

EXECUTIVE SUMMARY

0.1 INTRODUCTION

From the commercial point of view, the most important synthetic manganese dioxide is electrolytic manganese dioxide-EMD. Though anodic oxidation of Mn^{2+} salt to manganese dioxide goes back to 1830, yet the usefulness of EMD was not recognised until 1918. EMD has the ability to function superbly as solid state oxygen electrode in dry cell battery over a wide range of discharge conditions. Manganese dioxide, manganese binoxide, manganese black, battery manganese, manganese peroxide all are represented by the chemical formula MnO_2 .

The composition of synthetic manganese dioxide range from $MnO_{1.7}$ to $MnO_{1.98}$, with varying contents of lower valent manganese, foreign cations (e.g K^+ , Na^+ , Ba^{2+}), hydroxyl ions and water molecules. At least six distinct modifications of manganese dioxide have been characterised (α , β , γ , σ , ϵ and ramsdellite) which differ according to their degree of crystallisation and content of foreign ions. The β - modification, as in mineral pyrolusite is not only the least reactive form of MnO_2 , but also highly crystalline. By contrast, γ - MnO_2 is poorly crystalline and much more reactive both chemically and electrochemically. MnO_2 mostly γ - modification is produced by electrolytic process and is called electrolytic manganese dioxide, EMD and is battery active. The other main source of manganese dioxide is the natural ore which is available in pure form only in some African countries like South Africa, Gabon and Zaire. Though EMD is relatively a new commodity, yet it is one of the fastest growing synthetic manganese product primarily due to high growth rate of dry cell battery, electronic component market, and high capacity cells used in military or other-wise. High quality dry cell batteries require EMD containing 90-92% γ - MnO_2 and together with acetylene black it forms the depolarising mix. EMD has the appearance of black powder, with particle size of $<74 \mu m$ (-200 mesh) density 4.2 - 4.5 g/cm^3 , bulk density 1.7 - 2.5 g/cm^3 and surface area 30-60 m^2/g . Recent studies reveal that EMD consists essentially ϵ phase crystal structure along with γ structure, with 1% lower manganese oxides and 3-5% chemically bound water. The other sources of battery active manganese dioxide are chemical manganese dioxide, CMD, and activated manganese ore. IS: 11153-1984 is the Indian specification for MnO_2 for dry batteries.

Although trial of EMD production for battery use were attempted from time to time since about 1934, industrial scale production was not initiated until the end of World War II. The first commercial plant (Tokyo Shibaura Electric Company) came up in Japan in 1944. More or less simultaneously USA also commenced commercial production of EMD based on their own developed technology. However, the development in Japan was much faster compared to USA. By 1952, Japan mastered the technology and became leading producer of EMD in the world. Japan used at the beginning lead/lead-antimony anode, while USA used both lead/lead-antimony and graphite as anode. With the change of time and technology, most of the manufacturers in the world switched over to titanium as anode material, while the cathode material is either lead or graphite. Currently, Japan is experimenting with Zirconium as cathode material. Presently, Japan is meeting about 40-45% of world requirement while USA meets about 16-18%.

0.2 RAW MATERIAL AND PROCESS OF MANUFACTURE

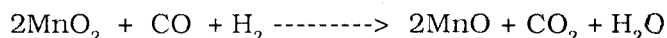
For the manufacture of EMD, manganese ore is the raw material. India has vast deposits of low, medium and high grade manganese ores, but the minerals do not occur in the form in which they are primarily required to function as effective depolariser in the dry cell batteries. Indian deposits mostly occur as pyrolusite, cryptomelane, psilomelane and manganite along with hematite, goethite, limonite, silica, phosphorous and potassium as impurities. None of these ores are suitable for direct use in the battery as natural depolariser. India has no deposit of ramsdellite or natural γ - MnO_2 and rhodochrosite, $MnCO_3$. The latter does not require pre-reduction or calcination for further processing to produce EMD. In order to get the desired product, i.e. EMD, the operations involved are :

- i) Manganese dioxide being insoluble in sulphuric acid, the ore is reduced to manganese oxide, MnO .
- ii) Leaching of manganese oxide with sulphuric acid, which is mostly practised or hydrochloric acid leading to formation of manganese sulphate or manganese chloride solution, respectively.
- iii) Purification of manganese sulphate or manganese chloride solution to remove impurities.
- iv) Deposition of manganese dioxide in an electrolytic cell on anodes to get EMD.

