ANODES FOR ALUMINIUM PRODUCTION

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ABSTRACT

Anodes used for aluminium production play an important role in the electrolytic process. Though information about aluminium technology is available, the theoretical and practical aspects and modern trends in the nature of anodes are scattered. An attempt is made to consolidate the various particulars in order to present an overview of the present status of the anodes. An insight into the studies conducted for predicting the mechanism of anodic reactions and products has been made. Emphasis has been made on the development of 'inert-anodes', leading to pollution-free aluminium cells operating at higher energy efficiencies.

INTRODUCTION

The current world production of aluminium is around 12 million tons per annum and India's share amount to 2 lakh tons. The entire production of the metal is by the Hall-Heroult's electrolytic process.

In the Hall-Heroult's cell, aluminium is obtained by the electrolysis of aluminium oxide dissolved to the extent of 5% in a cryolite melt at about 1000°C using carbon or carbonaceous material as the consumable anode. The overall reaction is reduction of alumina according to the following equations :

$$2 Al_2O_3 + 3C \qquad 4 Al + 3 CO_2 \quad (1)$$
$$Al_2O_3 + 3C \qquad 2 Al + 3 CO \quad (2)$$

The carbon anodes are hence continuously consumed during the course of electrolysis.

Theoretically at 100% and 85% current efficiencies the carbon consumption for reaction (eq. 1) should be 333 kg and 388 kg per ton of aluminium, whereas it will be 666 and 776 kg/ton for reaction (eq. 2). But data collected from industrial cells show that the exit anodic product is a mixture of 80-50% CO_2 and 20-50% CO, amounting to a consumption of 420-550 kg of carbon per ton of aluminium. The excess consumption of carbon may also be due to the Boudouard reaction in which CO_2 is converted into CO by the carbon. The consumption of carbon works out to be about 7% of the total cost of production of the metal.

Thermodynamically, the enthalpy for reaction (eq. 1) at 1000°C at a partial pressure of 1 atmosphere for oxygen is around 550 kg. The energy required to produce 1 kg aluminium is only 5.64 KWh/kg, compared with 8.69 KWh/kg for the decomposition of aluminium oxide to the elements in the absence of carbon. It is therefore evident that energy is saved at the expense of carbon and hence the use of carbon as an anode material.

Mechanism of anode consumption : The principal anodic product is carbon dioxide in industrial cells. The primary reaction is supposed to be the electrolytic decomposition of Al_2O_3 to give oxygen at the anode followed by the chemical reaction between the oxygen and carbon to yield the oxide of carbon as per the following equations :

$$Al_2O_3 \longrightarrow 2 Al + 3/2 O_2 \qquad .. (3)$$
$$O_2 + C \longrightarrow CO_2 \qquad .. (4)$$
$$O_2 + 2C \longrightarrow 2CO \qquad .. (5)$$
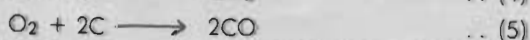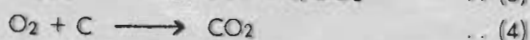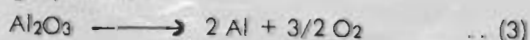
A study of reactions (eq. 4) and (eq. 5) indicates that thermodynamically reaction (eq. 5) is favourable, but in practice reaction (eq. 4) is the dominant one. This has been substantiated by taking into account the partial pressure of oxygen at anode which becomes too high for reaction (eq. 5) to take place. The anode carbon is not considered to take a leading role in the reaction. The anode is said to be covered with a film of gas, which produces a shielding effect, resulting in a higher anodic overvoltage. The E_0 for reaction (eq. 1) is 1.16 V at about 1000°C whereas the observed value ranges from 1.4 to 1.8 V.

