

## BATTERY MANGANESE DIOXIDE — A SURVEY OF ITS HISTORY AND ETYMOLOGY\*

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### Summary

Manganese dioxide was known two thousand years ago. It was described by Plinius. Later, Basilius Valentinus named it "Braunstein", the brown-stone. Its chemical nature was recognized by Scheele and his student Gahn. Its first application in the field of batteries seems to have been by Ritter. Following Leclanché's invention it has been used on a large scale in dry batteries. In 1977 about 300 000 metric tons of battery grade manganese dioxide were consumed. More than 50% of the oxide is derived from natural ores, and about one third is obtained as electrochemically deposited dioxide.

### Zusammenfassung

Braunstein war schon vor zweitausend Jahren bekannt. Er ist von Plinius beschrieben worden. Später nannte ihn Basilius Valentinus "Braunstein", den braun machenden Stein. Seine chemische Natur ist von Scheele und seinem Schüler Gahn aufgeklärt worden. Seine erste Anwendung in der Batterietechnik hat er durch Ritter gefunden. Seit der Erfindung von Leclanché wird er in grossem Umfang in Trockenbatterien benutzt. 1977 sind rund 300 000 t Batteriebraunstein verbraucht worden. Mehr als 50% davon waren natürliche Braunsteinsorten, ungefähr ein Drittel war elektrochemisch abgeschieden.

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### 1. History and etymology

Manganese dioxide was well-known in antiquity. Caius Plinius Secundus Maior (23 - 79 A.D.) described in his *naturalis historia* natural manganese dioxide as the "female" magnes, in contrast to the "male", magnetite, which we now know as  $\text{Fe}_3\text{O}_4$ . The term "magnes" remained in use up to the Middle Ages. Manganese dioxide ( $\text{MnO}_2$ ) was referred to as "magnesia", while tri-ferrictetroxide ( $\text{Fe}_3\text{O}_4$ ) was called "magnesium".

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\*To commemorate the retirement as Editor of Mr Derek Collins.

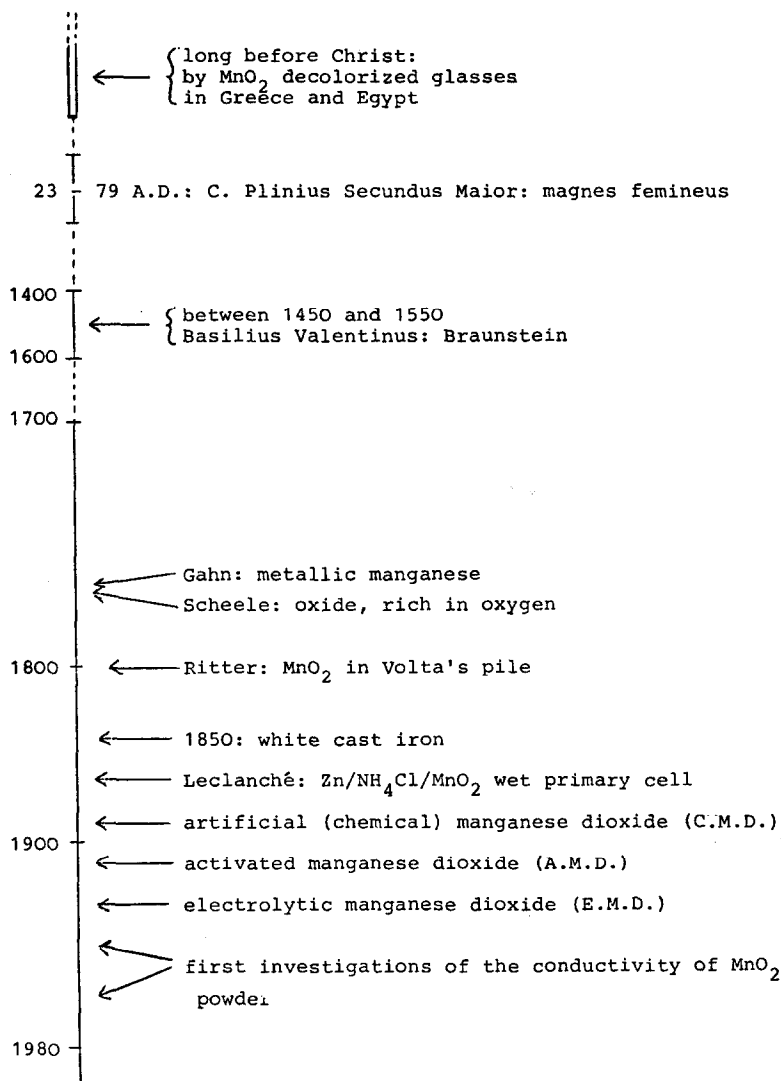


Fig. 1. History of the naming and uses of manganese dioxide.

