Crushing and grinding of electrodeposited manganese dioxide

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INTRODUCTION :

Electrolytic manganese dioxide, for use as an efficient depolarizer in dry cells, is produced by the electrolysis of a solution of manganese sulphate and sulphuric acid at a temperature of 95°C. As the electrolysis proceeds, manganese dioxide is deposited in thick adherent form on the anodes. The anodes are taken out when the deposited manganese dioxide attains a thickness of 15—25 mm in about 10—15 days on continuous operation. The thickness of the EMD deposited on the anode depends on the current density and the duration of electrolysis. The anodes after taking out of the electrolytic cells are washed thoroughly with water to remove the carried over electrolyte and hot air dried. The sudden fluctuation in temperature, on lifting the anodes from the hot electrolytic cell and washing, cracks the EMD deposit. After drying, the deposits are easily stripped from the anodes by mild striking.

The stripped manganese dioxide deposits are in flake form. This has to be crushed and ground to —200 mesh/—325 mesh according to the requirements of the customers without contamination of iron, alumina, silica or any other impurities since these will bring down the MnO_2 content of the product to lower levels and the activity of the EMD for dry cell applications will fall down. Thus the crushing and grinding of electrodeposited manganese dioxide is one of the most important process steps in the production of EMD. The maximum permissible impurity levels in electrolytic manganese dioxide are given in Table 1. Besides, the stripped deposit may contain upto 5% moisture and 2% entrapped acid. Hence the material of construction of the equipment used for crushing and grinding of of EMD should be such as not to contaminate the product and also should be able to withstand the corrosive nature of the acid content of the product (1).

Experimental :

Fig. 1 gives the processing steps of the deposited EMD which goes for dry cell applications. The anodes with deposited manganese dioxide are washed in cold water and hot air dried. After stripping, the EMD is either dry or wet ground. The ground product is then washed thoroughly with water to remove the contained acid and the pH of the product is adjusted with sodium carbonate solution. This is then filtered and dried below 110°C.

Since sulphuric acid is entrapped in the deposited manganese dioxide, the parts coming in contact with the product during crushing and grinding cannot be fabricated out of ordinary materials. The material of construction of the machine parts coming in contact with the product are generally made of acid resistant special stainless steel or porcelain.

The contamination of a particular sample of EMD by iron and silica on grinding in steel rod mill and porcelain mill to 80% —325 mesh are given in Table 2. It can be seen that grinding in steel rod mill increases the iron content to about 0.5%, considerably higher than the prescribed limit. The impurity content levels

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with agate mortar is given for reference purpose only. It is interesting to note that while the silica content with agate mortar is found to be trace only, with porcelain ball mill it rises to 0.14%.

The published information on the processing of electrodeposited manganese dioxide are few. The available information on the practices followed in various plants in India and abroad are discussed below.

Fig. 2 gives the practice followed at the EMD plant of Union Carbide (India) Ltd., Thane, Bombay (2). At Union Carbide, roll crusher is used for crushing the flakes and dry grinding is carried in a ball mill.

Japanese Practices :

In one of the Japanese plants, it is reported that after the removal of the raw EMD from the electrode, the material is air dried and then ground in a stone mill. The ground EMD is then subjected to ten washing operations. At each wash, about 14 cu. meter of water are used per ton of EMD.

A typical process followed in another Japanese plant (3) mentions that when the thickness of the deposit reaches 10—30mm, the anodes are usually pulled out of the cell and the deposit is removed by means of mechanical shock. The flake is washed with hot water to remove the oil and electrolyte solution. Then it is dried in a rotary drier, crushed and finally washed thoroughly with water. After washing, the powder is neutralised with ammonia, soda ash or sodium hydroxide as a dilute solution in order to neutralise free acid and adjust the pH of the final product. After pH adjustment, the EMD powder is filtered and dried. The final powder is dried with hot air (85°C) and adjusted for particle size distribution and finally packed.

