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## 1. Introduction [1]

Manganese compounds occur in all oxidation states from  $-3$  to  $+7$ , with  $+2$ ,  $+4$ , and  $+7$  being the most important. Most of the species in which Mn displays a negative valence state are anionic; for example, the ion  $\text{Mn}(\text{CO})_5^{3-}$  [obtained by vigorous reduction of  $\text{Mn}_2(\text{CO})_{10}$ ] contains Mn in the  $-3$  state. The  $-2$  oxidation state can be found in a complex of manganese with phthalocyanine, whereas manganese in the  $-1$  state is represented by the manganese pentacarbonyl ion  $\text{Mn}(\text{CO})_5^-$ . Ions representing the various positive valences display characteristic colors, as indicated in Table 1. The color of a particular ion in solution is not always the same as that of the corresponding solid compound. Thus, solid MnO is light green,  $\text{Mn}(\text{OH})_2$  is white, and  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$  are black. Liquid  $\text{Mn}_2\text{O}_7$  is green under reflected light but deep red under transmitted light.

Given the multitude of valence states for manganese compounds, redox reactions are of great importance. Under suitable pH conditions, compounds containing manganese with a valence

of  $+3$  or more are effective oxidants. Furthermore, tri-, penta-, and hexavalent manganese compounds tend to undergo disproportionation reactions under the influence of  $\text{H}^+$  and  $\text{OH}^-$ :



The divalent state is generally regarded as the most stable, at least in acid to neutral media. Tetravalent manganese is also quite stable as  $\text{MnO}_2$  under moderately acid and moderately alkaline conditions, while the heptavalent state displays maximum stability around pH 7. Precipitated manganese(II) hydroxide is oxidized at room temperature by oxygen to tri- and tetravalent manganese oxides in the presence of traces of alkali, while conversion to manganates (i.e., the penta- and hexavalent states) requires much higher temperatures and high alkali concentrations ( $\geq 180^\circ\text{C}$  for 60–70% KOH). The basicity of the manganese oxides decreases (and the acidity increases) with increasing valency. Thus,

**Table 1.** Ionic species of manganese

Ion	Valence	Color
Mn <sup>2+</sup>	+ 2	pink
Mn <sup>3+</sup>	+ 3	red
Mn <sup>4+</sup>	+ 4	brownish black
MnO <sub>4</sub> <sup>3-</sup>	+ 5	blue
MnO <sub>4</sub> <sup>2-</sup>	+ 6	green
MnO <sub>4</sub> <sup>-</sup>	+ 7	purple

MnO behaves as a basic anhydride, MnO<sub>2</sub> is amphoteric, and Mn<sub>2</sub>O<sub>7</sub> is an acidic anhydride. Even though manganese in its highest valence state (+ 7) resembles chlorine (i.e., perchlorate), its general reactivity corresponds more closely to that of iron.

## 2. Manganese Oxides

### 2.1. Manganese(IV) Oxide

#### 2.1.1. Properties

Manganese(IV) oxide [1313-13-9], MnO<sub>2</sub>, *M<sub>r</sub>* 86.93, is deep black to dark brown and practically insoluble in water. It is more commonly referred to as manganese dioxide, occasionally as pyrolusite. Pyrolusite (German: Braunstein) is also the name of a specific MnO<sub>2</sub>-containing mineral. The purest manganese dioxide – corresponding rather closely to the formula MnO<sub>2</sub> – occurs in the form known as the β-modification. The compositions of other natural or synthetic manganese dioxides range from MnO<sub>1.7</sub> to MnO<sub><2.0</sub> with varying contents of lower-valent manganese, foreign cations (e.g., K<sup>+</sup>, Na<sup>+</sup>, Ba<sup>2+</sup>), hydroxyl ions, and water molecules. At least six distinct modifications of manganese dioxide have been characterized (α, β, γ, δ, ε, and ramsdellite) [2, 3], which differ according to their degree of crystallization and their content of foreign ions. The β-modification (as in the mineral pyrolusite) is not only the least reactive form of MnO<sub>2</sub> but also the most highly crystalline, and it comes the closest to having a stoichiometric composition. By contrast, γ-MnO<sub>2</sub> is nearly amorphous and much more reactive both chemically and electrochemically. When heated up to 500 °C, manganese dioxides frequently release water and/or undergo phase transitions; above 500 °C they liberate oxygen. Between 500 °C and 600 °C