Anodic overvoltage measurements indicate that the mechanism of anode reaction is identical with the established theory of carbon consumption wherein the CO_2 formed is to some extent reduced to CO by Boudouard reaction through the formation of an intermediate C-O compound. The overvoltage of 300-500 millivolts is ascribed to the slow decomposition of the C-O compound.

Double-layer capacitance measurements in the system cryolite-alumina melt with graphite, industrial type carbon and vitreous carbon show that vitreous carbon has a low capacitance (30-60 μF/cm^2), compared with graphite/baked carbon (200-700 μF/cm^2). This high capacitance is due to the roughness and porosity of the material. This measurement has been found helpful in predicting the surface behaviour of the anode material and serves as a basis for selection of a suitable anode.

Gas analysis studies have confirmed that the carbon consumption was close to the theoretical value. However, the anode weight loss was found to be higher due to 'dusting'.

The available information does not prove whether the actual 'anode mechanism' is a diffusion-controlled process or charge transfer process. Adsorption studies interpret the mechanism as a charge-transfer process followed by chemisorption of the discharged oxygen atom. It has been proved beyond doubt that CO_2 is formed as the primary anode product in industrial high-capacity cells operating at current density above 0.5 A/cm^2. The presence of small amount of carbon monoxide in the anode gas is only due to a secondary reaction.

Quality of carbon material : The consumable anode carbon plays an important role in aluminium production. The selection of a suitable material requires strict quality control to yield a homogeneous product satisfying mechanical, physical and chemical properties. The material should have : (a) high electrical conductivity; (b) low thermal conductivity; (c) high mechanical strength; (d) high density; (e) low porosity (less than 25%); (f) resistance to electrolyte melt; (g) high thermal stability; and (h) high degree of chemical purity.

A high chemical purity is absolutely necessary since even small traces of metallic impurities will adversely affect the electrolysis and contaminate the metal. Vanadium is considered to be most harmful because it not only affects the purity of the metal but also increases the thermal erosion of the anode. The tolerable limits of impurities are :

Sulphur	12000-40000	ppm	Magnesium	110	ppm
Iron	120-470	"	Gallium	14	"
Silicon	90-390	"	Chromium,	)	
Nickel	80-230	"	Manganese,	)	
Sodium	200	"	Lead, Tin &	)	10	"
Calcium	120	"	Boron (total)	)	

The coke used should have high C/H ratio. Since calcination is a dehydrogenation process, lower C/H ratio prolongs the period of coking Sulfur in more than permissible limit causes microporosity and decreases the density of the material.

DEVELOPMENT OF ANODES

Though the aluminium electrolytic process has not undergone significant changes since its first cell operated in 1888-89, considerable development has taken place in the fabrication and assembling of the anode with a view to conserve energy, bringing down anode consumption and environmental hazards and increase the ease of operation. The development of the anodes is closely related with the design of the cell. The nature of developments that have taken place during the past hundred years is given in Table I.

Table I : Development of anodes.

Stages	Period	Current (KA)	Anodic current density (A/cm²)
Pre-baked (discontinuous)			
I. First cell with one anode	1888-1889	4	6.50 - 6
II. 30-40 circular anodes	1890-1895	6-8	4.0 - 2.5
III. 4-8 block anodes	1892-1894	4-8	1.6 - 1.4
IV. 11-14 block anodes	1898-1925	8-20	1.1 - 1.0
V. a) Packets of block anodes	1928-1930	12-30	1.1 - 0.9
b) -do-	1930-1960	30-100	1.0 - 0.8
c) -do-	1965 onwards	150-225	0.85-0.7
Soderberg			
I. 1-2 Soderberg anodes	1935-1950	30-45	0.8 - 0.7
II. Larger Soderberg anodes	1953-1954	60	0.75-0.7
III. a) Assembly of larger Soderberg anodes	1955-1957	70-80	0.7 - 0.65
b) -do-	1957 onwards	130-150	0.6 - 0.59

From the Table it could be seen that mainly two types of anodes are being used in the industrial aluminium cells. The prebaked anodes were only used till 1935 and the Soderberg anode came into existence thereafter. Prebaked anodes are preferred at locations where cost of energy is increasing and stringent environmental conditions are insisted upon. Higher capacity cells prefer to operate with prebaked anodes whereas cells with a production capacity of < 10,000 TPA favour Soderberg anodes. The method of fabrication, operation and characteristics of the various anodes employed in industrial cells are described hereunder.

