

# EXTRACTION OF MAGNESIUM, TITANIUM AND ALUMINIUM

## *Emerging Technological Options Relevant For India*

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### INTRODUCTION

Magnesium, titanium and aluminium are classified as light metals. They are extensively in structures and components where the strength/weight ratio is an important factor determining the choice of the metal. India possesses vast reserves of these metals in its minerals, in the form of oxides, silicates, carbonates etc. Developments in technologies for the extraction of these metals have been driven by the need to reduce the cost of production and make the utilization of these metals and their alloys viable in industrial application. The processes must have no adverse impact on the environment, too. Cost of raw materials, cost and availability of reducing agents and the cost of energy are the major factors that determine the viability of any process for the extraction of these metals. Magnesium and titanium are fast emerging as the favoured metals in the manufacture of automobile components due to their high strength/weight ratio and excellent properties at high temperatures. The high cost of production of these metals has severely limited the exploitation of this huge emerging market. Therefore, the focus is on developing alternative technologies to reduce the cost of production of these metals. The technology for the extraction of aluminium is well established. Attempts are being made to reduce the impact of the extraction process on the environment and also to reduce the energy consumption. Another interesting attempt has been to use carbon as a reducing agent for the reduction of the oxide. The relevance of the emerging technological options for India will depend on the type of raw materials available; the cost of the same; the energy resources available and the preferred scale of operation.

### MAGNESIUM

#### *Sources*

Magnesium is occurs as the oxide, carbonate or silicate in nature. On an average, the earth's crust contains about 2.1% magnesium [1]. Sea water is another major source, its magnesium content being about 0.13 % by weight [2]. Dolomite ( $MgCO_3 \cdot CaCO_3$ ) and magnesite ( $MgCO_3$ ) form the predominant terrestrial sources of magnesium. Magnesium silicates such as olivine, serpentine and asbestos are being increasingly used for the extraction of the metal. Indian reserves of the metal have been estimated to be at 30 million tonnes [2]. The dolomite reserves in India are estimated to be about 4608 million tones and those of magnesite to be 22 million tonnes [3]. The vast coast-line of India provides an inexhaustible source of magnesium in the form of sea-water. An important source of magnesium which has been largely ignored in

India is its silicate. Silicates such as the Olivine and Serpentine occur as overburden during the mining for minerals such as chromite and also during the mining of diamonds. In addition to these, pyroxenite, another silicate of magnesium, is mined extensively in many areas. None of these silicate resources are being considered for the extraction of the metal in India, at present.

### ***Applications***

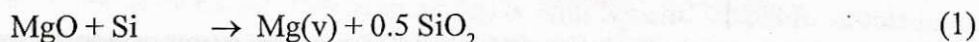
Alloys of magnesium have good corrosion resistance and also have a good machinability. They also can be worked by any of the fabrication processes such as casting, rolling, welding etc. They have good dimensional stability and damping capacity [3]. About 44% of the world production of magnesium is used as an alloying addition for strengthening aluminium [4]. Cast metal components used in the automobile industry form the next major application, using about 32% of the metal produced. This sector is growing very fast due to the thrust in the industry for increasing the fuel economy and the consequent search for materials with high strength/weight ratio. Desulfurisation of steel, which uses about 7% of magnesium produced in the world, is the next major application of the metal. These three sectors account for practically all the magnesium produced in the world. The utilization of magnesium in the automobile industry was limited by the insufficient corrosion-resistance of magnesium, produced largely by the electrolytic route. With the availability of high purity magnesium which possesses very good resistance to corrosion, the use of the metal in the automobile has steadily increased. The major producers of automobiles use about 5 kg of the metal in each vehicle manufactured in the form of various components. It is estimated that the use can go up to 100 kg per vehicle, if the cost factor is favourable [5]. The Passat platform of Volks Wagn is already using 14 kg of magnesium and it is projected that this can go up to 42 kgs per unit. Anticipating a large demand for magnesium in the manufacture of automobile components, major auto manufacturers like Volkswagan, Ford and Hyundai have invested in green field projects for the extraction of magnesium [5]. The annual production of magnesium worldwide was reported to be 7,26,000 tonnes during 2006 [6].