MnO<sub>2</sub> is converted into Mn<sub>2</sub>O<sub>3</sub>, and above 890 °C into Mn<sub>3</sub>O<sub>4</sub>. Manganese dioxide acts as an oxidant toward readily oxidizable materials, its own valency changing from + 4 to + 3 or + 2. For example, under acidic conditions manganese dioxide oxidizes chloride ions to chlorine; hydrazine and hydroxylamine to nitrogen; iron (II) to iron(III); carbon monoxide to carbon dioxide; alkylbenzenes to aromatic carboxylic acids, ketones, and, in some cases, aldehydes; and oxalic acid to carbon dioxide.

In the presence of strong alkalis and at elevated temperature, however, manganese dioxide is itself readily oxidized by oxygen to manganese (V) and (VI) compounds. Other noteworthy properties of the various MnO<sub>2</sub> modifications include their sorptive and ion-exchange capabilities and their catalytic and electrochemical activities. The latter is of great importance to the dry-cell battery industry, which consumes large amounts of “battery-active” MnO<sub>2</sub> (especially the γ- and ε-modifications) for use as a depolarizer (→ Batteries)

#### 2.1.2. Natural Manganese Dioxide

Only about 5% of the world production of manganese ore (totalling about 27 × 10<sup>6</sup> t/a) is consumed in nonmetallurgical applications. In 1976, the following approximate tonnages of manganese ore were associated with applications other than steel making [4, p. 331]:

For dry cell batteries (battery-active ore plus ore consumed in the production of battery-grade electrolytic manganese dioxide and chemical manganese dioxide)	500 000 t/a
In brick and ceramic coloring, including in glass manufacture	200 000 t/a
In welding rod manufacture	200 000 t/a
For the production of Mn chemicals and diverse chemical and metallurgical products	450 000 t/a
Total	1 350 000 t/a

Within limits, these consumption figures are probably still applicable, because world ore consumption in 1976 (24 × 10<sup>6</sup> t/a) was only slightly less than that in 1986 (25 × 10<sup>6</sup> t/a), and about 5% is still consigned to metallurgical uses. Organic MnO<sub>2</sub> oxidations are generally carried out in the presence of sulfuric acid, and they lead to manganese sulfate as a byproduct (see Chap. 3).

Oxidation of aniline by  $\text{MnO}_2$  in the presence of sulfuric acid was once the main industrial route to hydroquinone, but since the late 1960s this technique has been largely replaced by other methods, at least in the Western world. For more information on the synthetic applications of native manganese dioxide, see [5, pp. 36–37].

Several processes are known for the recovery of manganese from low-grade  $\text{MnO}_2$ -containing ores (Mn content < 20 wt%) [6, pp. 727–731; 7], but they are currently of little practical significance since high-grade manganese ores (Mn > 40 wt%) are widely available at moderate prices.

### 2.1.3. Synthetic Manganese Dioxides

#### 2.1.3.1. Commercial Forms

Several types of synthetic manganese dioxide are produced commercially for specific end uses. In principle, synthetic manganese dioxide can be prepared either by a strictly chemical route (*chemical manganese dioxide, CMD*) or by electrochemical methods (*electrolytic manganese dioxide, EMD*).

Procedures leading to CMD include the oxidation of Mn(II) salts or lower manganese oxides, reduction of permanganates, thermal decomposition of manganese(II) nitrates, thermal decomposition/oxidation of manganese carbonate, and disproportionation of Mn(III) compounds.

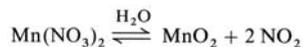
Manganese dioxides obtained by reduction of permanganate are commonly known as *manganites*. They correspond to the  $\delta$ -modification of  $\text{MnO}_2$  and should actually be regarded as salt-like combinations of hydrous manganese dioxide and cations of base-forming metals (e.g.,  $\text{K}_2\text{O} \cdot 4 \text{MnO}_2$ ). The metal portion is exchangeable against other cations. Such manganites [which are actually alkali manganates (IV)] are often obtained as byproducts from technical permanganate oxidations, but they may also be synthesized intentionally by direct reduction of permanganate (e.g., with manganese(II) salts). Until the late 1960s, the manganites were important in the manufacture of dry cells because they are highly active depolarizers. Manganites for this purpose were produced and sold in Europe under such trade names as Manganit and

Permanox. However, in recent years they have been largely displaced by electrolytic manganese dioxide (EMD) and the other types of chemically prepared manganese dioxide (CMD) described in Section 2.1.3.2.

