \text{——} Be(OH)F + F^1$$

Then evidently, current efficiency calculated on the basis of beryllium hydroxide formed, will be higher than 100. But work of Sengupta[7] on the titration of beryllium fluoride solution with alkali by thermo-metric and conductometric methods shows that no insoluble basic salt as mentioned above is formed. Hence it is presumed that the high current efficiency is due to the fact that a part of beryllium oxide is formed as a result of other physical process, such as adsorption, requiring no electrical energy.

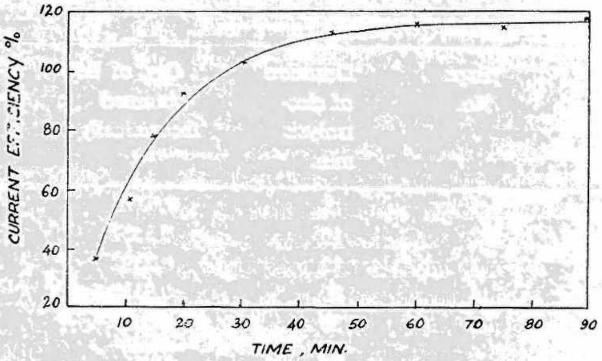

FIG. 3—*Influence of time of electrolysis on apparent current efficiency.*

TABLE II—EFFECT OF VARYING CURRENT DENSITY ON APPARENT CURRENT EFFICIENCY

Expt. No.	Cathodic current density amp/sq. dm.	Qty. of BeO obtainable theoretically g.	Qty. of deposit obtained experimentally g.	Apparent current efficiency %	Recovery
[Series A (wt. of BeO) in catholyte 3.035 g., duration of electrolysis 1 hr.]					
1	0.93	0.1166	0.0390	33.45	1.29
2	1.85	0.2332	0.1435	61.52	4.73
3		0.3498	0.2900	82.88	9.56
4	3.70	0.4665	0.4350	93.26	14.33
5	5.55	0.6997	0.7630	109.00	25.14
6	7.40	0.9328	1.0690	114.60	35.22
7	9.25	1.1660	1.3040	111.80	42.96
8	11.09	1.3990	1.5980	114.20	52.66
9	12.94	1.6320	1.9240	117.90	63.40
[Series B (wt. of BeO) in catholyte, 1.5175 g., duration of electrolysis, 1 hr.]					
1	1.85	0.2332	0.2134	91.49	14.06
2	3.70	0.4665	0.5020	107.60	33.07
3	7.40	0.9328	1.0400	111.50	68.50
4	9.25	1.1550	1.1860	101.70	78.12
5	11.09	1.3990	1.1040	79.89	72.73
[Series C (wt. of BeO) in catholyte, 0.7588 g., duration of electrolysis, 1 hr.]					
1	1.85	0.2332	0.2640	113.20	34.78
2	3.70	0.4665	0.5120	109.70	67.47
3	5.55	0.6997	0.6449	92.80	85.57
4	7.40	0.9328	0.5700	61.10	76.11
5	11.09	1.3990	0.5100	36.45	67.20

TABLE III—EFFECT OF VARYING THE DURATION OF ELECTROLYSIS ON APPARENT CURRENT EFFICIENCY

(Temp. 32°-34°C., anolyte, 70 cc. of 10% sodium chloride solution; volume of catholyte, 250 cc.)

Expt. No.	Duration of electrolysis min.	Qty. of BeO obtained theoretically	Qty. of deposit obtained experimentally	Apparent current efficiency %	Recovery %
1	5	0.0778	0.0282	36.28	0.93
2	10	0.1552	0.0890	57.24	2.93
3	15	0.2332	0.1811	77.64	5.70
4	20	0.3110	0.2840	91.33	9.36
5	30	0.4665	0.4750	101.80	15.65
6	45	0.6997	0.7869	112.30	25.90
7	60	0.9328	1.0690	114.00	35.22
8	75	1.1660	1.3270	113.60	43.73
9	90	1.3990	1.6400	117.10	54.04

That this hypothesis is correct will be evident from the following analytical data.