Ireland :

The processing at the EMD plant of Mitsui Denman (Ireland) Ltd. (4) is shown in Fig. 3. The EMD block is transferred to a 'finishing' plant for physical and chemical treatment. The block is first washed to remove any residual paraffin wax and electrolyte solution, dried, crushed and washed again. The EMD is then conditioned with an alkaline solution to neutralise free acid and adjust the pH of the final product. After further washing, the conditioned MnO_2 is dried in a rotary dryer, after which it is pulverized using a ring-roller mill (5).

As can be seen from the above, not much details of the equipment used are available from the published information of the various EMD plants abroad. The practices followed and the equipment used/proposed for crushing and grinding of electrolytic manganese dioxide from 10—25 mm size to —250/—325 mesh in a pilot plant and a commercial plant based on the technology developed at NML are given in Fig. 4 and 5 and Tables 3 and 4 respectively.

Fig. 4 shows the equipment and lay out of the processing section of an EMD plant set up in Rangoon (Burma) by NML/NRDC under the Technical & Economic Exchange programme. The pilot plant has a capacity of 50 kg EMD per day. The washed dried flakes of EMD are crushed in a roll crusher and then ground in a wet ball mill 45 cm x 45 cm. Details of the equipment used are given in Table 3.

The processing flow diagram in a proposed 2500 tonne per annum EMD commercial plant is presented in Fig. 5. A 1.5 tonne per hour capacity hammer mill is proposed with all the contact parts made out of stainless steel. The hammer mill is to crush the product from 10—25 mm size to 3—4 mm. The crushed material is ground in a wet ball mill (stainless steel 316) with a capacity of 0,75 tonne per hour with high density alumina ball charge. The ground material after washing, neutralising, centrifuging and drying has to be fed to a soft pulveriser after passing through a vibro classifier, material of construction of which is stainless steel 304. All the contact parts of the pulveriser, having capacity 750 kg per hour, are also

made of stainless steel 316. Details of the equipment proposed for a commercial plant are given in Table 4.

Conclusion

The crushing, grinding and washing of deposited electrolytic manganese dioxide is one of the most important process steps in the production of EMD suitable for dry cells. If the crushing and grinding equipment are not properly designed, it would result in the total rejection of the product by the dry cell industry either due to the particle size of the final product or the impurity levels, though the deposited EMD may be extremely pure.

Acknowledgement :

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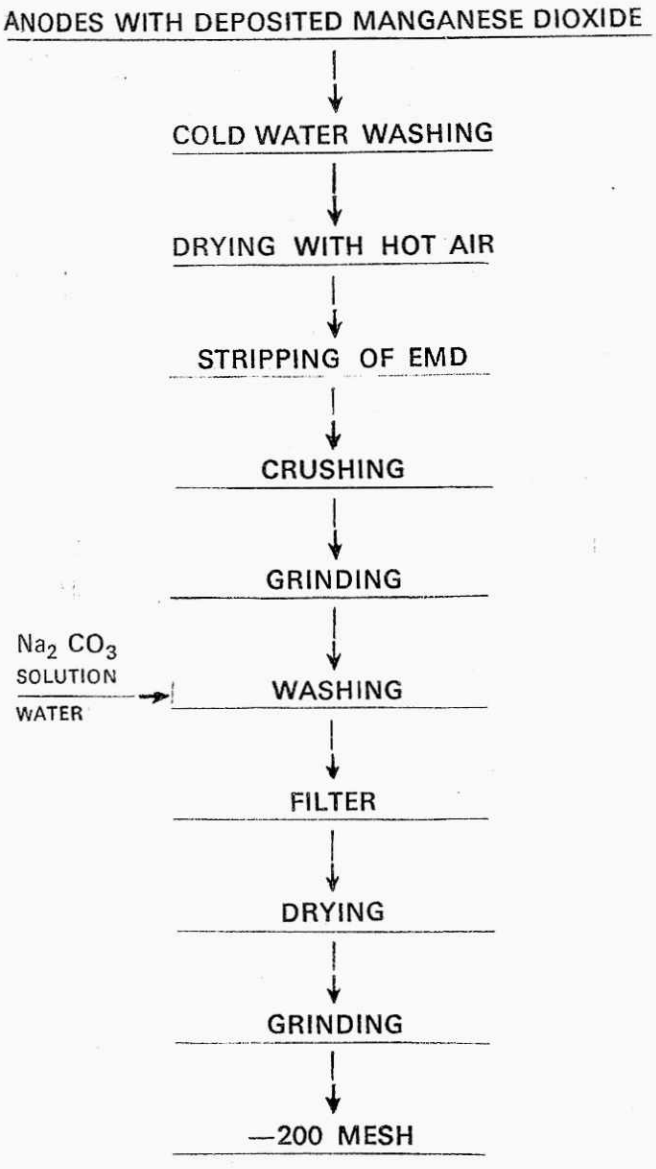

