Quality Criteria in the Selection of Manganese Dioxide for use in Leclanche Dry Batteries

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MANGANESE DIOXIDE is one of the most essential ingredient in the formulation of Leclanche Dry Cells. Most of the Indian Dry Cell manufacturers prefer to use either imported natural African Ore or Synthetic electrolytic manganese dioxide, or a mixture of both, but they neglect and avoid using Indian ores In their formulations. It is presumed that Indian ores cannot be used to get the desired service characteristics. There have not been any quality criteria based on raw ores from which they can be assessed for their final service characteristics. Any individual quality characteristic, like, manganese dioxide content, total surface area, pore volume constitutional water, crystal phase, hydrazine activity, pH-EMF relationship, kinetics of the recuperation reaction, particle size, presence of impurities, has not given any useful information for the selection of Indian ores.

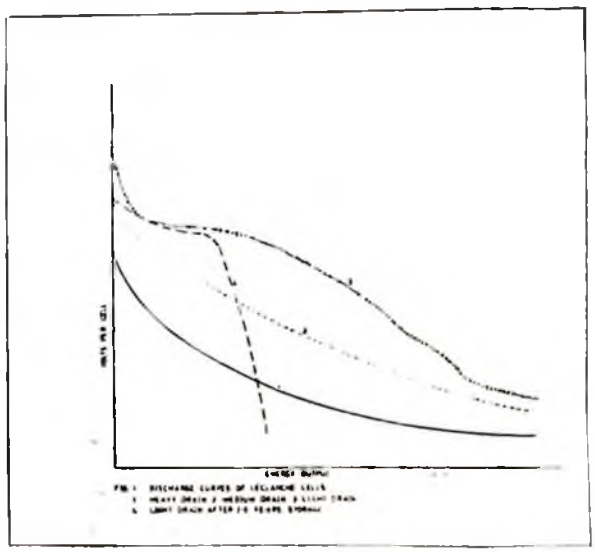
An attempt has been made to derive certain ratios from the above individual quality characteristics and to correlate these ratios with the service characteristics of of the dry cells made from them. From these ratios it has been derived that a 50 : 50 mixture of Electrolytic Manganese Dioxide with an Indian ore is in all respects comparable to natural African ore, and can easily conform to IEC specifications in 4 ohms and 40 ohms tests. There is also a suggestion that this ratio could also be raised to 60 : 40, or even upto 70 : 30, with increasing proportion of Indian Ore It is suggested that there seems to be some synergistic effect of gamma phase of EMD when mixed with alpha and beta phases of natural ores. On economic grounds also these mixtures of Indian Ores with EMD can be considered With this being successful, we can save upto Rs. 6 crores annually in our import bill. All Indian Battery Cell manufacturers have to take initiative and explore the vast resources available in India.

