Production of Electrolytic Manganese Dioxide

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THE principal application of electrolytic manganese dioxide is for the cathode material (or cathode depolariser) in dry cells. The authors have developed a process to produce electrolytic manganese dioxide, suitable for the use in dry cells from the manganese sulphate liquor obtained either from ferromanganese slag (Mn 28%) or low grade manganese ore (Mn < 40%). In case of the slag, the slag was directly leached with dilute sulphuric acid whereas low grade ore was leached with ferrous sulphate/ferrous sulphate + sulphuric acid or roasted first with ammonium sulphate/ferrous sulphate and then leached with hot water to solublise manganese as sulphate. The leach liquor thus obtained was purified and then electrolysed using titanium anode and stainless steel cathode as lead anode resulted in impure products. The crystal modification of the product was examined by X-ray diffraction method and found to be of γ-variety. DTA analysis of the sample showed similar curves to that of γ-manganese dioxide and the deplorisation study indicated that the product would be suitable for the use in dry cells. Further, the chemical composition of the product was found to match with the standard specifications for the battery industry. The paper also incorporates an approalmate estimate producing 1 T/day and 3 T/day EMD from ferromanganese slag.

MANGANESE dioxide of some special type is mainly used as a depolarizer in the Laclanche cell. As the depolarizer, manganese dioxide undergoes following electro-chemical and chemical reactions under normal condition of discharge.

$$MnO_2 + 2NH_4^+ + 2e^- = 2\,MnOOH + 2NH_3$$
$$2MnOOH + 2NH_4^+ = MnO_2 + Mn^{2+} + 2NH_3 + 2H_2O$$
$$MnO_2 + 4NH_4^+ + 2e^- = Mn^{2+} + 4NH_3 + 2H_2O$$

In this scheme the direct product of electro-chemical reaction is Manganite, MnOOH. The manganese dioxide used in this type of cell is of different grades, such as (i) natural manganese dioxide (ii) activated manganese dioxide, (iii) chemical synthetic manganese dioxide and (iv) electrolytically prepared manganese dioxide (EMD). In general, battery grade ores are characterised by their poor crystalline nature. They consist largely of γ-MnO_2 and in some cases cryptomelane or the nearly amorphous δ-MnO_2. Since the natural ore or activated natural ore are not suitable for sophisticated batteries, the present trend is to make appropriate varieties of MnO_2 by means of chemical or electrochemical method. There are several methods of preparing a synthetic MnO_2 by a chemical process. But the MnO_2 produced in this route cannot compete economically and also quality wise with electrolytic manganese dioxide. EMD is high purity manganese dioxide obtained from manganese ore by electrolytic process, and is the most powerful and most efficient depolarizer. It imparts a much longer life to both torchlight and transister cells, it is also used in the production of manganese based alloys, chemical paints, ceramics, glass and varnishes.

Production and demand of EMD : The production of dry batteries has received great impetus due to buoyant internal and export demand. Their production increased from 477 millions Nos. in 1969 to 804 million nos. in 1978 and compounded at an average annual growth rate about 7.7%. With this growth rate, the production is projected to touch 1255 million nos. by the end of 1984. In the light of projections made recently by the department of electronics[1] the demand may register further increase, as there is now a rapidly growing market for cassette tape recorders, electronic calculators, torches, transistors etc. In step with the increasing production of dry cells, the demand for MnO_2 will also increase in the coming years.