FIG. 1 : PROCESSING OF DEPOSITED EMD

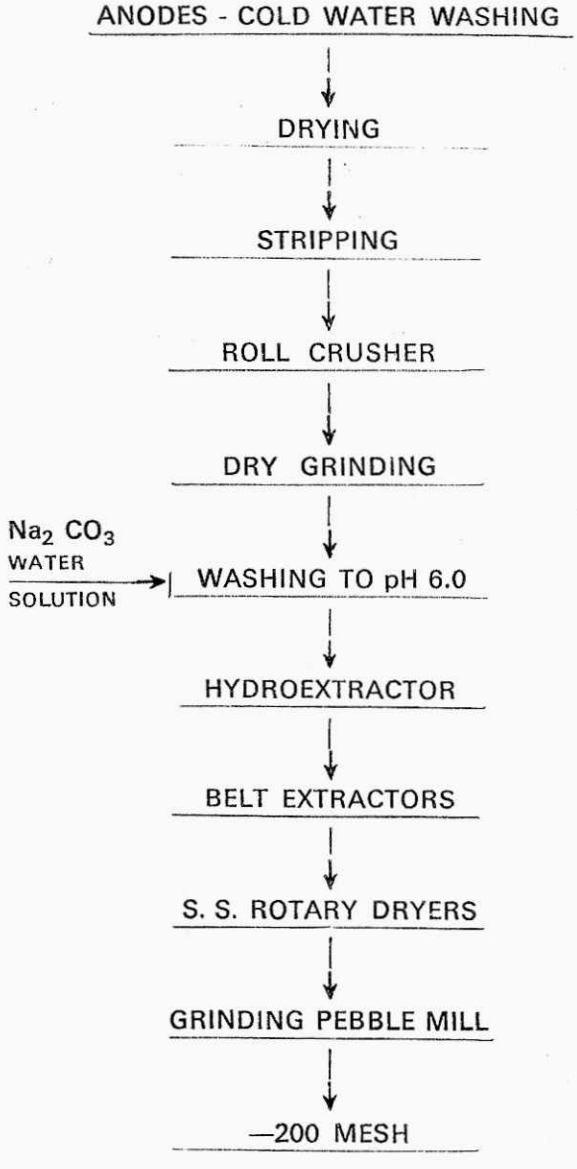

FIG. 2 : PROCESSING AT UNION CARBIDE (I) LTD. THANE, BOMBAY.