INDIA is one of the largest producers of manganese ore in the world[1]. These ores are of the manganese dioxide type, popularly known as pyrolusite ores. Manganese dioxide is one of the most essential ingredients in the formulation of Leclanche Dry Dells or Batteries. Traditionally Dry Cell Manufacturers have relied upon either imported natural African ore or synthetic electrolytic manganese dioxide, known as EMD in short, or a mixture of both[2]. But they have neglected and avoided using Indian ores in their formulations, primarily because they have to restructure their formulations and study the most convenient mix giving best or equlvalent results. The manganese ores are mostly classified as low or high grade depending on the manganese dioxide contents[3] while the selection of manganese dioxide for use in the Dry Cell formulation depends upon its Ampere-Hour-Capacity and ability to satisfy the requirements in relation to the intended applications[4]. All the natural and synthetic forms of MnO_2 do not perform equivalently[5]. Several attempts have been made to assess the suitability of the manganese dioxide for commercial dry cell manufacture, and the results have failed to give any comprehensive solution, even though useful guidelines have been evolved based on these results[2]. MnO_2 content, total surface area, pore volume, constitutional water, crystal phase, hydrazine activity, pH-EMF relationship, Kinetics of the reccuperation reaction particle size, presence of impurities, etc, have been said to be contributing to the depolarizing ability of manganese dioxide[2] for which sole purpose it is used in the dry cell formulations. It has been fairly well established that it is the gamma (γ) varity of manganese dioxide, with suitable physical, chemical, eletrochemical and catalytic properties, that serves as an efficient cathode depolariser[3] Recently, Nallaperumal *et al.* ([2]) have presented a study of the correlations of properties of natural Indian Manganese Dioxide with service characteristics in Leclanche Dry Batteries and compared their results with natural African ore and EMD to derive relevant conclusions with the hope that battery technologists could find ways and means of realising the full potential of ores in commercial dry cells. Aravamuthan *et al.* have also presented a study of the influence of electrolytic parameters on the properties of EMD prepared from chloride electrolyte([4]) and the developmental studies employing titanium anodes([6]). The estimated demand for EMD for the production of dry cells of various types is around 10,000 tons per annum([6]). It is estimated that the quantity of EMD in the total Manganese dioxide needed for dry cells is only about 30%([7]). From this it would be evident that the requirement of natural manganese ore would be about 25,000 tonnes per annum.

DISCUSSION

Nallaperumal et al.[2] observed that no single property of the manganese dioxide was capable of explaining the service performance of the dry batteries, but they contributed to the understanding of the MnO_2 behaviour in combination. Batteries with EMD alone and African Gabon ore alone met IEC specifications in both 4 ohm and 40 ohm tests (600 minutes to 0.9 V and 150 hours to 0.9 V resp.) while none of the Indian ores was good enough to meet the IEC standards. In the ampere hour output, for which there is no international standard. Indian ores were far below EMD and African Gabon ores, particularly in the high drain application and at higher Cut-off ie the low-drain application. Crystal phase of MnO_2 is an important factor in the service ou put. Presence of γ phase, both in natural and synthetic MnO_2 characterized by poor crystallinity, partial hydration and X-ray diffraction patterns help to increase the activity[3]. From amongst the Indian ores there was no indication of any superiority over one another. They[2] suggested that since Indian ores by themselves with commeraial formulations, did not meet international srandards, a blend of EMD or African Gabon ore could be resorted to.

Comparison of Table I and Table II indicates that % MnO_2 in manganeae ores was not indicacative of the battery perfoimance[2]. Same was true for constitutional water. Surface area shows some relationship with the service performance, and the higher the surface area, the better the service perfo.mance. But this relationship has some influence of other factors, as can be seen from the values of Indian ores A & B. Even though the difference in the surface area is very marginal, 3.3 and 3.1 m^2/g. resp., the service performance at 4 ohm test is 139 and 85 min. to 1.2 V, 336 and 283 min. to 1.1 V, and 515 and 443 min. to 1.0 V, and then again the figures drop to 606 and 602 min. to 0.75 V. Similar observations can be made for Indian ores C and D also. The service performance of a dry cell cannot be stated as a single definite value[1]. The performance characteristics will vary as a function of load, temperature, and length of time the cell is stored before use. If the load is too severe, i e., if the energy is drawn too rapidly from the cell, diffusion effects, both in the electrolyte and in the solid state, do not allow the current to continue to flow at its original rate and the cell does not function efficiently. When the energy is drawn more slowly, the diffusion effects are minimized and the working voltage holds up well. Too slow withdrawal of energy introduces another source of depletion. In this case, the time required to exhaust the cell is so extended that shelf deterioration, inherent in all dry cells, is sufficient to detract from the cell's available energy and so reduces its electrical output. The optimum lies between the heavy and the light drain service conditions. These effects are shown in Fig. 1[3]. Efficient use of the battery's energy may still be obtained with a relativeiy heavy drain if the discharge periods are very short or the rest period constitutes a large portion of the over all time.