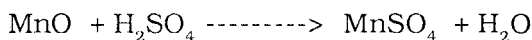
- v) Removal of EMD from anode surface, grinding/pulverising and neutralisation.
- vi) Drying, grinding/milling and packing of EMD.

EMD is generally produced from high-grade (50% Mn) manganese dioxide ore. Medium or low grade ore can also be used depending on impurities. Major countries exporting ore are South Africa & other African countries, South America, Mexico and India.

Generally, rotary kiln is used for the reduction of the ore using coke, coal, furnace oil or natural gas. Pile roasting with natural gas also done.

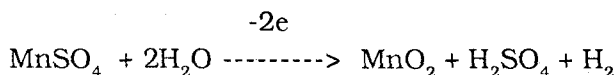


About 90 to 97% of MnO_2 is reduced to the soluble form MnO during reduction in the region of 800-900° C or more depending on the reducing agent and equipment used. The reduced ore (calcine), Mn_2O_3 , is preferably wet ground in ball mill to finer particle size for better leaching by acid solution. The slurry from the ball mill is then leached with the depleted electrolyte from the EMD cells, to which make up acid (98% sulphuric acid or 30% hydrochloric acid) is added. In the sulphate route, depending on the plant size, 2/3 stages of leaching is performed, in agitated tanks, at ambient temperature to 85°C, either in batches or continuously. By controlling pH, temperature, aeration and addition of MnO_2 ore or small quantities of EMD, the iron impurities along with potassium is precipitated as a complex salt, jarosite. The main reaction during leaching is as under :

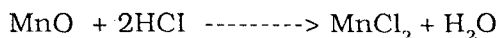


The manganese sulphate slurry is then treated in a thickner. The clear solution is filtered so also the thickened sludge. Because the process circuit is closed loop, it is not desirable to add sodium or ammonium ions which would build-up in the circuit and affect the quality of EMD produced. The clear filtered manganese sulphate solution is then treated with BaS or H_2S to remove heavy metals like copper, nickel, cobalt and some iron while the pH is maintained around 5.5 to 6.5 depending on impurities. A test for completion of sulphiding is carried out. The solution is filtered, some times thickened and then filtered to remove the impurities. A polishing filter is also used and the liquor is

stored prior to electrolysis containing about 150g/l manganese sulphate. The EMD electrolytic cells are not standard. Each EMD manufacturer has designed and constructed his own cell reflecting location and the capacity of the plant. The cells may be concrete, mild steel rubberlined, fibre glass reinforced plastic and acid proof tiles lined. The anodes are graphite, lead or titanium while the cathodes may be graphite, copper or lead. The overall cell reaction is



Generally, the anode surface is large and current density is 50-100 Amps/sq.m. The ratio of anode to cathode area is generally 2 to 1. Once the EMD deposit reaches a critical thickness, the cell is taken out of line and anodes stripped. Hydrogen liberated at cathode escapes to atmosphere acting as a gas lift in the cell aiding electrolyte circulation. The cell is kept covered with oil or wax to conserve heat and decrease loss of vapours and acid/MnSO₄ mist along with escaping hydrogen. The cell operating parameters are critical. Because of large number of variables like cell temperature, anode current density, sulphuric acid concentration, manganese sulphate concentration, impurities in solution and anode-cathode spacing the commercial EMD cell operates under various conditions which are proprietary information. The contents in the cell are maintained at about 90-95° C, heated by live steam, steam coil or electricity. The current efficiency is in the range of 90-97%; operating voltage 2.1-2.5. Depleted cell liquor is regenerated by leaching manganese oxide with sulphuric acid (make-up) followed by purification, for reuse. The EMD deposited on anodes are broken/ground, washed, entrapped acid neutralised with NaOH or Na₂CO₃, pulverised and dried at relatively low temperature. The final packing is done in air tight conlainers. In the chloride process, which is being experimented in different parts of the world, leaching of the calcine is done in hydrochloric acid and the main reaction is as under :



The rest of the process right from manganese ore reduction is more or less identical to sulphate route process.