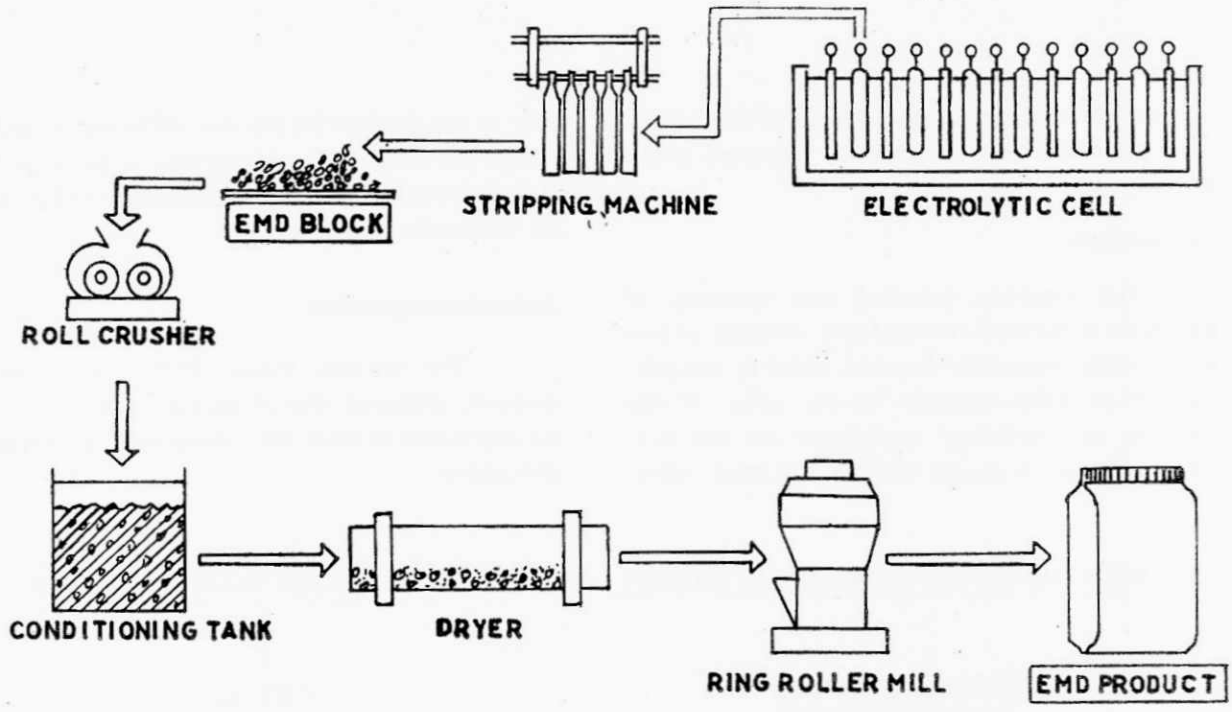

FIG. 3 PROCESSING OF EMD AT MITSUI DENMAN PLANT. IRELAND.