Also of interest is the *hydrated manganite*, better known as *active manganese dioxide*, used in organic syntheses under nonaqueous, neutral conditions. Manganese dioxide of this type is generally prepared from  $\text{MnSO}_4$  and  $\text{KMnO}_4$  under strictly controlled conditions. Numerous methods are available for the preparation of “active” manganese dioxide. Many involve oxidation of a  $\text{Mn}^{2+}$  salt with  $\text{KMnO}_4$ , but  $\text{NaClO}_3$  or  $\text{O}_3$  are also used as oxidants. In a typical procedure, a solution of manganese sulfate (151 g/2.87 L) is added with stirring to a solution of potassium permanganate (105 g/2 L), and the resulting suspension of hydrous  $\text{MnO}_2$  is stirred at 60 °C for 1 h. After filtration and washing, the precipitate is dried to a constant weight at 60 °C [8, p. 122]. These conditions lead to precipitated  $\text{MnO}_2$  in the poorly crystallized but very reactive  $\gamma$ -form. It is a specific oxidant whose uses include dehydrogenation (e.g., the preparation of unsaturated aldehydes and ketones from unsaturated alcohols) and coupling reactions.

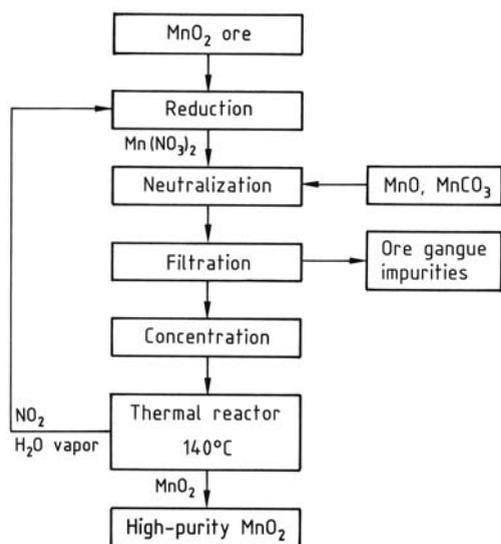
Mention should also be made of the increasing use of manganese-dioxide-based *oxidation catalysts*, particularly for air pollution abatement (removal of volatile organics, destruction of ozone) [9, 10].

Another commercial CMD is a *high-purity manganese dioxide* used in the manufacture of high-purity lower manganese oxides as well as ferrites (ceramic magnets) and thermistors for the electronics industry. This product (99.5 wt%  $\text{MnO}_2$ ) is obtained by thermal decomposition of manganese nitrate:



For a description of the original manganese nitrate process developed by IG Farbenindustrie (Bitterfeld) in the 1920s, see [11]. A later modification of this process by Chemetals has been utilized at a plant in Baltimore since the early 1970s [12, 13] (Fig. 1).

A concentrated solution of manganese nitrate (made from  $\text{MnO}_2$  ore by reaction with  $\text{NO}_2$ ) is first purified and then thermally decomposed at about 140 °C in a well-agitated, externally



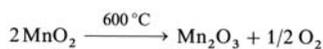
**Figure 1.** Manufacture of high-purity manganese dioxide  $\text{MnO}_2$  (Chemetals process)

heated reactor. The resulting  $\beta$ -manganese dioxide precipitates as a fine, free-flowing powder; the nitrogen dioxide coproduct is recycled to generate new manganese nitrate. Chemetals' production capacity for high-purity manganese dioxide is about 6000 t/a.

### 2.1.3.2. Synthetic Manganese Dioxides for Dry Cells

From a commercial standpoint the most important synthetic manganese dioxides are those that are electrochemically active and are therefore useful as depolarizers in dry-cell batteries. Electrochemical or battery activity of  $\text{MnO}_2$  results from a favorable combination of such factors as crystal structure, surface area, porosity, and chemical purity. Battery activity is not readily predictable; the only reliable way of establishing this property is by an actual performance test in a battery.

One important type is the so-called *activated manganese ore*, actually a semisynthetic product. It is made by roasting a high-grade oxidic manganese ore containing at least 80 wt%  $\text{MnO}_2$  but with low or no battery activity at 600 °C. The product is then treated with hot sulfuric acid.