0.3 CAPITAL EQUIPMENT

The capital equipment required for EMD plant are all indigenously available and they are jaw crusher, roll crusher, ballmill, rotary kiln (oil fired), Rotary dryer etc. Both titanium and graphite as anode and cathode material are available in India including fabrication facilities; only titanium sheets are imported. All pollution control equipment like cyclone separator, bag filter, pulse-jet filter, venturi scrubber, packed bed scrubber, various other dust handling equipments and even electrostatic precipitators are available indigenously. Lead is an imported material mostly.

0.4 STRUCTURE AND STATUS OF INDIAN INDUSTRY

Union Carbide India Ltd, with an installed capacity of 4500 TPA is operating an EMD plant at Thane, Maharashtra since 1971. Manganese Ore India Ltd., MOIL has commenced commercial operation of its 700 TPA plant near Nagpur, since 1991. The licensed capacity of this unit is 4000 TPA. Both the units are registered with DGTD. UCIL is a public limited company. Union Carbide Corporation, UCC of USA has substantial interest in UCIL. MOIL, under Ministry of Steel and Mines is owned by Government of India (51% share) and the balance share holding is equally distributed between State Governments of Maharashtra and Madhya Pradesh. MOIL is also engaged in the mining of manganese ore while UCIL is a leading manufacturer of dry cell, chemicals and plastics. Another unit T.K. Chemicals Ltd, Trivandrum, was engaged in the manufacture of EMD between 1977 end and mid 1984. It was the first plant to commence commercial production of EMD with indigenously technology from National Metallurgical Laboratory, NML, Jamshedpur. At present only two EMD plants are in operation. UCIL purchased their technology and engineering design from UCC, USA, in 1963-64. MOIL is using indigenously technology of IIT, Madras/NML, Jamshedpur. MECON, Ranchi, is their engineering consultant. The project cost of 700 TPA plant is Rs. 3.6 crore. Magno Mining Co. Ltd., MMCL, has obtained license for a 2500 TPA EMD plant now enhanced to 4000 TPA. The plant will be located at Bobbili, Andhra Pradesh. They are currently operating at 1 TPD Venture Capital Fund project with NML technology. The present installed capacity of EMD is 5200 TPA.

0.5 DEMAND/EXPORT/IMPORT

The demand of EMD in India has not picked up along with increase in capacity of dry cell manufacturing units which has grown from 1642 to 2095 million pcs. between 1985 and 1991 in terms of installed capacity. The average growth rate is about 3.6% between 1985 to 1991. The consumption pattern of EMD per dry cell remained at 4.5 gm for one unit while for the others the same is below 3 gm, on an average against international standard of 7.5 gm/cell. This is attributed to high cost of indigenous and imported EMD which has been substituted by indigenous and imported ore, and chemical manganese dioxide. All these are far less active compared to EMD. EMD has been imported as well as exported. The conservative estimated demand at present is about 9000 TPA and by 1999-2000 the same should touch 11000 TPA. Export potential of EMD is very high with plenty of raw material in reserve. According to Indian Bureau of Mines, Nagpur, the recoverable reserves of manganese dioxide is 7 lakh M.T. out of total reserves of 1542 lakh M.T. EMD industry in Japan is virtually surviving on imported ores while exporting about 50% of their product. Instead of exporting manganese ore, India should export EMD as a value added product.