Prebaked anodes (discontinuous) : Petroleum coke and bituminous tar-pitch are the most commonly used starting materials. The specifications of the petroleum and coal tar pitch are given in Table II.

Table II : Specification of coal tar and petroleum pitch

Properties	Coal tar pitch	Petroleum pitch
Softening point, °C	100-125	124
Coking value, °C	50-60	54
Density, gm/cc	1.18-1.34	1.27
Benzene insoluble, %	5-30	16
Quinoline insoluble, %	8-25	2
Ash content, %	0.01-0.3	0.1
Sulphur content, %	0.2-6.5	1.5

Prebaked anodes are produced by moulding 70-80% aggregate coke and the balance with pitch as the binder and then baking in separate gas fired or oil fired furnaces at 1000°-1300°C. Spikes/studs are inserted to carry the current. Addition of inhibiting agents to the binder such as natural or artificial graphite, alkali salts, aluminium fluoride, and boric oxide, have been tried and found to improve the mechanical and electrical properties. Graphite in particular, when added to the extent of 10%, has been found to increase the conductivity and reduce the oxidizability. Addition of boric oxide has an inhibition action on the combustion of carbon. It is reported that during baking, the boric oxide particles equalize the reactivity of the basic carbon material and of the binder coke by reducing air oxidation.

The baking temperature has considerable effect on the consumption of carbon during electrolysis and is found to be near theoretical if the temperature of baking is maintained at 1300°C for four to five hours. Texture, surface qualities and apparent densities of the baked anode determine the mechanical and electrical properties of the anode. The aim is to obtain a dense anode with lower specific surface.

Prebaked anodes, either round or square in cross-section, weigh up to 90-100 kg. A multiple of such anodes is used in the cell to achieve a current density of 0.8 to 1.0 A/cm² in cells of 150 KA and above. Individual anodes are raised or lowered to maintain the proper position with respect to the bath as and when it is consumed. They are replaced at intervals.

Apart from carbon monoxide and carbon dioxide, the exhaust fumes contain particulate materials containing fluorides. The distribution of fluorides are reported to be 45% HF, 35% fine and 20% coarse particulates.

A flow chart showing the fabrication of pre-baked anode is given below and a typical cell with pre-baked anode is shown in Figure 1.
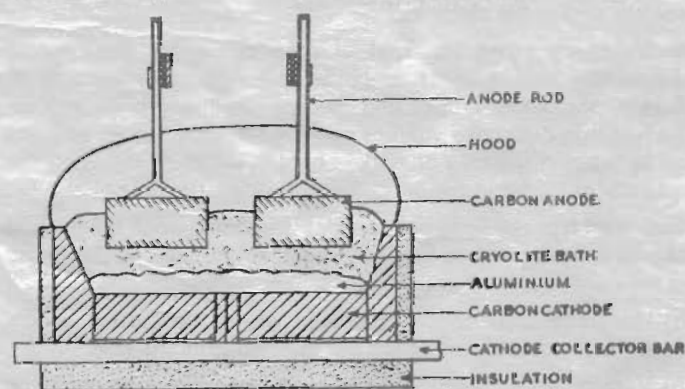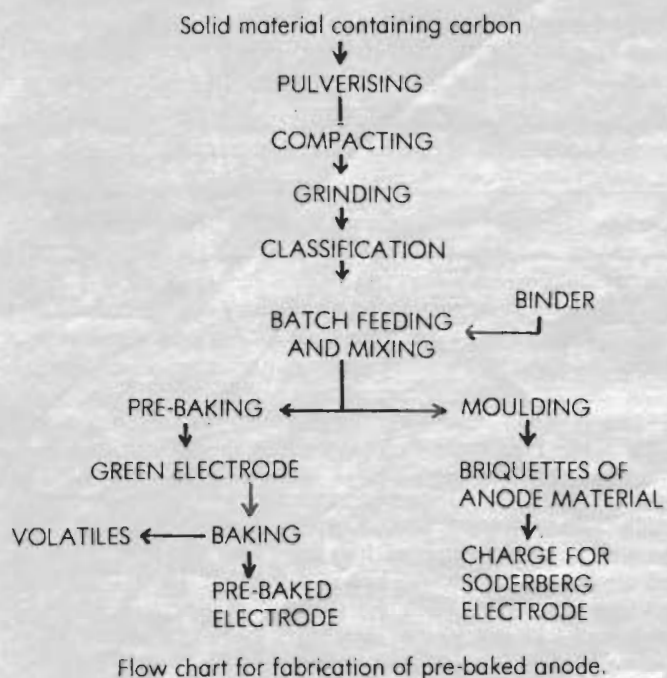