The translation of the different names for manganese compounds from one language into another is not always easy. In German, for example, a general term exists, comprising the multifarious manganese oxides above trivalent manganese: the German word "Braunstein", verbally translated "brown stone"; but this translation does not meet the requirement. The term "Braunstein" came into use no earlier than the 15th or 16th century, see Fig. 1. It was coined by the mysterious Basilius Valentinus or whoever adopted this name.

The origin of the term "Braunstein" could have three roots. Today it is the collective term for all manganese oxides higher than trivalent. Most of these are black or, at least, dark grey. Only one species is really brown: the

wad, found in the Siegerland mountains of the Federal Republic of Germany. In earlier days, however, Basilius found it difficult to distinguish between manganese minerals, for, indeed, many of them are brown. Natural manganite\*  $\gamma\text{-MnOOH}$ , for example, is familiar to the painter as "manganese brown" or "bister". The mineral braunite, a silicate of trivalent manganese, is used as the dark brown pigment "umbra", which in Latin means "shadow". Natural hausmannite ( $\text{Mn}_3\text{O}_4$ ) exhibits a red-brown colour. Some brown iron ores contain up to 10% manganese, some manganese ores contain iron and have a rusty appearance. Thus, it is not beyond the bounds of possibility that Basilius had a brown stone on his desk, which he had doubts of as female magnes or magnesia, and called it "Braunstein"\*\*\*.

In German textbooks of chemistry, another version of the origin is obstinately maintained. Basilius is said to have discovered that a pleasing brown colour can be imparted to grey earthenware by the addition of "Braunstein". This, however, was already well known in ancient Greece. Therefore, this origin of the word does not seem to be very likely. It has been asserted that the third root arises from the fact that Basilius had discovered, by chance, that the addition of *large quantities* of these ores resulted in the dark brown glass used to make the well-known Hock wine bottles.

Glass is a homogeneous, amorphous mixture of silicates, borates, etc. It is coloured green-yellow in the presence of iron; much less with  $\text{Fe}_2\text{O}_3$  than with  $\text{FeO}$ . The addition of *small* amounts of manganese dioxide changes the iron to the less coloured oxidized state and forms a faint violet manganese silicate. Its colour is complementary to the remaining  $\text{Fe}_2\text{O}_3$  colour, thus appearing white to the eye. Actually, it is a very light brown. Excess manganese (and excess iron) imparts a deep brown tint to the glass. The ancient Egyptians modified the colour of glass by the addition of manganese dioxide, and the same procedure was familiar to the experts in Greece. In German textbooks the translated term "glass makers soap" is found, but it is not widely used in Germany.

Even without knowing the roots, nevertheless we can state that the general denomination "Braunstein" is of German origin, and has penetrated into only a very few other languages. The author is aware of the word in four languages only!

- in German: Braunstein;
- in Dutch: bruin steen;
- in Hungarian: barnako (which means brown dwarf);
- in Polish as the loanword: braunstyn.

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\*The term "manganit" was used as the registered trade name of a chemically precipitated manganese dioxide by Messrs. Nikolaus Branz, Berlin, F.R.G. It was a manganese dioxide of high activity and high in water content.

\*\*Even in 1929 a well-known mineralogist called a natural  $\text{Mn}_2\text{O}_3$  "Hartbraunstein". A black species of  $\text{Mn}_3\text{O}_4$  was designated "Glanzbraunstein" or "schwarzer Braunstein".

These words denote manganese oxides and hydroxides above the trivalent oxidation state, between  $Mn_2O_3$  and  $MnO_2$  with various water contents. The words belong to the colloquial language. In these four languages, the more technical term "Mangan-Dioxid", etc. is mostly restricted to varieties of nearly exact  $MnO_2$  composition, with only small deviations from the stoichiometric formula. This must be kept in mind when translating scientific papers, technical notes, or patents.