Electrolysis was carried out under the following conditions: anolyte, 70 cc of 10 per cent sodium chloride solution; catholyte, 250 cc. of solution containing 0.7137 g. of beryllium oxide; current 0.5 amp., cathodic c.d., 1.85 amp/sq.dm; and duration of electrolysis, 2 hr.

The slurry obtained after electrolysis was filtered and the residue on the filter paper pressed between filter pads. The moist hydroxide was weighed and dried to constant weight at 110°-115°C. The dried hydroxide was then analysed for fluorine,

TABLE IV—EFFECT OF ADDING SODIUM CHLORIDE TO CATHOLYTE ON APPARENT CURRENT EFFICIENCY

(Anolyte, 70 cc. of 10% sodium chloride solution ; catholyte, 250 cc., containing 0.6632 g. of BeO ; duration of electrolysis, 1 hr. ; cathodic current density, 3.70 amp./sq.dm ; temp., 32°-34°C.)

Expt. No.	Qty. of sodium chloride added %	Bath voltage at start V	Bath voltage at end V	Qty. of BeO obtainable theoretically g.	Qty. of deposit obtained experimentally g.	Apparent current efficiency %
1	nil	11.3	10.00	0.4665	0.5060	108.5
2	0.5	9.5	7.00	0.4665	0.5041	108.1
3	1.0	9.9	6.50	0.4665	0.5074	108.7
4	2.0	8.0	6.00	0.4665	0.5053	108.3
5	4.0	5.7	5.25	0.4665	0.5059	108.5

beryllium oxide, silica and oxides of iron and aluminium.

Wt. of moist hydroxide — 8.6550 g.
Wt. of dry hydroxide — 0.9754 g.
Wt. of ignited oxide — 0.5285 g.
Wt. of water lost during drying — 7.6796 g.
Wt. of the complex fluoride present in residual solution in the filter paper pressed sample* — 0.0858 g.
Wt. of beryllium oxide contained in 0.0858 g. of the complex fluoride — 0.0164 g.
Wt. of beryllium oxide due to adsorption — 0.0345 g.
Wt. of impurities ($SiO_2.Al_2O_3$ Fe_2O_3) present in the oxide — 0.0370 g.

∴ Beryllium oxide formed due to electrolytic action only.

= Wt. of the oxide−(wt. of impurities−wt. of beryllium oxide due to adsorption−wt. of beryllium oxide due to residual solution in the filter paper pressed sample).

$= 0.5285-(0.0370-0.0345-0.0164)$

$= 0.4406$ g.

Wt. of beryllium oxide theoretically obtainable $= 0.4665$ g.

∴ Theoretical current efficiency

$$= \frac{0.4406\times 100}{0.4665} = 94.48 \text{ per cent}$$

$$\text{Apparent current efficiency} = \frac{0.5285\times 100}{0.4665}$$

$$= 113.3\%$$

DISCUSSION

The formation of beryllium hydroxide during electrolysis is essentially a chemical process. When a hydrogen ion is cathodically discharged, a hydroxyl ion is also released which travels towards the anode. The hydroxyl ions thus released react with sodium beryllium fluoride leading to the formation and precipitation of beryllium hydroxide.

The observed characteristics of the reaction can be explained if following two assumptions are made:—

(1) That initially a soluble basic beryllium salt is formed due to the interaction of hydroxyl ions with sodium beryllium fluoride. Tananaev and Deichman[8] have shown that such a salt is formed in solution.

(2) That the soluble basic salt can further react with hydroxyl ions to form beryllium hydroxide which is then precipitated.

The results given in Table I show that the current efficiency is lowered by stirring. Stirring produces more of the soluble basic salt and consequently the current efficiency is diminished. Stirring may also facilitate the escape of hydroxyl ions to the anode chamber, thus lowering the current efficiency.