Fig. 1 : Prebaked anode

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Solid material containing carbon
              ↓
         PULVERISING
              |
         COMPACTING
              ↓
          GRINDING
              ↓
       CLASSIFICATION
              ↓
                         BINDER
                           |
      BATCH FEEDING ←───────┘
       AND MIXING
              |
      ┌───────┴───────→ MOULDING
      ↓                     ↓
PRE-BAKING ←          BRIQUETTES OF
    ↓                 ANODE MATERIAL
GREEN ELECTRODE             ↓
    ↓                  CHARGE FOR
VOLATILES ← BAKING     SODERBERG
    ↓                  ELECTRODE
 PRE-BAKED
 ELECTRODE
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Flow chart for fabrication of pre-baked anode.

The pre-baked anodes usually operate at higher current densities and a considerable portion (nearly 35% of the anode) remains unutilised as a 'butt'. This calls for supplementing with a new anode atleast once in a week thereby leading to operational difficulties. In order to operate it continuously in high capacity cells at lower current densities, efforts were made in the development of the 'self-baking Soderberg type anodes'.

Soderberg anode : Unlike the discontinuous pre-baked anodes, these anodes are of the self-baking type in which a 'green paste' of carbonaceous material is continuously formed in the pot itself during the reduction process. The green paste is a mixture of petroleum coke (65-70%), pitch blend and coal tar (25-35%). The anode itself is a rectangular steel casing into which the green paste is continuously fed and compressed. The casing serves as a retainer to hold and support the 'green paste' during the baking operation. The lower end of the casing dips into the cell so that the 'green paste' is preformed and baked by the heat of the cell itself prior to its use. As the electrode is consumed during electrolysis, it is pushed down by addition and compression of new paste.

There is not much of difference in the quality of the carbon used, as compared to the one used in the pre-baked type. The pitch used for self-baking should have a comparatively lower softening point i.e., 55°-120°C as against 100-125°C in pre-baked, since use of hard pitches presents additional problems in providing the contact pins in the electrode.

In Soderberg paste, the kind of coke aggregate particle size distribution and quantity of binder are restricted, because of fluidity, shrinkage, cracks and mechanical strength of anodes. Pitch with a high coke value is preferred since it makes possible an increase in quantity of coaked binder, without increasing the quantity of binder in the anode.

Two main types of Soderberg anodes depending upon the method of providing connecting lead have been developed and put to use in the cells (Figures 2 and 3) :

a) Horizontal-spike-anode (HSA) in which the current enters through contact pins which are inserted from the side.

b) Vertical-spike-anode (VSA) : The current enters through the pins inserted vertically from above.