0.6 TECHNOLOGY

UCIL is operating their plant with imported technology since 1971. It was a proven technology from UCC, USA. With technology upgradation, UCIL claims to have upto date technology if not the state of the art technology. In India, technology developed by NML after 20/22 years or more of efforts, was first commercialised by TKCL in mid seventies but the said venture did not last long. Central Electromechanical Research Institute, CECRI, Karai Kudi, is involved in EMD technology development for nearly 30 years following manganese chloride route instead of manganese sulphate route (used by most of the EMD manufacturers) has yet to go through commercialisation step. Institute like IIT, Madras also has a patented process for EMD. Going by various patents, papers and activities of NML, CECRI and IIT it is evident that the technology for EMD is available indigenously. The real test lies in commercialisation. A consortium effort on the part of NML, CECRI and IIT backed by engineering and consultancy capability of MECON, Ranchi, and expertise of Indian engineering

industry could provide effective indigenous EMD technology in about 3/4 yrs. The gaps in areas like calcination, energy consumption and product finishing, can easily be tackled. UCIL has been able to improve upon energy consumption from 4150 KWH in 1981 to 3200 KWH in 1990-91 besides fuel oil consumption from 1550 litres to 1050 litres during the same period per MT of EMD. NML's EMD technology was given to CRS, Myanmar in 1979 under ITEC programme.

0.7 TECHNOLOGY SUPPLIER AND ENGINEERING CONSULTANTS

National Research Development Corporation Ltd., New Delhi, a Government of India Enterprise under Ministry of Science and Technology serves as a vital link in the innovation chain and acts as a prime vehicle for technology transfer in this country. Over more than 30 years of its existence, the corporation has established linkages with a large number of technology generating agencies and has become a repository of indigenous technologies particularly those generated at public funded R&D institutions. NRDC works in close association with major research institutions like Council of Scientific and Industrial Research, Indian Council of Agricultural Research, Indian Council of Medical Research and Defence Research and Development Organisation. The Corporation has in reserve more than 2,000 technologies and executed more than 3,000 license agreements since its inception in 1953. The basic indigenous EMD technology suppliers and engineering consultants are:

- National Metallurgical Laboratory, Jamshedpur, Bihar
- Central Electro-Chemical Research Institute, Karaikudi, Tamilnadu
- Indian Institute of Technology, Madras, Tamilnadu
- Engineering Consultants - Metallurgical & Engineering Consultants (India) Limited, Ranchi, Bihar, Engineers India Ltd. and Dalal Consultants & Engineers Pvt. Ltd., Bombay.

Union Carbide India Ltd, Calcutta, can also be considered as a source of technology in India. Besides basic technology suppliers, there are quite a few individuals as consultants in the field of EMD having research and operational experience.

0.8 INTERNATIONAL SCENARIO

Japan is the largest producer of EMD, followed by Europe, Latin America and others. First patent on EMD was taken in Japan in 1929. Though Japan and USA commenced commercial production more or less simultaneously, between World War II or immediately after, Japan's progress was faster through simultaneous R&D work. Japan's current capacity is 72,000 TPA which was 52,000 TPA in 1982. USA and Canada jointly have the capacity of 31,000 TPA. If Japan's interest in Europe is taken into consideration, then the Japanese controlled capacity comes to about 50% of world capacity which stands at about 2,24,000 TPA, taking into consideration the new plants in Australia, Brazil and Mexico compared to 1,53,000 TPA in 1982. Japan is the largest exporter of EMD, accounting for more than nearly 50% of its production. The world growth rate in EMD in the 1980s was about 10%. The present growth rate is 6-7%. The plant capacities vary between 4,000 to 15,000 TPA. All the producers export substantial quantities of EMD. In 1986 world demand was placed at 1,28,000 TPA which is 1,62,000 TPA currently.

There are at least four operating companies like Toyo Soda Manufacturing Company Ltd., (now TOSO Corporation), Mitsui Mining & Smelting Company Ltd., Daiichi Carbon and Japan Metals & Chemicals Corporation which can offer technology compared to only two companies like Union Carbide Corporation and Kerr-McGee Chemical Corporation of USA. USA and Japan are considered 'have not' as far as raw material for EMD is concerned. Installed capacity in India which was 4,000 TPA in 1982, is 5,200 TPA now, accounting for only 2.5% of world capacity. Though India has vast reserves of low, medium and high grade manganese ore, yet thrust towards value added product like EMD is lacking. R&D activities by world's producers of EMD have kept their technology always on the fore-front. Their R&D efforts are directed towards conservation of energy, new type of cathode material, better cell and anode design, combat pollution, use of low grade ore, etc.