In the Russian language special types of low-grade manganese dioxide are called "buri marganetz", translated "dark brown manganese". In spite of this, the most important Russian manganese ore, the pyrolusite ( $\beta$ - $MnO_2$ ), is called "marganzivaja ruda": simply "manganese ore". The literal translation of the German term "Braunstein", namely, "buri kamenii", will be as little understood in Russia as will "brown stone" in the English speaking countries, "pierre brune" in France, "pietra bruna" in Italy, or "piedra morena" in Spain. "Brown stone" leads to confusion with brown coal. In the battery industry different terms are very often used, e.g., "calanas" in Spain, or "tchiaturi" in Russia, which simply denote the location of the mine. Despite even large deviations from the true quadrivalent stoichiometry, in English "manganese dioxide" is used instead of "Braunstein", in French it is "bioxide de manganèse" or simply "manganèse", in Italian "perossido di manganese", in Spanish "manganeso", and in Russian "marganzivaja dwuo-kis"\*.

Karl Wilhelm Scheele (1742 - 1786) discovered in about 1780 that heating manganese dioxide with sulfuric acid resulted in the liberation of oxygen. A few years later, J. G. Gahn (1745 - 1818), one of Scheele's students, reduced manganese dioxide to metallic manganese. Before his discovery, "magnesia" was considered as an iron ore. Gahn called the new metal "manganese". This designation again, is astonishing, and its origin is not quite clear. Hearsay has it that Gahn changed the "female magnesia" into "manganesia" to prevent confusion, or to adopt the spelling of the word to the Italian pronunciation of the nasal sound "magn". The other possibility is that in the Greek language "manganitzein" means "to clean", self-evidently well-known to the learned man Gahn, as he well knew that glass and iron can be refined by his "manganesia". Everyone teaching chemistry knows to his constant regret that even today manganese (Mn) is easily confused with magnesium (Mg). Furthermore, brown spar, a dirty brown species of dolomite ( $[Ca, Mg]CO_3$ ) is confused with the reddish manganese spar or rhodochrosite ( $MnCO_3$ ), with rhodonite ( $MnSiO_3$ ), or with braunite, even by chemists.

## 2. A few remarks about the economy

During the year 1978, about 10 million metric tons of manganese dioxide ore have been mined throughout the world. About 90% of this was low-grade ore, with 30 - 50%  $MnO_2$  involved with large amounts of trivalent man-

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\*The Russians really call it marganetz with "r" and not with "n".

TABLE 1

Consumption of battery grade manganese dioxide in 1977 according to Matsumara [1]

Country or Region	Consumption (tonnes)
North, Central and South America	69 000
Western Europe (including F.R.G.)	101 000 (12 000)
Eastern Bloc countries	42 000
Japan	24 000
Asia without Japan	49 000
Africa and Middle East	17 000
World	302 000
Estimated sale	1300 million DM 750 million US \$ 300 million £

gane and gangue, the latter very often containing a great deal of iron. Most of the recovered manganese ore is reduced to ferromanganese and related alloys, used for deoxidation of steel. The manufacture of white cast iron also needs a great deal of manganese, as does the manufacture of Mn-alloyed steels, Mn-containing Al and Mg alloys, and electric resistor wires. Industrial chemical processes need manganese ores as bases for permanganates, paint dryers and manganese fertilizers. Other areas of application are in colouring bricks, in the manufacture of safety matches, the removal of iron from water, and anticorrosion treatment of steel.

About 3% of the mined manganese dioxide is used in batteries: high grade, very pure natural ores, or synthetic species. Johann Wilhelm Ritter (1776 - 1810) as early as 1799 applied manganese dioxide to the positive electrodes of Volta's pile. The Belgian railroad engineer Georges Leclanché (1839 - 1882) in about 1864 invented the wet zinc/manganese dioxide primary cell, the ancestor of our contemporary dry cells.

From a paper by Matsumara [1] it can be seen that in 1977 about 300 000 metric tons of battery grade manganese dioxide were consumed. A geographic breakdown is given in Table 1. More than 50% were natural ores, the remainder being either activated natural ores or synthetic manganese dioxide. The latter were produced from somewhat larger quantities of natural ores. The processing yield for the activation of natural ores or for the production of synthetic manganese dioxides is of the order of 75%, relating to the Mn content in the final dioxide and the raw material. Thus, the mined quantity consumed for battery manufacture is of the order of 350 000 metric tons, as given above. The total quantity increases gradually, at a rate of about 3% per year, with an increasing proportion of synthetic manganese dioxides. The price is between 3 and 8 deutschmarks per kilogram\*, depending

\*Equivalent to approximately 0.75 - 2 US \$, or to 0.3 - 0.9 £s per lb.