Of the C.E./c.d. curves A, B and C (Fig. 2) the curve A corresponds to the highest concentration of the beryllium salt in the electrolyte. In this curve, current efficiency gradually rises from a low value to a maximum value where it remains steady for a wide range of current density. Here the concentration of the beryllium salt is high and will, therefore, favour the formation of the soluble basic salt. The current efficiency is therefore low at low current density. When the current density is increased favouring precipitation of the hydroxide it increases the current efficiency. Maximum current efficiency is obtained when all the hydroxyl ions produced are available for precipitating the hydroxide.

If the concentration of the beryllium salt is low, the formation of the soluble basic salt will decrease and the formation of the precipitated hydroxide will increase resulting in an increase of current efficiency.

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* Calculated on the basis that 10 cc. of stock solution weighs 10.0277 and contains 9.9169 g. of water and 0.1108 g. of sodium beryllium flouride.

This is evident from the curves B and C (Fig. 2) where the current efficiency goes on increasing for the same value of current density in the lower range.

The curves also reveal that lower the initial concentration of the beryllium salt the lower is the current density required for obtaining maximum current efficiency. This can be explained as follows: when the concentration of the beryllium salt is low, the maximum formation of the soluble basic salt can be achieved at low current density as only a small number of hydroxyl ions will be required for the purpose. This will also help in obtaining maximum precipitation of the hydroxide at relatively lower current density than when the beryllium salt concentration is high. The current densities required for obtaining maximum current efficiency for beryllium salt solutions of concentrations 3.03, 6.07 and 12.14 g/l. respectively are 2, 6 and 8 amps/sq.dm. (curves C, B, A, Fig. 2).

When the current density required for maximum current efficiency is exceeded, the concentration of hydroxyl ions in the system is increased as a result of the increase in current density. The concentration of hydroxyl ions is considerable compared to the concentration of beryllium salt in the solution and all the hydroxyl ions present will not get the chance of reacting with the beryllium salt to form the insoluble hydroxide and will migrate towards the anode chamber; as a result, the current efficiency will be lowered. Thus curve C, representing the lowest concentration, records a fall at 2 amp/sq.dm. and curve B representing an intermediate concentration, records a fall after 6 amp/sq.dm.; curve A, representing the highest concentration of the beryllium salt, does not show any fall within the range studied. It may, however, be assumed that the current efficiency will begin to fall when the current density is greater than 14 amp/sq.dm. Thus it is seen that increasing beryllium salt concentration shifts the critical current densities (indicating a fall in current efficiency) towards higher values.