Vertical spike anodes have replaced the horizontal spike anode for the following advantages :
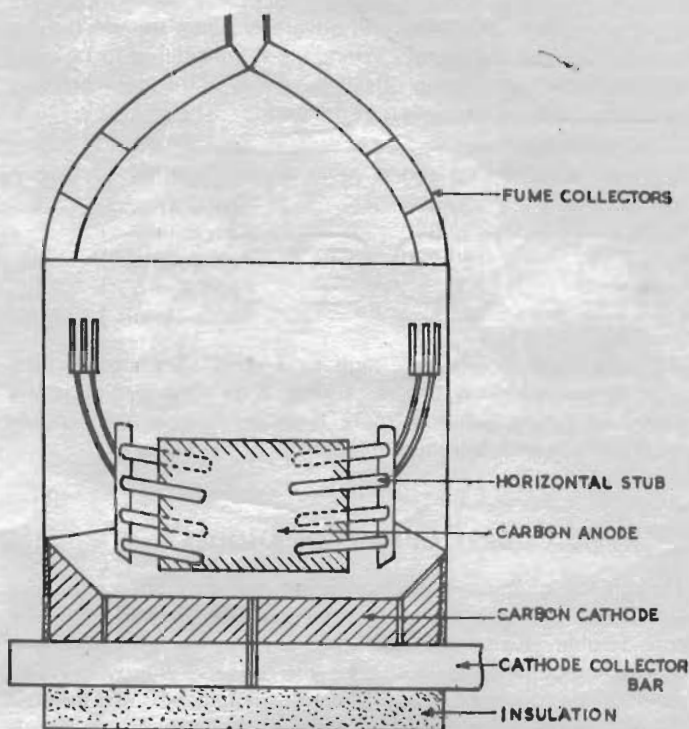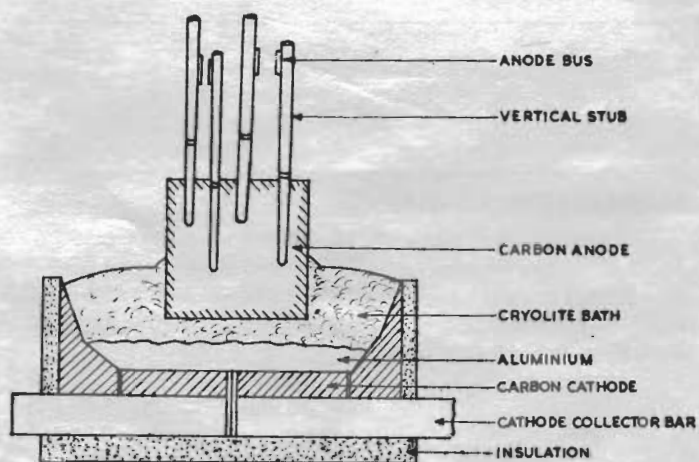

Fig. 2 : Soderberg anode (Horizontal) HSS

Fig. 3 : Soderberg anode (Vertical) VSS

a) The use of a consumable aluminium casing inside the permanent casing is avoided.

b) The pot gases can be collected in a concentrated form.

Current densities of the order of 0.6-0.8 A/cm² have been used in industrial cells operating at 150 KA and above. The major drawback in the use of Soderberg anode are the obnoxious fumes in the pot room, due to the *in situ* volatilization of the green paste. To obviate this, large size hoods are to be provided for extraction of the fumes. Nearly 100 times of infiltrated air to the volume of anodic gases has to be handled. The fluorine content in the exhaust gas of HSA is similar to the pre-baked one whereas in VSA, it is almost double (i.e., 80-90% HF), posing serious environmental hazards.

The salient features of the two types of anodes are summed up in Table III.