Though India has large resources of manganese dioxide ore, most of these cannot be used for dry cell manufacture as it possesses a high iron content and it does not have the desired crystalline structure. So the country has all along been dependent upon imports. The imported ore is generally blended with the indigenous ore. Imported-indigenous mix of 70 : 30 may be considered suitable for a good cell. On the basis of this ratio, an overall estimate of MnO_2 requirement in India during the period 1983-84 is given in Table 1. At present, India's demand for EMD is

TABLE 1

Statistics on Battery Grade MnO_2 Requirement of India during the Period 1983-84

Overall Estimaes in Tonnes	Imported Compononent In Tonnes	Indigenous Components in Tonnes
50,000	35,000	15,000

In case Emd is used, the consumption Pattern will be

Overall Estimates in Tonnes	EMD in Tonnes	Natural ores In Tonnes
50,000	15,000	35,000

met through both imports and indigenous production. There are now two producers of EMD namely Union Carbide (India) Ltd. with an installed capacity of 2,500 tonnes/yr. and M/s. T. K. Chemicals with a capacity of 1,000 tonnes/yr. Statistics on indigenous production and imports of EMD and battery grade ore is given in Table 2.

TABLE 2

Statistics on Import of EMD and Battery Grade Manganese dioxide ore by India and Indigenous Production of EMD in India

Year	Import of EMD in Tonnes	Indigenous Production of EMD in Tonnes	Import of Battery Grade ore in Tonnes
1973-74	389	1480	4123
1974-75	32	2341	2776
1975-76	39	702*	5550
1976-77	67	2300	2050
1977-78	208.9	N.A.	5963

* Plant shut down for 6 months.

Technology for production of EMD : The most commonly used technologies for the production of EMD are based on the electrolysis of $MnSO_4$ solution. Technological developments in the production of EMD relates mainly two routes — electrolysis of $MnSO_4$ solution or $MnCl_2$ solution. The sulphate route has got advantages over the chloride route because of the choice of material of construction of the cell, of the electrodes etc. Thus the sulphate electrolysis is the convenfional route for the production of EMD. The only change made in the earlier developed technologies has been in the use of new materials for electrodes and in electrolysis conditions.

Outline of production process : Manganous carbonate and manganese dioxide ores are the major sources of raw material for EMD. In the case of MnO_2 ores, since the ore does not dissolve in H_2SO_4, the ore must be roasted with a reducing agent (oil or carbon) in order to convert it to MnO which dissolves easily in H_2SO_4. The leach liquor after usual purification is electrolysed, using lead alloy or graphite anodes at about 90°C to produce EMD.

Process developed at R. R. L. Bhuvaneswar : Extraction of Manganese : At the Regional Research Laboratory processes were developed to extract manganese into solution from (i) Ferromaeganes slag (both high and low manganese content slags) and (Ii) Low grade manganese ore. Ferromanganese slag, both low manganese content slag[2] (Mn = 12%) and high manganese content slag[3] (Mn = 28%) were leached with dilute sulphuric acid to extract manganese value. For the extraction of manganese from the low grade manganese ore, the following routes were adopted

i) Ferrous sulphate/Ferrous sulphate + H_2SO_4 leaching[4].
ii) Ferrous sulphate roasting, followed by hot water leaching.
iii) Ammonium sulphate roasting followed by hot water leaching[5].

The influence of several variables like the amount of reagent, temperature, duration etc. on the extraction of manganese from both the slags and ores were studied and optimum conditions were carried out.

The main constituents of ferromanganese slag are silicates of Mn, Ca and Al. These slags are of little use and some types of it are simply dumped. In India the slag obtained from ferromanganese plants varies between 12-30% of manganese. As the slag contains comparatively high manganese value with a negligible amount of iron it may be used as a suitable raw material for making EMD. At Regional Research Laboratory extraction of manganese from two types of slags were studied i.e. (i) high manganese content slag (HMC slag) containing 28% manganese from FACOR, A. P. and (ii) low manganese content slag (LMC slag) containing 12% manganese from Joda plant, Orissa, to evsluate the feasibility for using the slag to produce EMD. The

composition of both the slags are given in Table 3 The results at optimum conditions are reported in Table 4. It may be observed that in case of HMC slag only 1.4 times stoichiometric quantity of H_2SO_4 is required to extract about 80% of Manganese but in case of LMC slag it requires 4.5 times stoichiometric quantity of H_2SO_4 to extract almost the same amount of manganese when all other parameters are kept constant.