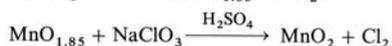
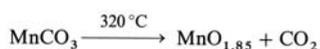


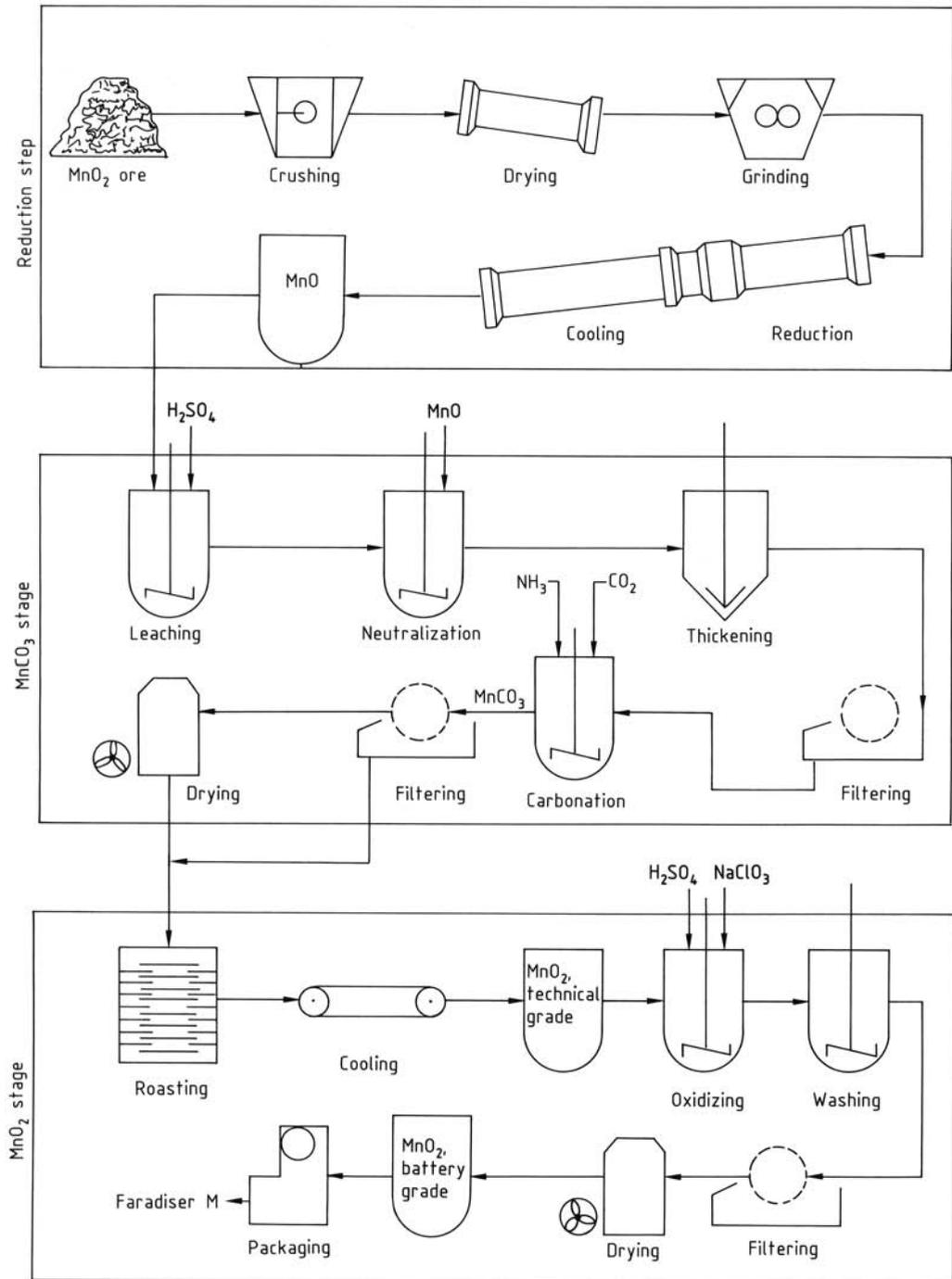
The second reaction is a disproportionation of trivalent manganese leading directly to battery-active  $\gamma$ - $\text{MnO}_2$ . The coproduct  $\text{MnSO}_4$  must be separated by leaching with water. Activated manganese ore is somewhat less effective as a depolarizer than EMD or fully synthetic CMD (see below), but it is still produced in France at a rate of several thousand tonnes per year under the names Ergogene and Philodyne.