Table III : Salient features of anodes

S.No.	Characteristics	Pre-baked anode	Soderberg anode
1.	Energy requirement, KWh/ton	14,000	15,000
2.	Carbon consumption, Kg/ton	450-500	520
3.	Current efficiency, %	90-91	86-88
4.	Cell voltage, V.	4 to 4.1	4.3 to 4.4
5.	Bath voltage, V.	3.35	3.1
6.	Voltage drop at anode, mV.	200-300	500-600
7.	Current density, A/cm^2	0.65-1.3	0.65-0.90
8.	Electrical resistivity, ohm.cm.	5-6	7-8
9.	Inter electrode distance, cm.	4-5	5-6
10.	Specific investment cost	High	Low
11.	Specific production cost	Low	High
12.	Fluoride consumption, Kg/ton Al	28-30	32-34
13.	Fume treatment	Not required	Necessary
14.	Operation	Easy	Cumbersome
15.	Thermal conduction	High	Low
16.	Porosity	Below 20%	25%
17.	Suitability	Suitable for greater plant output	Favourable for smaller plant (less than 10,000 TPY)

Continuous pre-baked anode : The combination of two entirely different processes in the Soderberg anode, namely, the preforming of the anode and electrolysis within the cell room was considered detrimental in view of the evolution of gaseous hydrocarbons which form the nuclei for the condensation of fluorides posing health hazards.

The 'Erftwerk cell of Vereingte Aluminium — Werke-A.G.' solved this problem as early as 1955 by the development of the continuous pre-baked anodes. This in essence is to segregate the coking process of the 'green paste' out of the cell room into chamber furnaces with the ultimate aim of developing pre-baked anodes for continuous operation, thus eliminating anode butts.

A set of carbon blocks is placed on top of the used blocks dipping in the melt. A gluing paste connects the new block with the old stub. Thus the pre-baked anodes which were hitherto discontinuous are made to function continuously adding to the economy and ease of operation of the process.

The consistency of the paste should be capable of becoming plastic during slow heating, and sufficiently viscous so that it does not flow down easily under pressure. As the glued surface enters the hot zone, coking of the paste layer takes place, effecting a perfect contact. During this process the required electrical conductivity is attained.

The electrical contacts are given by copper/steel pins entering from the sides, at an angle of 20° downwards. The pins are rammed into the anode during the fabrication stage. In cells up to 130 KA, current densities of 0.6 A/cm^2 have been used which is lower than used in discontinuous pre-baked anodes or almost equal to that of Soderberg anodes.

Multiple slab anodes : In order to overcome some of the disadvantages of the pre-baked and Soderberg anodes but at the same time retaining all the beneficial factors, a new type of anode 'Multiple slab anodes' was employed successfully in 3000-4000 A capacity cells.

The anode is made by sandwiching carbon slabs between steel current-conducting plates. The use of long slabs in separately removable bundles considerably reduces labour in anode setting. Flat current-conducting plates ensure better contact between the surfaces, thereby reducing voltage losses at the contact. The intervening steel plates protect the carbon slabs from air oxidation, thereby lowering carbon consumption. The voltage drop in the slab itself is only 200 mV as against 300 mV and 500 mV in pre-baked and Soderberg anodes respectively.

Inspite of many attractive features this type of anodes has not been commercialised and perhaps a re-examination is worthwhile.

Graphite anodes : Various types of graphitized carbon have been tried in large laboratory trials and found as a suitable substitute for the carbon anode. However, due to the prohibitive cost of the material, industrial usage of graphite as a consumable anode has not been attempted. Graphite has been used as the only anodic material for use in the developing technology of aluminium production through the electrolysis of anhydrous aluminium chloride either in monopolar or bipolar cells. In this process, there is no anode consumption since the anodic product is chlorine and not oxygen. The cells are also operated at substantially lower temperatures.