TABLE 3

Chemical Composition of Ferromanganese Slags, Particle size-100 Mesh (BSS)

Constituents	High Manganess Content Ferro-Manganess Slag, %	Low Manganess Content Ferro-Manganese Slag, %
MnO	36 96	16 00
SiO_2	30 96	24.51
CaO	11 43	24.11
MgO	0.32	7.34
Al_2O_3	15 05	20.27
Fe_2O_3	2.23	2.03
Insoluble	4 35	5.84

TABLE 4

Chemical Composition of Low Grade Manganese ore, Particle size-100 Mesh (BSS)

Constituents	%
MnO_2	61.38
SiO_2	4.90
Fe_2O_3	15.50
Al_2O_3	5.50
CaO	9.10
Insoluble	4.35

The slag after reaction with H_2SO_4 produced a thick slurry which posed great difficulty for solid-liquid separation. However, later this problem was successfully solved.

The chemical composition of the low grade manganese ore is reported in Table 5. Of the different processes adopted for the extraction of manganese from low grade manganese ore, $FeSO_4$/$FeSO_4 + H_2SO_4$ leaching seems to be most effective, with more than 90% of manganese value extracted When $FeSO_4$ alone was used as a leachant, it resulted in a thick slurry which was difficult for solid-liquid separation. But when H_2SO_4 (8% or above) was added to $FeSO_4$ solution, the solid-liquid separation problem was solved, with 97%

TABLE 5

Optimum Conditions for the Extraction of Manganess from Ferromanganese Slag & Low Grade Manganese ore

A.

Raw Meterial	AMT. of Acid (Times Stoi-Chio. Qnty.)	Time Min.	Temp. °C	Solid-Liquid Ratio	Mn Extrn. %
HMC Slag	1.4	30	27	1 : 5	79.82
LMC Slag	4.5	30	27	1 : 5	82.57

B.

Raw Material	AMT. of $FeSO_4$ (Times Stoi-chio Qnty.)	AMT. of H_2SO_4 %	Time Min.	Temp. °C	Solid-Liquid Ratio	Mn Extrn. %	Total Fe G/L
Mn ORE	1.0	–	60	90	1 : 10	91.4	3.90
Mn ORE	1.0	8	60	90	1 : 10	96.6	15.26

C.

Raw Materials	AMT. of $FeSO_4$ (Times Stoi-chio Qnty.)	AMT. of $(NH_4)_2SO_4$ (Times Stoi-chio Qnty.)	Time Min	Roasting Temp. °C	Mn Extrn. %
Mn ORE	1.2	–	45	650	73.23
Mn ORE	–	1.2	60	650	70.40

Mn extracted. But iron content in the solution increased 3 times than leaching with $FeSO_4$ alone (Table 4).

In cases of roasting either with $FeSO_4$ or $(NH_4)_2SO_4$ followed by hot water leaching the maximum manganese value extracted was only about 70% (Table 4). The advantage of this route over direct leaching with $FeSO_4$/$FeSO_4 + H_2SO_4$ is (i) it possesses no filtration problem and (ii) the leach liquor contained almost negligible amount of iron. When the roasted ores were leached with hot dilute H_2SO_4, there was a little increase in manganese extraction but 10–15% iron was extracted.

Purification of leach liquor : In order to oxidise Fe^{+2} ion to Fe^{+3} ion in the leach liquor obtained from ferromanganese slag leaching air was passed through the solution and its pH was raised to 4.5-5.5 to precipitate out iron as $Fe(OH)_3$ In case of leach liquor obtained from the treatment

of low grade manganese ore, Fe^{+2} ion oxidation to Fe^{+3} ion was carried out by adding MnO_2 ore (fine powder) and bubbling air through the solution and finally raising the pH to 4.5-5 5. Small amount of other impurities (Pb^{++}, Ni^{++}, Co^{++}, etc.) were also coprecipated with either $Fe(OH)_3$ or SiO_2. The precipitate was filtered and a clear manganese sulphate solution was obtained.