### **PRODUCTION**

Magnesium is produced through two primary routes: (a) the silico-thermal reduction of the oxide and (b) electrolysis. The first route relies on the reduction of magnesium oxide in calcined dolomite or magnesite using ferro-silicon. Reduction is carried out at temperatures around 1200-1600°C. The process is carried out under vacuum and the vapour of magnesium is condensed away from the main reactor. The purity of the metal produced by this route can be as high 99.95% [7]. Magnesium is also produced by the electrolysis of the anhydrous magnesium chloride or through the electrolysis of dehydrated carnalite,  $MgCl_2 \cdot KCl$ . The both are maintained usually at temperatures less than 700°C. It is difficult magnesium better than 99.8% pure, through the electrolytic route.

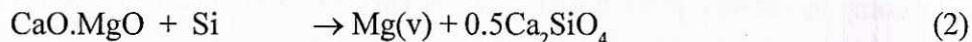
#### ***Silico-thermic Reduction***

In this process, magnesium oxide is reduced with silicon. The Pidgeon process, the Magnetherm process and the Bolzano process use this reduction reaction.



### ***The Pidgeon Process***

Calcined dolomite is used as the source of magnesium in this process. The oxide is reduced with ferro-silicon. Briquettes of mixture dolime powder and ferro-silicon are charged into a steel retort. The retort is evacuated and sealed. A pressure of 0.1 mm Hg is maintained inside the reactor [1]. The charge is heated to 1200°C through external heating of the steel retort. Gas or electricity is used as the source of heat. Magnesium vapour is produced by reduction and condenses in the cooler regions of the retort. The reaction cycle time is about 8 hours [8]. At the end of this period, the retort is opened and the solid magnesium is recovered. The reduction reaction is given by:



The equilibrium constant is given by

$$K = \exp(-\Delta G^0/RT) \quad (3)$$

$$K = (P_{\text{Mg}} \cdot a^{0.5}\text{Ca}_2\text{SiO}_4) / (a_{\text{CaO} \cdot \text{MgO}} \cdot a^{\text{Si}}) \quad (4)$$

Here,  $P_{\text{Mg}}$  is the partial pressure of magnesium and  $a_i$  is the activities at equilibrium. 'R' is the gas constant and 'T', the temperature. Assuming the activities of the oxides to be equal to unity and estimating the activity of silicon from appropriate models, the partial pressure of magnesium can be estimated. Ferro-silicon containing 65-90% silicon can be used. The process consumes 30 kWh of energy per kg of metal produced [1]. The retort is made of heat-resistant steel and is usually 25 cm in diameter and 300 cm long. Lower pressure (0.1 mm Hg) of operation gives dense magnesium crowns whereas fine, inflammable crystals are formed at high pressures. The traditional process uses horizontally placed retorts. Recent developments aim at perfecting a technology using retorts held vertically [10,11]. The traditional process suffers from low heat and mass transfer leading to high energy consumption and low productivity. This process has high capital cost and requires more area. It is not suitable for large scale production. The vertical retort process attempts to overcome these drawbacks of the conventional process.

### ***The Bolzano Process***

The Bolzano process is similar to the Pidgeon process in principle. The reactor is a brick-lined vertical cylinder. Briquettes of mixture of calcined dolime and ferro-silicon are placed on a charge support system. The charge support system is heated through electrical resistance heating. Thus, heating internal to the reactor, unlike the Pidgeon process. The temperature of operation is 1200°C and a pressure of 30 mm Hg is maintained inside the reactor. Magnesium vapour formed during reduction condenses in the cooler regions of the reactor and is collected at the end of the reduction cycle.

### ***The Magnetherm Process***

MgO dissolved in molten slag is reduced with ferro-silicon in the Magnetherm process. The slag contains about 55% CaO, 25% SiO<sub>2</sub>, 15% Al<sub>2</sub>O<sub>3</sub> and 5-6% MgO. The slag is maintained at a temperature of 1550°C in a cylindrical reactor lined with brick and carbon. Heat is generated through electrical resistance heating of the molten slag using graphite electrodes. The slag is