Porous gas anodes : Some preliminary investigations on the use of porous gas anodes have been carried out. In essence these types of anodes have a semblance with fuel cells in which the anodic oxygen is allowed to react preferentially with a fuel so that the main carbon anode is saved from consumption and dimensional stability is ensured. Hydrogen/methane/carbon monoxide is injected onto a porous carbon electrode which gives a depolarizing effect, resulting in a reduction of the anodic potential by about 0.5 V. Unfortunately, the water formed reacts with the electrolyte, increasing fluorine emission. Besides, the clogging of the pores with the soot formed hampers the normal behaviour of the anode. Magnetite, when used as a porous anode by flushing carbon monoxide, was found to disintegrate.

Though porous gas anodes possess the advantage of dimensional stability and reduced energy consumption, yet the future use of these types of anodes in commercial cells appears to be less promising. The main advantage of this lies in the utilisation of a cheaper carbon in the place of costly petroleum coke.

Metal anodes : Base metal itself to be used as an inert anode, has been under investigation. The metal has to withstand the corrosive electrolyte and the liberated oxygen gas bubbles at high temperatures. The anodic dissolution is avoidable if the EMF of the couple, 'Al-metal', is lower than the EMF of the cell reaction (2.19V) at 1000°C. It has been reported that various metals such as nickel, iron, copper and platinum are suitable as anode materials due to the formation of a thin passive film.

Composite anodes : Recently an unique process has been described in which a composite anode, made up of graphite plates coated with purified aluminium oxide admixed with small

quantities of powdered coke, is used in the electrolysis of aluminium chloride-sodium chloride melt at 700°C. The anodic product is carbon dioxide and there is no chlorine evolution, which indicates an *insitu* chlorination of the aluminium oxide, a component of the anode. It is claimed that the conversion efficiencies were almost theoretical.

Oxide anodes : The current trend in aluminium technology is the search for a suitable permanent anode material which will permit continuous, unattended cell operation for prolonged periods. Efforts made in this direction have resulted in the use of metallic oxides as a suitable substitute for the anodic carbon. Since these anodes do not undergo any appreciable dimensional change, the inter electrode distance remains unaltered. In view of the above, cells can be operated at reduced interpolar gap, thereby reducing the energy consumption. The electrical energy saved in conventional anode due to the anodic depolarisation by oxidation of carbon is off-set by higher inter-electrode distance.

Anode consisting of pure oxides of metal, ferrites, more complex oxides of spinel, perovskite, delafossite, pyrochlore, schellite and rutile with electronic conduction, have been studied. All these types of anodes can be conveniently fabricated by any one of the known methods of ceramic technology. The anodes have been fabricated with or without a substrate. The selected oxides should have low resistivity, chemical and thermal stability and low porosity. The sturdiness and suitability of these compacted oxide anodes have been tested on a pilot plant scale over extended periods of two to three months.

Oxide compositions have also been tried with success in 'Alusuisse-Bipolar Electrode Cell', in which, the inert anode material is used in conjunction with cathode material of graphite, borides, nitrides and silicides of titanium or zirconium. These cells operate at one volt higher than the conventional cells. This increased voltage has to be offset by proper design considerations to reduce the inter-polar gap.

CONCLUSION

An overview of the various types of anodes that are currently in use as well as other alternative anodes are dealt with. It could be seen that the developments in the anodes have all been centered around carbon or carbonaceous material on an industrial scale and a real substitute for the carbon is yet to emerge. The recent developments are giving much emphasis in operating cells at lower current densities to avoid environmental pollution. Though the Soderberg anode was considered as an improvement over the pre-baked anodes in the early 50's, ecological awareness has pushed the Soderberg anode into the background. New smelters are exclusively based on pre-baked anodes, leaving the existing plants employing Soderberg anodes to operate with some improved technique.

In the light of the above, development of a suitable permanent anode will open up new design possibilities which will facilitate continuous, unattended cell operation with considerable energy savings. To conceive of future aluminium smelters operating with bipolar electrodes in which oxide composites are incorporated as the anode is not an exaggerated idea. Once this is accomplished it will no doubt dramatise the aluminium technology.

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