Electrolysis of manganese sulphate liquor and production of EMD :

Process Chemistry : On electrolysing on aqueous solution of manganese sulphate, manganese dioxide is produced at the anode and hydrogen at the cathode.

At anode :

$$2Mn^{2+} \rightarrow 2Mn^{3+} + 2e^- \quad \ldots\ldots(4)$$

$$2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+} \quad \ldots\ldots(5)$$

At cathode :

$$2e^- + 2H_2O \rightarrow 2H^+ + H_2 + 2O^{2+} \quad \ldots\ldots(6)$$

The complete reaction may be written as

$$MnSO_4 + 2H_2O = MnO_2 + H_2SO_4 + H_2 \quad \ldots\ldots(7)$$

For every mole of $MnSO_4$ consumed in the reaction there is production of 1 mole of H_2SO_4. Fleischmann, Thirsk and Tordesillas[6] have studied the kinetics of the electrodeposition of γ-MnO_2 on Pt-electrodes. They concluded that the slow stage of the reaction is a rate determining dehydration to for γ-MnO_2.

$$Mn(H_2O)_{n-1}(OH)_{ads} \rightarrow MnO_2 + (n-2)H_2O \quad \ldots(8)$$

A detailed investigation[7] has shown that the degree of crystallinity of the gamma type varies with electrolyte and type of anode used.

Operating condition

Electrolysis using Pb-Sb anode : The purified leach liquor was taken for electrolysis after addition of suitable additives. The speciality of the bath used in the present study was that the electrolyte was in the pH range (pH 4-5) and the electrolysis was carried out at room temperature using lead antimony anode and steel cathode. Storey et al's[8] pointed out that if the temperature of electrolysis were low, beta type MnO_2 would be produced. But in the present conditions of electrolysis the authors obtained γ-MnO_2 at room temperature electrolysis which contradicts storey et al's[8] findings. The bath composition and electrolysis condition established are in Table 6. The MnO_2 obtained was washed with hot water to remove any electrolyte and dried. The dried sample was ground and finally washed throughly with water. After washing, the material was neutralized with NH_4OH as a dilute solution in order to neutralise free acid and to adjust pH of the final product. After pH adjustment, the EMD was filtered and dried at 100-110°C for 2 hrs.

TABLE 6

Bath Composition and Electrolysis Conditions Using Pb-Sb Anode

Mn	—	30 - 70 GPL
NaS_2O_4	—	10 - 20 GPL
H_3BO_3	—	10 - 20 GPL
Temperature - Room Temperature		
C.D. - 0.2 - 1.0 A/dm^2		

Analysis of EMD : The EMD thus obtained was subjected to chemical analysis. Some physical and electrochemical tests were conducted to find out its suitability as a dry cell cathode depolarizer. The results are given in Table 7. It may observed that the EMD obtained thus satisfies almost all the requirements for dry cell specifications (Table 8) except that the lead content is high.

TABLE 7

Specifications of EMD Produced Using Pb - Sb Anode

MnO_2	—	88-90%
Mn	—	56-58%
Fe	—	0.1%
Pb	—	1.0-3.0%
Acid Insoluble (HCl) — Nil		
pH	—	4.5
X-Ray Structure - Gamma MnO_2		
DTA	—	Similar to Gamma MnO_2
Depolarisation Test - Results Similar to Gamma MnO_2		

Electrolysis using Ti anode : Titanium is well known for its mechanical stability and chemical resistance. It can be successfully used for the production of EMD because of its hardness, stability to acids such as HNO_3, H_2SO_4 or 5% HCl, high electrical conductivity and ease of preparation[9]. In the preparation of EMD lead or lead alloy electrodes proved unsatisfactory since these did