semi-molten at this temperature and consists of a mixture of solid and liquid phases. The activity of MgO in the slag is unity with respect to the pure oxide. Reaction takes place between molten slag and liquid ferro-silicon. The reaction chamber is evacuated and a pressure of 30-100 mm Hg is maintained. Magnesium vapour is produced by the reduction of the slag by silicon. The vapours leaving the reaction chamber is condensed in a condenser to liquid and collected in a crucible. Calcined dolomite and alumina in the size range 3-30 mm is charged along with ferro-silicon. The cycle time is about 18 hours. The process consumes less than 9 kWh of energy per kg of magnesium produced [1]. The grade of magnesium produced is inferior to that obtained by the Pidgeon process. The metal has to be refined further after collection from the condenser crucible to obtain the desired purity. About 90% of the magnesium charged is recovered in the condenser [12]. However, the recovery is 75% at the ingot stage. The Magnetherm process has the advantage of flexible production capacity which can be adjusted quickly depending on the demand [13]. The equilibrium vapour pressure of magnesium can be increased if aluminium is used as the reducing agent and the reduction temperature is increased. The possibility of producing magnesium at atmospheric pressure is being explored exploiting these principles in the traditional Magnetherm process [14]. This can overcome the need for operating the process under vacuum. MAGRAM (Magnesium Recovery from Asbestos) is a modification of the Magnetherm process [15]. This process attempts to introduce flexibility of raw material and slag composition to improve the economics of the process.

### ***Carbothermic Reduction***

The natural availability of carbon in the elemental state and its low cost makes it an attractive reductant for the production of magnesium. Plants based on the carbothermic reduction of magnesium oxide were in operation during World War II [16]. However, this practice was abandoned subsequently due to technological problems. Reduction with carbon requires high temperatures (1800-2000°C) [1]. The magnesium vapour produced quickly reacts with CO gas formed, at lower temperatures and MgO is regenerated. A submerged-arc furnace was used for the reduction of the oxide at 1950-2000°C. The magnesium vapour was rapidly quenched in a stream of hydrogen gas and recovered. Current research at CSIRO focuses on cooling the magnesium vapour at a rate of 1,00,000°C/second. The group is confident of developing a carbothermic reduction process that can be an alternative to the Pidgeon or electrolytic process [17].

### ***Magnesium through Electrolysis***

About 75% of world's magnesium was produced through the electrolytic route until about a decade ago [18]. The process consists of the electrolysis of the electrolysis of anhydrous magnesium chloride, MgCl<sub>2</sub>. The cell feed of dehydrated magnesium chloride is produced by chlorination of MgO or MgCO<sub>3</sub>. Alternatively, aqueous magnesium chloride solutions (brines) or hydrous Carnalite (MgCl<sub>2</sub>·KCl·6H<sub>2</sub>O) can be dehydrated to produce the feed [1]. Caustic magnesium oxide from sea water or natural magnesite can be chlorinated in the presence of carbon to produce the chloride feed. The chloride is electrolysed at 700-800°C in a brick-lined vessel or a steel shell. Steel cathodes and graphite anodes are used. Magnesium metal floats on top of the electrolyte. Cell voltage is 5 to 7 V [8]. Current density varies from 2000 to 8000

Am<sup>2</sup>. A part of the current is for generating heat through ohmic resistance. Current efficiency varies from 0.75 to 0.95. Recombination of dissolved chlorine and magnesium is the major source of reduced current efficiency. The process consumes about 10 to 20 kWh of energy for 1 kg of magnesium produced. Preparation of the required quality of cell feed is a major challenge in this process. The electrolytic route is characterized by high maintenance cost due to the deliquescent and corrosive nature of MgCl<sub>2</sub>. If the process is not operated continuously, the re-commissioning of the idle plant is expensive.

### ***The Magnola Process***

This process utilizes asbestos mine tailings, present as a silicate of magnesium, serpentine (3MgO<sub>2</sub>·SiO<sub>2</sub>·2H<sub>2</sub>O), for the extraction of the metal. The tailings contain 24% magnesium. The serpentine is leached to produce a brine of magnesium chloride. The brine is purified and dried to produce granules of magnesium chloride. The granules are melted in an electrolyte and electrolysed to produce magnesium [19].

### **TECHNOLOGY OPTIONS FOR INDIA**

500g of magnesium is used for desulfurising every tonne of steel produced. Every passenger automobile is expected to use 5 kg or magnesium in the form of various components. Steel and the automobile industry are expanding very rapidly in India. The traditional market for the metal as an alloying addition is also growing though not as phenomenally. An estimate shows that the requirement of magnesium in India would about 10,000 tonnes per annum. There is practically no production of the metal in India.