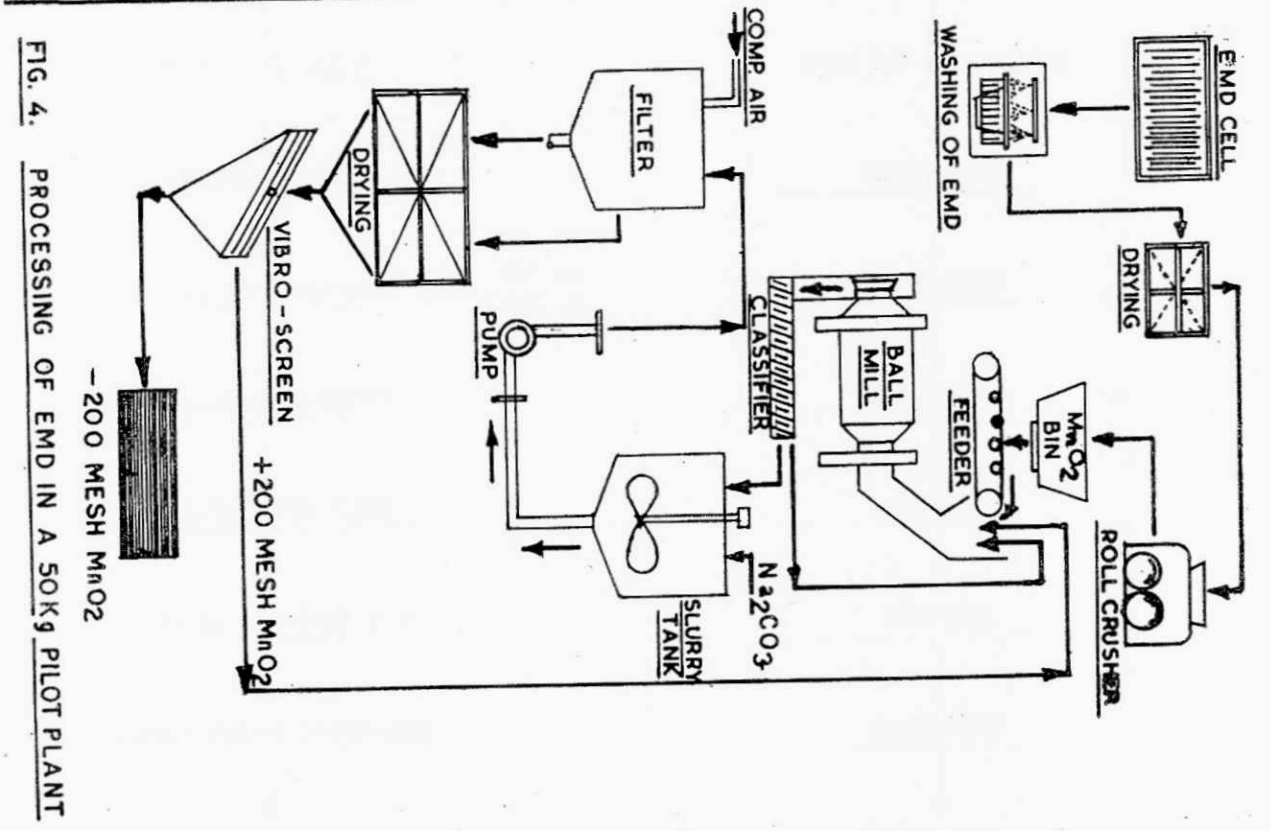

FIG. 4. PROCESSING OF EMD IN A 50Kg PILOT PLANT

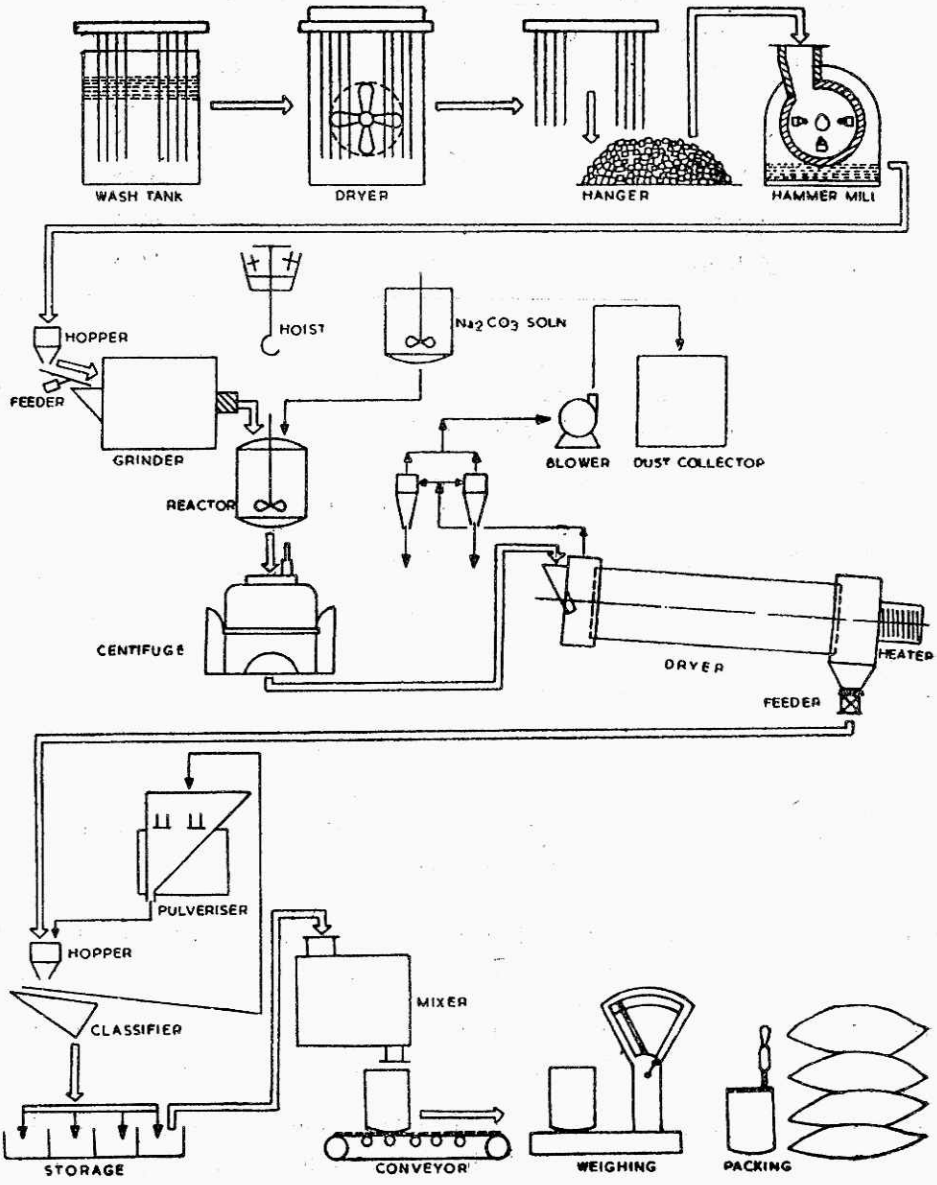

FIG. 5. PROCESSING OF EMD IN A 2500 TONNE PLANT

TABLE—1 : Specification of Electrolytic Manganese Dioxide

Constituents	Percentage
Manganese dioxide	90.00 Min
Moisture	3.00 Max
Matter insoluble in HCl	1.00 Max
Iron	0.05 Max
Lead	0.10 Max
Copper	0.002 Max
Sulphate	1.5 Max

TABLE—2 : Iron and silica contents on gringing EMD in steel rod mill & porcelain ball mill

Constituent	Grinding in		
	Agate Mortar	Steel rod mill	Porcelain ball mill
Iron	0.035	0.49	0.05
Silica	Trace	0.10	0.14

TABLE—3 : Equipment used in a pilot plant (50 kg/day) for processing of depositsd EMD

Roll Crusher	—	Capacity 100 kg/hr manually fed, Feed size 10—15 mm; crushed size 3mm, 5 HP Motor.
Wet Grinding Mill with Classifier	—	Ball Mill 450 mm x 450 mm, Capacity 10 kg/hr of the final product, 3 HP Motor. Spiral Classifier ½ HP Motor.
EMD Slurry Tank	—	800 mm dia x 750 mm ht., 6 mm M. S. sheet lined with 3 mm FRP Stainless Steel stirrer with reduction gear and drive motor.
EMD Slurry Pump	—	Capacity 1.5 m^3 /hr at 15 meter height.
Neutral Slurry Filter	—	NUTSCHE Filter. stainless steel sparkler type filter, worked under air pressure.
Tray Dryers	—	Oven for drying final EMD