TABLE 8

Represntative Compositions of Electrolytic MnO_2 Samples

Composition	U.S.%	Japan%	India%
MnO_2	85 Min	90 Min.	91 9
Mn	58 Min	—	59.4
Fe	0.03 Max	0.05 Max.	0.1
Silica	0.50 Max	—	—
Alkali & Alkaline Earth Metals	1.00 Max	—	—
Pb	0.20 Max	0.10 Max	0.1
Cu	—	0.002 Max	—
Heavy Metals	0.03 Max	—	—
SO_4	—	1.50 Max	1.1
Moisture	—	3.00 Max	2.1
Acid Insoluble	—	—	0 36

not yield a product of satisfactory purity, especielly activity[10]. Graphitized electrodes are most widely used in practice. But these are now a days replaced by metallic ones because of their large volume, instability under conditions of high temperature electrolysis in presence of free H_2SO_4 etc. Thus the present trend is to use Ti, platinum coated-Ti, Ti-Mn alloy, TiC - coated Ti, RuO_2 coated Ti etc.

Lead-antimony anode was replaced by Ti anode in the present work to get a better product. It was observed that under the optimum condition established earlier using Pb-Sb anode, power consumption was unexpectedly high with Ti anode. Thus the electrolysis bath was optimised by studying the variables like manganese concentration, temperature of electrolysis, amount of H_2SO_4, current density etc. using Ti anode and stainless steel cathode. It was observed that during electrolysis the bath voltage increases after a certain period of time. This is perhaps due to the non-conductive layer of Ti-oxide film on the Ti surface.

The anodic behaviour of Ti in hot H_2SO_4 (20 g/l) and acidified $MnSO_4$ (100 g $MnSO_4$/l) solutions was studied by Dzhaparidze et al[11]. They showed that the minimum anodic current densities in these solutions are 2.4 and 0.45 mA/cm² respectively. Accumulation of oxides together with MnO_2 deposition occurred in acidified $MnSO_4$ solution. The potential did not increase before the complete coverage of the electrode with Ti_3O_4 3-4 TiO_2 oxide film. The voltage increased sharply with complete coverege of the Ti surface by this film. Kelly[12] also reported that Ti shows typical passivity behaviour in H_2SO_4 solution. An active/passive peak is formed in the anodic polarization curve. In order to prevent this phenomenon the authors used small amount of NaF in the bath composition and it worked excellently. Jshino et al[13] used NaF as a de-passivator which exerted a positive influence. Ti-oxides dissolve chemically in acidic flouride solution[14]. When F^- is added to the H_2SO_4 electrolyte, the general form of the polarization curve remains unchanged but the current both in active and passive regions are increased[15]. The dissolution mechanism in the peak and near passive regions has been studied by Caprani[16]. From a recent study Kelly[17] suggested that the rate of Ti dissolution is controlled by an almost constant electric field in the surface film. The dissolution rate of the film is dependent for a given electrolyte. The presence of F^- is expected to play an important role since TiO_2 dissolve in acidic flouride solution[14]. The electrolysis bath optimised by the authors using Ti anode, could be used for prolonged period for producing EMD with more than 90% current efficiency. The bath composition and electrolysis condition for producing EMD is reported in Table 9.

TABLE 9

Bath composition and electrolysis condition using Ti anode

Mn	—	50 — 100 GpL
H_2SO_4	—	< 50 GpL
NaF	—	< 1 GpL
Temperature	—	85 — 95°C
C.D.	—	Max. 1A/dm²

The EMD obtained as flakes was easily groundable. It was washed with hot water to remove any electrolyte adsorbed. Then it was dried, crushed and finally washed throughly with water. After washing, the EMD powder was neutralized with NH_4OH solution in order to neutralize the free acid and to adjust the pH of the final propuct. After pH adjustment the EMD powder was filtered and dried at 100-110°C for 2 hours.

Analysis of EMD : Generally speaking, there are two main requirements for a battery grade MnO_2. The first is the chemical composition of the material and the second is the battery characteristic of MnO_2. So chemical analysis alone does not give any assurance that the product will be a sufficiently active MnO_2 to meet the requirement of the battery manufacturers. As a consequence a number of physical and electrochemical tests are performed to determine the battery characteristics.