As discussed above, the electrolytic route throws several technological challenges to the manufacturer in the form of producing an anhydrous feed; operation of the cell and the high cost of maintenance. The process is heavily dependent on the availability of electric power at affordable price. The process is viable only if the production capacity is at least 15,000 tonnes per annum (tpy). The metallothermic reduction processes are viable even at a scale of operation of 500 tpy. The cost of maintenance is not high in this process. Production capacities can be quickly altered depending on demand with minimum impact on the techno-economics.

A silico-thermic reduction process such as the Pidgeon or the Magnetherm will be ideal for India. The Magnetherm process consumes less energy per kg of magnesium compared to the Pidgeon process. However, the latter process has had resurgence in the past decade mainly because of the exploitation of this process by the Chinese, leading to the shut down major industries such as the Pechiney in France and the ALCOA's unit in USA. The Chinese produced 5,26,000 tonnes of magnesium in 2006 based on the traditional Pidgeon process, compared to 2,00,000 tonnes produced by the rest of the world mainly through the electrolytic route [6]. The overwhelming dominance of the magnesium market by the Chinese has prompted several Indian manufacturers to consider adopting the Chinese model. Therefore, it is necessary to examine the factors that have contributed to the phenomenal success of this model. These can be listed as follows [20]:

1. Low capital cost (USD 300-400 per tonne) compared to the electrolytic process (10,000 USD/tonne of metal produced)

2. Direct use of fossil energy without conversion to electricity
3. Rapid turnaround of investment, i.e. short gestation period
4. Low cost of labour
5. Low cost of raw material, dolomite and low cost of coal [5].

Indian producers have to contend with high cost of raw materials, i.e. dolomite and ferro-silicon. They can take advantage of the large availability of natural gas in some parts of the country to provide the energy required at a low cost. A preliminary estimate of the cost of production indicates that the high cost of dolomite will be a critical deterrent. On the other hand, silicates of magnesium are available in mine tailings in many mining operations. These will prove to be a low-cost source of magnesium in India. It is possible to develop a process for the metallo-thermic reduction of the silicates dissolved in slags melting at relatively low temperatures, around 1400°C. Efforts have to be made to develop a suitable process based on this principle of silico-thermic reduction of these slags. This process has a potential to be highly competitive compared to the existing technologies.

## TITANIUM

### *Sources*

India possesses vast reserves of titanium in the form of oxides. About 374 million tonnes of Ilmenite, 21 million tonnes of Rutile and 14 million tonnes of leucoxene available in India account for about 20% of the world reserves of titanium minerals [21]. It is the fourth largest reserves available in any country. About 90% of the world reserves of the minerals is utilised in the production of Rutile which is extensively used as a pigment. Therefore, any discussion on the exploitation of these minerals should focus on the production of Rutile, apart from the extraction of titanium.

Titanium has a high strength/weight ratio and excellent corrosion-resistance. It has also got good strength at high temperatures. These properties make it an ideal structural material in applications under extreme conditions, particularly in the automobile industry which is keen to reduce weight of vehicles and improve the fuel efficiency. However, the application of the metal is severely restricted due to high cost. Whereas 1kg of steel sheet costs Rs.53; that aluminium costs Rs.500 the cost of the same weight of titanium is at least Rs.1500 [22]. Though the high cost is partly offset by the low density of titanium and the need to use less mass of metal for same volume application, it is still too costly to compete with other structural materials. Therefore, the metal is primarily used in aerospace applications where the cost factor is less predominant. Aerospace, chemical and electrical industries consume bulk of the titanium produced in the world. The petroleum industry and computer industry use titanium to significant extents. Medical prostheses form another major use of titanium. Major auto manufacturers such as Volkswagen and General Motors are using substantial quantities of titanium in auto components [23]. Though the metal has several potential applications, it is estimated that the current utilization of titanium is only 5% of the potential use. The annual world production of titanium was 1,24,000 tonnes in 2006 [24]. The high cost of production has dampened the production and utilization of this metal, compared with its closest rival in

the automobile industry, namely, magnesium. Intensive efforts are being made in many parts of the world to develop alternative technologies to produce the metal at low costs so that use of the metal would be commercially viable. However, there is hardly any alternative technology successfully demonstrated on any significant scale of operation. Most of these efforts are still in the development stage. The metal almost exclusively produced using the Kroll's process.