0.9 R&D EFFORTS, TECHNOLOGY ABSORPTION AND GAPS

In 1949-50, NML started laboratory scale investigation to develop a process for production of electrolytic manganese dioxide through the electrolysis of manganese sulphate. By 1952 the process was patented.

The process was scaled up from laboratory to semi-pilot plant level with the installation of 2 Kg/day unit in 1953-54. Realising the inadequacy of the semi-pilot plant to provide necessary design engineering data, a 50 Kg/day pilot plant was set up in 1959-60. The samples of EMD produced in this pilot plant were sent to two firms viz. Estrella Batteries and Ray-O-Vac, USA. The tests conducted by these firms found the samples acceptable to battery manufacturers. Further in 1965 NML provided UCIL with 500 kg of EMD for use in dry cell batteries. During this period, since the technology was not exploited commercially patent ran out its full life. The process was licensed to M/s Devidayal, Bombay in 1962 but not commercialised for various reasons. Though other parties showed interest in the process for commercialisation of the NML process it did not take place till TKCL came into the field. With the growth of dry cell battery industry, Ministry of Industrial Development proposed issuing of new licences for setting up of EMD plant by several units. The growth in demand coupled with the defence requirements during 1971 war gave a boost to the production of dry cell batteries leading to shortage of EMD in India. TK Chemicals Limited initiated setting up EMD plant in 1972 and appointed M.M. Suri and Associates as their turnkey consultant with NML technology. The plant materialised in 1977. In 1979, under Indian Technical and Economic Copoperation Programme, ITEC, NML installed an EMD pilot plant at Central Research Station, CRS, Rangoon, Burma (Myanmar) with lead antimony as anode material, which was also employed at TKCL. Subsequently, NML tried out graphite and titanium as anode material. CECRI/CSIR, Karaikudi, also commenced R&D work on EMD following manganese chloride route and process was patented in India in September 1964. CECRI have also developed patented process for treatment of titanium anode used in EMD cells. Both NML & CECRI have put in substantial number of years in R&D work on EMD, using lead-antimony, graphite and titanium as anode material. In 1984, Indian Institute of Technology Madras patented a process for the manufacture of EMD. UCIL purchased a proven technology from UCC, USA and started production of EMD from 1971. They have expanded their capacity, switched over to titanium anode, improved fuel, energy and raw material efficiency through in-house R&D. After TKCL's closure, NML technology was improved upon with respect to ore reduction, anode material, titanium in place of lead antimony and potassium removal to make it more competitive. The R&D work in NML, CECRI and IIT is continuing. Therefore, as far

as technology absorption is concerned it can be said that imported UCC technology adopted by UCIL is fully absorbed. Indian technology which is under going commercialisation with MOIL will definitely throw some light in areas like ore reduction, electrolysis, removal of impurities including potassium, filtration and product finishing which will call for technological innovation ultimately leading to the acceptance of the product by the consumer. Both NML and UCIL claim that they have developed process of removal of potassium impurities from leached solution.

10. THRUST AREA

R&D work including pilot plant studies by NML and CECRI if put together is quite substantial and the country must be benefited from their work. IIT Madras is also engaged in R&D work in EMD. With a view to commercialise the technology, the strong points of the technologies of NML, CECRI and IIT must be put together with active support of consultants like MECON. If need be, support of engineering industry also can be sought. The thrust should be to commercialise the indigenous technology by 1994-95. The problems encountered during commercialisation and technology transfer can be taken up with any of the R&D centres mentioned above.

11. RECOMMENDATIONS

- R&D institutes currently working on EMD should consider working jointly for process know-how optimisation and technology improvement leading to cost saving and commercialisation of the EMD technology in India and technology transfer to other countries like Far East, European and Latin American countries.
- To establish indigenous EMD technology as one of the world's commercial technology by 1994-95 (target year), a consortium approach from R&D laboratories and institutions as well as consultants, Indian engineering industry and various experts should be evolved at the earliest.
- Fresh capacity in EMD should be created to cater to domestic as well as export demand. The export of raw ore should be discouraged in favour of value added finished product.