A. *Chemical analysis :* Chemical analysis required to find out the percentage of the MnO_2 Mn, Fe, Pb, matter insoluble in HCl etc. were carried out to find out whether the product suits the specifications (Table 8) of the battery grade The results are reported in Table 10.

TABLE 10

Specifications of EMD produced using Ti anode

MnO_2	—	90% Min.
Mn	—	58% Min.
Moisture at 120°C	—	2.9% Max.
Pb	—	Nil
Fe	—	0.03% Max.
Matter insoluble in HCl	—	Nil
Alkali Metal	—	Nil
X-ray Structure	—	Gamma
DTA Analysis	—	The curve is similar to Gamma MnO_2
Empirical formula from Chemical analysis	—	$3MnO_2.H_2O$
From X-ray	—	$Mn_{1.1}O_{6.4}$-H_2O
Crystal Form	—	Orthorhombic
Depolarization test	—	Results similar to Gamma MnO_2
Sizing	—	92%–200 MESH
pH	—	4.5–5.5

B. *Physical Test :* Physical tests such as X-ray, D.T.A., Kerosene absorption, carbon dioxide evolution test etc. are some of the tests which indicates the activity of the MnO_2 to be battery grade.

(i) *X-ray analysis :* The relationship between the crystal structure and the depolarizer quality of MnO_2 samples has long been tantalized battery technologists. The term γ-MnO_2 is applied to synthetic as well as natural manganese dioxide characterized by poor crystallinity, partial hydration and typical X-ray pattern. The EMD obtained in the present study was subjected to X-ray diffraction analysis. The result shows that the product is γ-MnO_2 having crystal system orthorhombic and empirical formula $Mn_{1.1}O_{6.4}$-H_2O.

(ii) *Differential thermal analysis :* Differential thermal analysis peak temperatures reflect the thermal stability of the MnO_2, which is felt to be indicative of its reactivity in a Leclanche dry cell. γ-MnO_2 shows main vertical peak at 578°C which is the characteristic of its activity as a depolarizer The DTA curve taken on our sample shows a very similar curve as the standard battery grade EMD.

C. *Electro-chemical test :*

Depolarization characteristic : The depolarization capacity is a function of many variables. e.g., MnO_2 content, crystal modification, state of the crystal, size of the crystallites and impurities. Thus the electrochemical method seems to be the best since it takes into consideration all the influences and directly reveals the depolarization properties of the MnO_2 in the test cell MnO_2/Zn. This view is supported by the operational practice. since the surest measure of the quality of MnO_2 is considered to be the discharge of commercially prepared cells.

The depolarizing activity of MnO_2 was determined in a suitably modified form of cell system developed originally by Appelt[18]. The discharge curve (potential vs. time) obtained at a constant current load, 40 mA, using the EMD produced here were exactly similar to that of electrolytically prepared γ-MnO_2.

Basing on the preliminary studies, a detailed bench scale study i.e. 3 kg EMD/day batch from ferromanganese slag (HMC slag) was made. The flow sheet of the complete process is given in Fig. 1. The other routes given in the flow sheet (Fig. 1) i.e. production of EMD from low grade manganese ore, either through $FeSO_4$/$FeSO_4$ + H_2SO_4 leaching or $FeSO_4$/$(NH4)_2SO_4$ roasting followed by hot water leaching, were carried out up to the extraction stage. After the extraction $MnSO_4$ is obtained in the leach liquor which can be purified and the same route to produce EMD as in case of ferromanganese slag mey be followed.