### ***Synthetic Rutile Pigment***

About 90% of the world reserves of titanium minerals are used in the production of  $\text{TiO}_2$  pigment. The basic raw material used in the production of pigment is Rutile, either or synthetic. Therefore, various processes have been developed to produce synthetic rutile from ilmenite which can be represented by the chemical formula,  $\text{FeTiO}_3$ .

### ***The Sulphate Process***

In this process, titanium sulphate is produced by digesting ilmenite or  $\text{TiO}_2$ -rich slag with conc. sulfuric acid. The sulphate is then hydrolysed and precipitated to form  $\text{TiO}_2$  pigment. The residue is a solid waste consisting of ferrous sulphate. Natural and synthetic rutile and leucosene are not attacked by sulfuric acid. Hence, only natural ilmenite and slag can be used as the feed material in this process [25]. This process produces anatase which is a form of  $\text{TiO}_2$ . This pigment is used in papers, ceramics and inks [26]. This process produces a large quantity iron sulphate effluent causing a major problem of disposal of this material.

### ***The Chloride Process***

Natural or synthetic rutile or  $\text{TiO}_2$ -rich slag can be used as the feed material in this process. The feed is chlorinated with chlorine gas in the presence of carbon to form titanium tetrachloride. The vapour is then heated in a mixture of oxygen and air to produce  $\text{TiO}_2$  pigment and liberate chlorine gas. An alternative process developed by Du Pont chlorinates ilmenite directly [27].

### ***Slag Process***

Ilmenite is reduced with solid carbon in a submerged-arc furnace to produce liquid pig iron and a slag rich in  $\text{TiO}_2$ . The slag is treated subsequently by one of the conventional routes to produce pigment-grade  $\text{TiO}_2$ . A pseudo-brookite phase which is quite suitable for treatment by the sulphate route is produced in the slag. If a rutile phase is produced, it can be treated only by the chlorination route. The slag usually contains some iron oxide to provide sufficient fluidity and ease of tapping. The  $\text{TiO}_2$ -content of the slag varies from about 74 to 90% [27].

### ***The Becher Process***

This process consists of oxidation of ilmenite to form pseudobrookite. This is followed by solid-state reduction with carbon at 1050-1160°C to form metallic iron and oxides of titanium. The metallic iron is subsequently leached out in aqueous solution containing ammonium chloride through a process of rusting. The resulting product contains up to 93%  $\text{TiO}_2$ . This is treated further to produce pigment.

### ***The Benilite Process***

Ilmenite containing 54-65%  $\text{TiO}_2$  is reduced at 900°C in a kiln using fuel oil [28]. Iron is reduced to the metal. It is leached out using hydrochloric acid at 2.5 atm pressure and 120-140 °C. The acid is regenerated by oxidizing the chloride to iron oxide. The acid is recycled.

The Reptile Technology chlorinates ilmenite in the presence of petroleum coke, above 1000°C. Ferrous chloride produced by the reaction is oxidized to recover ferric oxide. Synthetic rutile is recovered by wet sieving, tabling and magnetic separation [28]. Processes involving chlorination of partially reduced ilmenite and leaching of ilmenite with hydrochloric acid have been explored.

## PRODUCTION OF TITANIUM

TiO<sub>2</sub> is a highly stable oxide. In addition, oxygen has a high solubility in the metal. Therefore, it has not been possible to extract the metal from the ores through direct reduction either with carbon or other metals. Almost all the processes for the extraction of titanium, convert the oxide into a halide first. The halide is then either through the metallo-thermic route or through electrolysis.

### *Kroll's Process*

About 80% of titanium in the world is produced through the Kroll's process. TiO<sub>2</sub> is chlorinated in the presence of carbon to form the tetrachloride of the metal.