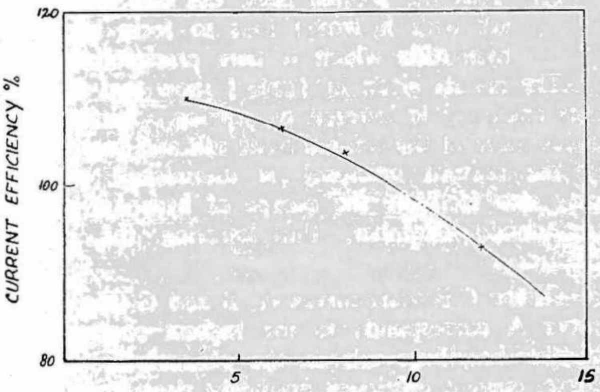

FIG. 4—*Variation of apparent current efficiency with concentration.*

From C.E./time curve (Fig. 3), it is found that the current efficiency gradually rises with time and ultimately reaches a maximum value. When the electrolysis is carried out for a short period, the total number of hydroxyl ions produced as well as their local concentration is small. Therefore, conditions are favourable for the formation of the soluble basic salt which lowers the amount of the precipitate and hence the current efficiency. When the duration of electrolysis is longer, a good amount of basic salt would have been already formed due to more hydroxyl ions being produced in the system. Local concentration of hydroxyl ions will also rise, as the rate of formation of hydroxyl ions is expected to preponderate over the rate of their diffusion into the bulk of the solution. This will increase the chances of the formation of a larger amount of precipitate. Thus current efficiency goes on improving with increase in the duration of electrolysis and ultimately reaches a maximum value and continues to remain in that state till the bath is depleted of a good amount of the beryllium salt. This 'induction period' (i.e. the period which elapses before maximum current efficiency is obtained) is due to the accumulation of increasing amounts of the soluble basic salt in the electrolyte. This is borne out by the results given below. The first experiment was done at a cathodic c.d. of 7.40 amp/sq.dm. for 1 hr. with 250 c.c. electrolyte containing 3.035 g. of beryllium oxide. The current efficiency obtained was 114.6 per cent. The filtrate from this stage was electrolysed at a cathodic c.d. of 370 amp/sq.dm. for 1 hr. The volume of the filtrate used was also 250 c.c. containing 1.966 g. of beryllium oxide. The first experiment was done under such conditions as would give the maximum current efficiency. Under these conditions the formation of the soluble basic salt which would be remaining in the filtrate would also be maximum. It was presumed that if the filtrate from the first electrolysis was re-electrolysed, it would give a higher current efficiency than would be obtainable if a fresh solution of the same concentration was used. The current efficiency obtained in the second electrolysis was 117.7 per cent., whereas with a fresh solution of the same concentration the current efficiency would be only 105 per cent. (Fig. 4). This shows that the electrolyte in the second electrolysis contained the maximum amount of the soluble basic salt produced during the first electrolysis and no time was lost in the formation of the soluble basic salt in the second electrolysis prior to the formation of the hydroxide.

ECONOMICS OF THE PROCESS

In absence of sufficient data it is not possible to work out the economics of the process. But an approximate idea can be formed from a comparative study of the electrolytic and the chemical processes. From data obtained by us in course of operating both the processes, we may arrive at some tentative figures regarding the cost of electrical power for the electrolytic process and the cost of chemicals for the chemical process. We have found that current consumption together with common salt required for the purpose will cost 14 annas per lb. of the oxide, whereas the chemicals would cost Rs. 6½ per lb. of the oxide. This wide difference is in fact only apparent and would be narrowed down to a great extent in actual operation on a bigger scale. The capital required for the electrolytic process is expected to be higher than what would be required for the chemical process. Regarding depreciation, the advantages gained by lower depreciation on the electrical equipment may be out weighed by higher capital expenditure necessary for the electrolytic process. The higher depreciation on the equipment for the chemical process on account of their liability to corrosion and chemical attack may be offset by their lower cost and easy replaceability.

In fact at this stage, it is rather difficult to say which of the two processes would be best suited for operation. We have studied the chemical process[3] on large-scale experiments and have calculated that the cost of production in our case becomes comparable with that obtained elsewhere, particularly, in America. In seems, it will be worthwhile to try the electrolytic method on the same scale and compare it with the chemical process regarding per unit cost of production.

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DISCUSSIONS

GROUP : BERYLLIUM

Dr. Jagdish Shankar (*Atomic Energy Establishment, Bombay*) : What is the purity of the beryllium obtained by this method ?

Mr. P. B. Chakravarty (author): The purity obtained is generally between 96/97 per cent beryllium using, of course, a ceramic diaphragm in the electrolytic cell. But nowadays, as plastic diaphragms are available which are not attacked by hydrofluoric acid or floride solution, much purer product can be rightly expected.

Dr. Jagdish Shankar : For atomic energy work the purity required is of much higher magnitude. The purification of beryllium then becomes an involved process when one tries to reduce the impurity down to one part in a million. If, therefore, the method is to be developed for preparing beryllium of that high purity this particular point should be kept in mind.

Mr. P. B. Chakravarty : We could only produce a product of 99.99 purity (maxm.) by a special process.