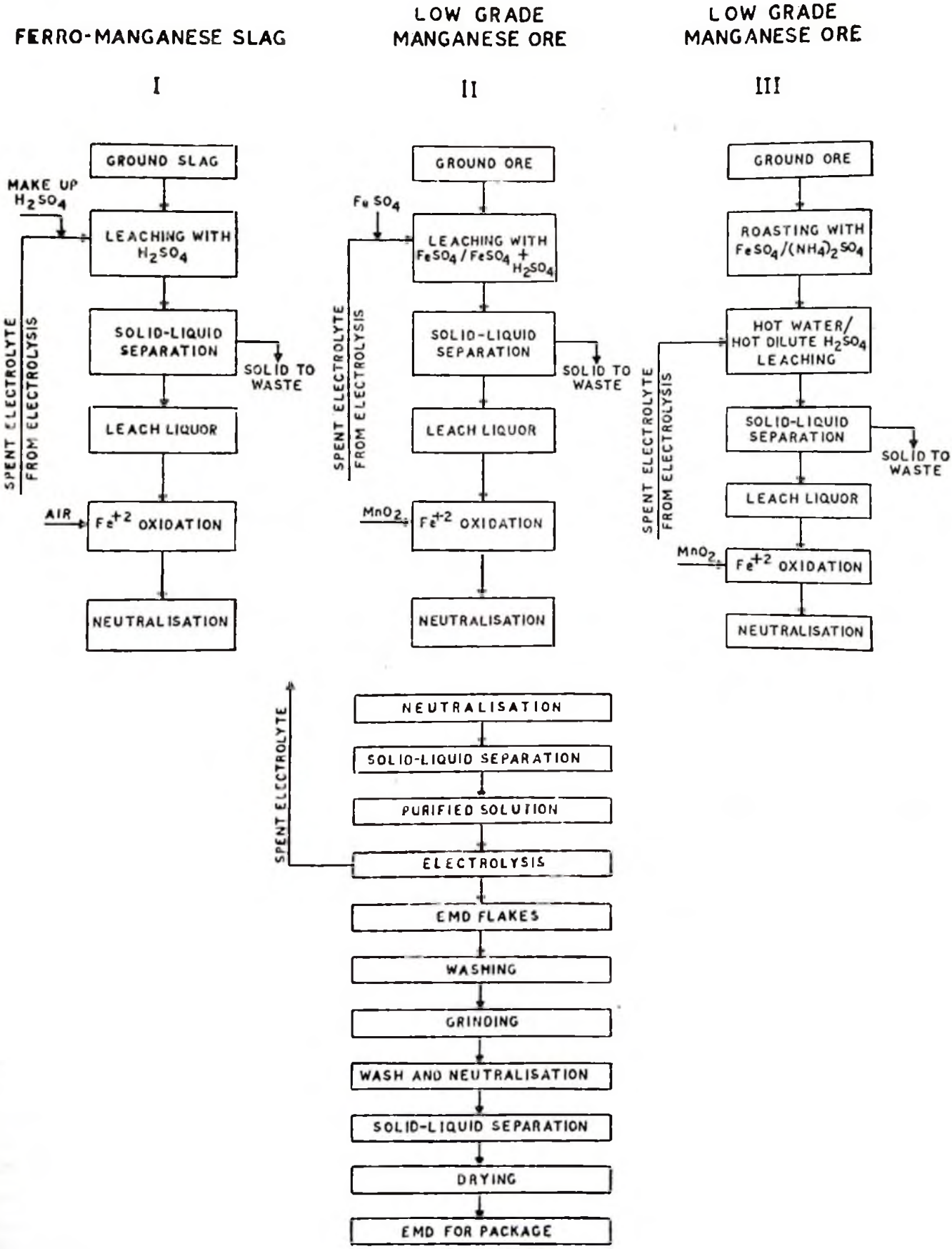


FIG.1 ROUTES FOR PRODUCTION OF EMD

An approximate cost estimation was made for the production of EMD from high manganese content ferro-manganese slag in 1 T/day and 3 T/day scale. In the first case the capital investment is around 36 lakhs rupees and the return will be 6 lakh rupees per annum, whereas in case of a 3 T/day plant the capital investment and return will be around 83 lakhs rupees and 27 lakhs rupees per annum. Thus it is observed that the profitability would be around 16% and 20% in case of 1 T/day and 3 T/day scale respectively.

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