TABLE 2

Crystal system of the five main families of the allotropic modifications of manganese dioxide according to Bode [3]

<i>Psilomelane</i> $C_{2h}^3(A2/m)$	approx (Ba, H <sub>2</sub> O)Mn <sub>5</sub> O <sub>10</sub> monoclinic	$a = 9.56 \text{ \AA}$ $b = 2.88$ $c = 13.85$ $\beta = 92.5^\circ$
$\alpha$ -MnO <sub>2</sub> $C_{4h}^5(I4/m)$	approx. MeMn <sub>8</sub> O <sub>16</sub> paratetragonal	$a = b = 9.82 \text{ \AA}$ $c = 2.86$
$\beta$ -MnO <sub>2</sub> $D_{4h}^{14}(C4)$	MnO <sub>2-<math>\Delta</math></sub> ( $0.01 < \Delta < 0.03$ ) holotetragonal rutile type	$a = b = 4.39 \text{ \AA}$ $c = 2.87$
$\gamma$ -MnO <sub>2</sub> $D_{2h}^{16}(EO2)$	MnO <sub>2-<math>\Delta</math></sub> ( $0.05 < \Delta < 0.5$ ) rhombic diaspore type	$a/2 = 4.64 \text{ \AA}$ $b = 2.86$ $c = 4.5$
similar are $\epsilon$ -, $\eta$ - and $\rho$ -MnO <sub>2</sub>		
$\delta$ -MnO <sub>2</sub>	MnO <sub>2+<math>\Delta</math></sub> ( $0 < \Delta < 0.01$ ) nearly rhombic diaspore type with enlarged elementary cell	$a/3 = 4.85 \text{ \AA}$ $b = 4.0$ $c/2 = 4.2$

on grade, quality, and brand. The total sale of battery grade manganese dioxide is about 1300 Mio DM (750 Mio US \$, or 300 Mio £), the total sale of the batteries made from it is about 4000 Mio DM (2300 Mio US \$, or 950 Mio £). Ninety per cent of the batteries are dry cells, having aqueous solutions of *sal ammoniac* and zinc chloride as the electrolyte. The remaining 10% of the batteries make use of other electrolytes, mostly caustic potash lye. At present, cells with electrolytes dissolved in organic liquids, and cells with lithium as the negative electrode, do not play any significant role in the total number of manufactured cells.

### 3. Contemporary battery grade manganese dioxide

Manganese dioxide ores are found in a large number of different mineral species, having different manganese dioxide content, different electrochemical activity, different impurities, etc. These, however, may be placed unconstrainedly in a system of four allotropic modifications. A fifth modification can be prepared exclusively by chemical synthesis. Table 2 lists the crystal properties of these five modifications of manganese dioxide. Each modification comprises many individual species, which may differ considerably in appearance, composition, and electrochemical behaviour. In short, it is necessary to distinguish between the following modifications:

(a) *Psilomelane, hard manganese ore, Glaskopf*

Composition complicated, approximately  $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ ; mean degree of oxidation as low as  $\text{MnO}_{1.6}$ ; many impurities present: gangue, clay, iron, alkaline silicates, etc.

Psilomelane cannot be applied to batteries, because its degree of oxidation is very low, and because the ever present iron causes severe corrosion of the negative electrode.

(b)  $\alpha\text{-MnO}_2$ , the cryptomelane family with coronadite, hollandite, lithioporite

Composition about  $\text{MeMn}_8\text{O}_{16}$  with Me equal to Ba, 2K, 2Li, Pb with essential water. A fraction of the Mn can be replaced by Fe(III), Co(III), or Zn(II).

Mean degree of oxidation  $\text{MnO}_{1.85}$  or above. Lead free, pure ores are assigned for application to batteries, especially in the U.S.A. Synthetic cryptomelanes are known to the battery manufacturer, but seem not to have found broad interest, so far.

(c)  $\beta\text{-MnO}_2$ , polianite, pyrolusite, wad, soft manganese ore

Composition  $\text{MnO}_{2-x}$  with small oxygen deficiency  $x \leq 0.05$ . The typical natural manganese dioxide used in dry batteries for intermittent discharge at low rate.

Can be synthesized, e.g., by thermal decomposition of  $\text{MnNO}_3$  [2].

(d)  $\gamma\text{-MnO}_2$ , ramsdellite, nsutite

Composition  $\text{MnO}_{2-x}$  with oxygen deficiency  $x > 0.05$ . Found as natural battery grade ore, but to a large extent synthesized by numerous procedures. The  $\gamma$ -family exhibits numerous species with very different degrees of crystallization. Thus, several sub-modifications have been proposed:  $\epsilon$ -,  $\eta$ -, and  $\rho\text{-MnO}_2$ . However, it appears to be unnecessary to separate these from the  $\gamma$ -family.