Vibratory Screen	—	300 mm x 900 mm single deck feeder screen in aluminium. Screen construction with 200 mesh stainless steel screen, 0.75 HP Motor.

TABLE—4 : Equipment proposed for a commercial 2500 TPA plant for processing of deposited manganese dioxide

Hammer Mill	—	Capacity : 1.5 TPH; Feed size : 6mm—25mm; Crushed size : —10 mesh; Material of construction : Stainless Steel Complete with cyclone blower, dust collector, drive motor, etc.
Product Grinding Mill	—	Wet Grinding Tube Mill, Material handled : Crushed EMD; Capacity : 0.75 TPH., Feed Size : 3—4 mm; Product size : 325 mesh; Material of construction : Stainless Steel 316 Ceramic Ball Charge.
Reactor Vessels	—	Capacity : 5 Cu.m.; Material of construction : Steel plate 6 mm thick lined with soft rubber 3 mm thick.
Sodium Carbonate solution tank	—	Capacity : 1.5 Cu.m. FRP lined.
Centrifuge	—	Bottom Discharge; Basket dia 1200 mm, height 500 mm; Material of construction : Rubber lined steel.
Vibro Classifier	—	Capacity : 200 kg/hr. Material of construction : Stainless Steel 304.
Soft Pulverizer	—	Type : Vibratory Grinding Mill; Capacity : 750 kg/hr. Feed size : 10—15 mm (agglomerated lumps) Product size : —325 mesh; Material of construction : Stainless Steel 316; High density alumina balls.

References :

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