The chlorination process is usually carried out in a fluidized bed reactor. The reaction starts at about 600°C. After the initiation of the reaction, no heat is supplied to the system [29]. The vapours of titanium tetrachloride are purified through fractional distillation in stages and the high purity chloride is condensed. FeCl<sub>3</sub>, SiCl<sub>4</sub>, SnCl<sub>4</sub>, VOCl<sub>3</sub>, AlCl<sub>3</sub> are the major impurities present in the TiCl<sub>4</sub> vapours. TiCl<sub>4</sub> is reduced with magnesium to produce the metal.



The reduction is carried out in steel reactors. It is charged with magnesium which is melted at about 650°C in argon atmosphere. When the temperature reaches 700°C, purified TiCl<sub>4</sub> is charged into the reactor either as a liquid or as a gas. The reduction temperature is maintained to be around 850-950°C. Titanium sponge deposits on the walls of the reactor or is deposited above the molten magnesium. Molten MgCl<sub>2</sub> which collects below the liquid magnesium is drained off. The crude titanium sponge which contains entrapped magnesium and MgCl<sub>2</sub> is purified by distillation.

### *Hunter's Process*

This process uses liquid sodium as the reducing agent instead of the liquid magnesium used in the Kroll's process. The major advantages of this process are: (a) it requires stoichiometric amount of sodium for reduction as against the 130% stoichiometric amount of magnesium required in the Kroll's process; (b) the titanium sponge is more easily removed from the reactor vessel; (c) sodium chloride formed during reduction is easily removed by washing with water.

### *Electrowinning*

Titanium chlorides have been electrolysed to produce titanium. An electrolyte bath consisting of LiCl and KCl of composition close to the eutectic and containing dissolved TiCl<sub>4</sub> has been



used in an industrial operation. The bath was maintained at about 520-650°C [29]. Titanium produced by the electrolytic route is highly pure (>98% purity). But, it consists of loosely adherent dendritic crystals. This is a major drawback of the process. The current efficiency is very low due to the multiple valency states exhibited by titanium. The high vapour pressure of titanium chloride is another major limitation of this process. Special design of the electrolytic cell is required to overcome many of the technological problems. In spite of a long history of development, electrowinning has not been successful as an industrial operation. Practically all the titanium produced in the world is through the metallo-thermic reduction of the tetrachloride.

### ***The FFC Process***

In this process,  $\text{TiO}_2$  cathode is used along with carbon anode in a bath of  $\text{CaCl}_2$  maintained at about 900°C. Oxygen is removed from the cathode on application of a suitable voltage and transported to the anode. Titanium metal is left as a residue at the cathode at the end of this "deoxygenation" process. This process has attracted considerable attention in the past decade due to its potential to reduce the cost of production of the metal by about 40%.

### ***Recent Developments***

Intensive research is being carried out in many laboratories to develop a process that can produce titanium at a cost that can make it a viable alternative to other structural metals. In process being investigated by Ono Suzuki and co-workers [29-33], calcium is dissolved in molten  $\text{CaCl}_2$ .  $\text{TiO}_2$  is charged into this solution directly and reduced.  $\text{CaO}$  formed during the chemical reaction dissolves in the bath. It is decomposed by simultaneous electrolysis using carbon anode. In another process, the contact-less reduction of molten titanium chloride ( $\text{TiCl}_4$  or  $\text{TiCl}_3$ ) is carried out to use molten aluminium to reduce  $\text{TiCl}_4$ . The chloride is kept in a cathode chamber which is isolated from the anode chamber which contained the molten aluminium. A salt bridge served to transport the chloride ions [32].

## **TECHNOLOGY OPTIONS FOR INDIA**

Indian titanium reserves are predominantly in the form of ilmenite. They vary in grade depending on the location of the mines. Synthetic rutile is produced from these reserves using the sulphate route or the Bechar process. The Kroll's process technology has been developed in India and is being commercialized [33-35]. Apart from the problem of disposal of waste generated, the processes for the production of synthetic rutile suffer from the draw-back that these do not generate metallic iron which would be a valuable by-product. Similarly, titanium produced by the Kroll's process is very expensive and can not compete with other metals for bulk structural applications. A process that can reduce the number of process steps will substantially reduce the cost of production. A process similar to FFC process but can use ilmenite directly as the cathode recovering metallic iron and titanium will substantially reduce the cost of production. Similarly, attempts must be made to develop a process that can recover metallic iron along with  $\text{TiO}_2$  in the production of synthetic rutile from ilmenite.