(e)  $\delta\text{-MnO}_2$  without verbal name

Composition  $\text{MnO}_{2+x}$  with oxygen surplus or deficiency  $x \gtrless 0$ .  $\delta\text{-MnO}_2$  is synthesized on a practical scale by chemical procedures. It is added to less active natural ores in order to ameliorate load capacity and recovery of the batteries.

The most crystalline species is  $\beta\text{-MnO}_2$ , and the least crystalline  $\delta\text{-MnO}_2$ . Ritter and Leclanché both favoured  $\beta\text{-MnO}_2$  for battery application. In earlier times in Germany two species of  $\beta\text{-MnO}_2$  were known: the pure polianite from the Harz Mountains, and the less pure wad from the Siegerland Mountains. Leclanché mentions *expressis verbis* pyrolusite, mined at that time — just as today — mostly in the Caucasian mines of Russia.  $\beta\text{-MnO}_2$  shows a good electronic conductivity as compared with the other modifications. The first measurements of the conductivity of battery grade manganese dioxide, however, were not carried out until after 1925.

Until 1914, mostly  $\beta$ - $\text{MnO}_2$  had been applied in batteries. Later, starting with the U.S.A., Brazilian — and later, during the twenties — and Gold Coast ores came into use. Both are mixtures of  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $\text{MnO}_2$ . Ramsdell discovered the most highly crystallized  $\gamma$ -species, the mineral ramsdellite, in the thirties. Synthetic  $\gamma$ - $\text{MnO}_2$  was prepared and the general lattice of the  $\alpha$ -modification was evaluated by Glemser, again in the thirties. The first cryptomelane mines were opened in Montana, U.S.A. in the twenties. The lattice of the  $\alpha$ -modification was confirmed in the thirties, and the  $\delta$ - $\text{MnO}_2$  modification even later.

In addition to natural ores, synthetic manganese dioxides are widely used in batteries. The battery expert evaluates his raw material less by its modifications, but rather by its readiness for current generation. This property is called the “activity” and is evaluated by simple but reproducible test methods. Apart from a few exceptions, the activity can be represented by the origin of the manganese dioxide, and by its method of manufacture. Thus, battery grade manganese dioxides are commonly classified as follows:

*(i) Natural manganese dioxide (N.M.D.)*

The selected ore is used after simple beneficiation processes: picking out of stones, washing in jiggers of rheo grooves, crushing, milling, screening, seldom flotation. Mostly it is milled to about 60  $\mu\text{m}$ , approximately the IMM sieve 200 mesh\*.

*(ii) Activated natural manganese dioxide (A.M.D.)*

N.M.D. is partly reduced by roasting at 400 °C, followed by acid leaching. It results in disproportionation, Mn(II) is dissolved, Mn(IV) remains as spongy  $\gamma$ - $\text{MnO}_2$ . It is neutralized, washed, dried, disintegrated, and screened.

The Mn(II) solution is transferred to the fabrication of E.M.D. (see below). A.M.D. was introduced into battery manufacture in 1904. Most of these A.M.D. grades belong to the  $\gamma$ -family.

*(iii) Chemically prepared manganese dioxide (C.M.D.)*

Between 1888 and 1910, Weldon mud has been used in batteries. Its formula is approximately  $\text{CaOMnO}_2$ , a residue of the historic Weldon process for the fabrication of chlorine. In 1900, a residue of saccharine fabrication was found to be a well-suited battery additive. It is a water-rich, nearly amorphous material, belonging probably to the  $\delta$ -modification. Other processes consist in the oxidation of Mn(II) salt solutions by chlorine, chlorinated lime, hydrogen peroxide, ozone, etc. C.M.D. is added to the positive electrode in quantities up to 15% to adapt less active battery grade manganese dioxides to high discharge rates or to cold climates.

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\*IMM = Institution of Mining and Metallurgy, 100% passing through a sieve of 200 meshes per inch.



(iv) *Electrochemically deposited manganese dioxide (E.M.D.)*

An aqueous solution having about 100 g of  $\text{MnSO}_4$  per litre undergoes an electrolysis between inert electrodes at  $\text{pH} = 1$  and  $90^\circ\text{C}$ . At the anode, a hard crust of fairly well-crystallized  $\gamma\text{-MnO}_2$  is formed. It is struck off, milled, neutralized, washed, dried, and screened. E.M.D. was introduced into battery manufacture in 1918.

At present, about 55% of N.M.D., about 10% of A.M.D., about 5% of C.M.D., and about 30% of E.M.D. make up world consumption. However, important regional differences exist. In general, the relative consumption of E.M.D. is increasing.

### References

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