Hydrazine activity shows a similar relationship with service performance and the higher the hydrazine activity, the better the performance. EMD with highest value of 71.4 gives the highest values of service performance, followed by African Gabon ore and the Indian ores. From amongst Indian ores it is difficult to judge the superiority of any one of them over others, simply from these values of surface area and Hydrazine activity.

Crystal structure indicates that the Gamma (γ) phase gives the best service performance as is the case with EMD, the mixture of Gamma (γ), Beta (β) and Alpha (α) phases take the next position as is the case with African Gabon ore, while all Indian Ores with Alpha (α) and Beta (β) phases show very poor performence. It can be seen that eventhough the Indian ores show poor performence in the begining at 1.2 V, they gain the capacity in

long-drain as evidenced at 0 75 V in 4 ohm test. They show values only 60% of EMD. In 40 ohm test, they outurn EMD at 0.6 V drain. This signifies that EMD is good for immediate performence but Indian Ores are better for long-drain use.

If these observations could be judiciously blended, they can give very useful results.

Service performance of batteries is a test to be carried out by battery manufacturers on their finished goods. As this performance is affected by the raw materials input, the input quality criteria should be such that the should help to select good quality manganese dioxide. Determination of individual chemical dan physical characteristics fail to give any indication of the quality on which selection could be based. But the ratios worked out from these chemical and physical characteristics values are very useful in deciding the quality of manganese dioxide. Ratios mentioned under experimental for 1 to 6 are all expected to give a value equal to 1.5. The next criteria gives a total of these 6 ratios to be 9.0 for a good quality manganese dioxide. The next criterion gives a value, 100 − % Mno_2, to be equals to the value obtained by addition of values of ratios 1 to 6. And the last criterion gives a value as the difference between the value in 7 and value in 8 and this should be between 0.0 and 1 0 If all these ratios show values near to the expected value, the quality of manganese ore is considered good, but if they lack coherance in all criteria then the quality is not good but gradation can be made on the basis of the values obtained in the 9th test showing a value between 0.0 and 1.0.

The values obtained for various ratios and presented in Table III for EMD, African Gabon ore and the four Indian ores and the values for the various mixtures of Indian ore C with EMD indicate that these quality criteria can held in deciding the quality of manganese dioxide for use in the raw mix formulation for dry cell to get the best desired service performance of the battery. With this view in mind it helps us to decide that Indian Ore C in proportions of 50 : 50 and 60 : 40 with EMD shows promises of competing with the African Gabon are and should results in the Import substitution. Large resources of Indian ores should find application in admixture with EMD in the battery mix formulation eliminating the African Gabon ore.

Data presented in Table IV are calculated from Table II. They present the service performence of the batteries made from a mixture of EMD with Ind an Ore C in proportions of 50 : 50, 40 : 60, 30 : 70, 20 : 80. From amongst the 4 Indian Ores selection of ore C was made for mixing with EMD because, the ratio calculations for quality criteria presented in Table III showed its superiority over the other ores.

These values indicate that a 50 : 50 mixture of EMD with Indian ore C is in all respects comparable to African Gabon Ore, and can easily conform to IEC specifications in 4 ohms and 40 ohms tests. A further reduction of EMD to 40 : 60 and 30 : 70 or any other intermediate ratios also be considered as there is an indication that they can also show equal performence. There also seems to be some synergistic effect of gamma phase when mixed with alpha and beta phases and some actul mixtures of EMD with Indian Ore C when tested for service performence it may surpass African Gabon Ore even at a 30 : 70 level.

There is a strong suggestion to use these mixtures on economic grounds. We are importing more than 10,000 tons of African Gabon Ore every year and at landed cost of Rs. 6,000/- per ton, this can easily save Rs. 6 crores annually in our import bill. It is for the Indian Battery Cell Manufacturers to take the initiative and explore the vast resources available in India.

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