## **ALUMINIUM**

India possesses one of the largest reserves of high grade bauxite ore in the world, eminently

suitable for the extraction of aluminium. The Hall-Heroult's process has virtually been the only technology available for the production of the metal at affordable price. It has never faced any major challenge from any alternative process in spite of continued efforts to develop more cost-effective alternative routes. However, increasing competition from alternative materials for the substitution of aluminium in consumer goods and industrial components has forced the industry to intensify efforts to reduce the cost of production either through improvements in the existing process or through development of alternative technologies. Several technological advances have been made in the treatment of the ore as well as the operation of the electrolytic cells. Two of these developments are discussed here-one in the area of electrolysis process and the other in a new technology that has seen considerable development work. Discussion is limited to these because it would be difficult to do justice here to all the process improvements that have been taking place. Both the two concepts discussed here are relevant to the Indian aluminium industry and have a potential to make a large impact.

### ***Low-melting Electrolytes***

The best energy consumption achieved in the Hall-Heroult process is about 13kWh/kg of aluminium. About 50% of this energy is lost as heat from the process. The minimum anode carbon consumption is 0.4 kg per kg of aluminium. This is about 21% higher than the stoichiometric limit. The current density is about 1A/cm<sup>2</sup>, leading to a high investment cost [36]. The cryolite bath used traditionally in the electrolytic cell melts at 950°C. If this can be replaced with a bath with a lower melting, this will considerably reduce the heat loss from the bath and improve energy-efficiency. The industry has been exploring the possibility of using dimensionally stable cathodes and anodes. Such an approach will have several advantages. For example, use of inert anode will eliminate the emission of environmentally-offensive gases; eliminate the cost of production of carbon anodes and produce oxygen gas that can be used industrially. Corrosion and fracture at high temperatures have frustrated the development of dimensionally-stable electrodes [37]. Efforts are, therefore, being made to alternative electrolytic baths that can melt at low temperatures, around 750°C [37,38]. These baths are made from the fluorides of aluminium and alkali metals.

### ***Direct Carbo-thermic Reduction of Aluminium Oxide***

Al<sub>2</sub>O<sub>3</sub> can be reduced with solid carbon at high temperatures. These temperatures can be achieved with reactor technologies already available. Such a process will result in higher productivity compared to the Hall-Heroult process; reduce the capital cost up to 60% and energy consumption up to 38%. Many of the processes based on the carbo-thermic reduction have been tested at the pilot plant scale. ALCAN's electrothermal reduction; ALCOA's blast-arc and arc furnace reduction; Kuwahara process; Isukuba's low shaft furnace reduction and Reynold Metal Company's process are based on this principle. The carbo-thermic process has several advantages over the Hall-Heroult process [39]:

- (a) Two to four submerged-arc furnaces used in this process can replace 400-500 Hall-Heroult cells
- (b) Less investment in electrical equipment
- (c) Less requirement of floor area

- (d) Elimination of pre-baking of electrode
- (e) Freedom from fluoride problem
- (f) Less capital
- (g) Less operation cost
- (h) Less labour requiremnt

However, several technological problems have arrested the progress of the process beyond the pilot plant scale. Some of these are [39]:

- (a) Formation of several species ( $Al_4O_4C$ ,  $Al_4C_3$  etc.) at temperatures below aluminium formation affecting process balance, chemical equilibrium and overall conversion
- (b) at the actual temperature ( $>2100\text{ }^\circ\text{C}$ ), the solubility of carbon in the metal us about 35%, requiring an efficient decarbonisation process
- (c) Vapourisation loss in the form of volatile Al and  $Al_2O_3$
- (d) Efficient charge feed management to the furnace
- (e) Finding suitable furnace lining material and cooling system
- (f) Energy recovery from the off-gases as well as transport of materials at high temperatures.

#### TECHNOLOGY OPTIONS FOR INDIA

The Indian aluminium industry is quite aware of the need to reduce the cost of production of aluminium to remain competitive in the long term. It has shown considerable interest in both the technologies discussed above. Substitution of cryolite with alternative electrolytic baths and development alternative anodes and cathodes would be possible in the near future with focused efforts. Research and development work should be supported in this direction. The direct carbo-thermic reduction can e investigated in collaboration with international and national research groups, there by gaining a sharing of knowledge and experience.

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