### Chemical Manganese Dioxide (CMD).

Much more important than activated ores are the CMD products manufactured by the Sedema Division of Sadacem S.A. in Belgium under the trade names Faradiser M (for Leclanché and magnesium cells) and Faradiser WSZ (for zinc chloride batteries). The chemical compositions of the two products are practically identical: ca. 90 wt%  $\text{MnO}_2$  (primarily the  $\gamma$ -modification), 2 wt% water, plus minor amounts of lower manganese oxides. Critical trace impurities (Co, Ni, Cu, Mo) are kept below 0.001 wt%. Types M and WSZ differ in such physical properties as surface area and density. Typical particle sizes are 80% < 44  $\mu\text{m}$  for type M and 85% < 44  $\mu\text{m}$  for type WSZ.

The first step in the production process [13, 14] (Fig. 2) is the reduction of  $\text{MnO}_2$  ore to MnO using heavy fuel oil and a temperature of ca. 900 °C. The MnO is then treated with sulfuric acid to form manganese(II) sulfate. After careful neutralization with MnO to precipitate heavy metal impurities, solids are removed by thickening. The solution of  $\text{MnSO}_4$  is then treated with ammonium carbonate (by simultaneous addition of  $\text{NH}_3$  and  $\text{CO}_2$ ) to precipitate manganese(II) carbonate, ammonium sulfate being generated as a byproduct. The  $\text{MnCO}_3$  is separated and dry-roasted in the presence of air at about 320 °C to form a higher manganese oxide with the approximate composition  $\text{MnO}_{1.80-1.85}$ . Complete oxidation to  $\text{MnO}_2$  is achieved by treatment with  $\text{NaClO}_3$  in the presence of sulfuric acid. The key oxidation reactions may be represented as





**Figure 2.** Production of chemical manganese dioxide (CMD) according to the Sedema process [13]

Sedema introduced a process improvement in the course of expanding their production in which the  $\text{MnO}_2$  is transformed directly to  $\text{Mn}(\text{NO}_3)_2$  by reaction with nitric oxides. The procedure is similar to the first step in the Chemetals synthesis of high-purity manganese dioxide (see Section 2.1.3.1). The  $\text{Mn}(\text{NO}_3)_2$  solution thus obtained is treated with ammonium carbonate to give manganese carbonate (processed as before) and ammonium nitrate. The latter byproduct is more readily marketed as a fertilizer than the previously obtained manganese sulfate [15].

### Electrolytic Manganese Dioxide (EMD).

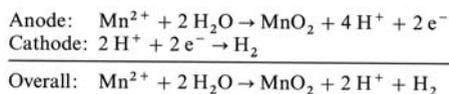
is the most important of the synthetic manganese dioxides even though it is a relatively new commodity. Practically all the EMD produced is used in the manufacture of dry cells and electronic materials such as ferrites.

The electrolytic preparation of  $\text{MnO}_2$  was discovered during the first half of the 19th century, but the outstanding suitability of the product as a depolarizer for dry cell batteries was not recognized until 1918 [16]. Commercial production started in Japan and the United States during the 1930s. By about 1952 the Japanese industry had perfected their technology to such an extent that the performance of dry cells made with EMD was about two to three times that of cells made with native battery ore [17]. Ever since, the Japanese EMD industry has maintained its world leadership in this field.

Electrolytic manganese dioxide is a black powder and typically contains 91 wt%  $\text{MnO}_2$  (mostly the hexagonal  $\epsilon$ -modification [18]), 3–5 wt% moisture, up to 1.3 wt% sulfate, < 0.02 wt% Fe, and very low residual concentrations (< 0.001 wt%) of such metals as Pb, Cu, and Co. The balance consists largely of lower manganese oxides. The true density of EMD ranges from 4.0 to 4.3  $\text{g}/\text{cm}^3$ , and its tap density from 2.2 to 2.3  $\text{g}/\text{cm}^3$ . The BET surface area is 40–50  $\text{m}^2/\text{g}$  [17] with a particle size of < 74  $\mu\text{m}$  (< 200 mesh).

The outstanding performance of EMD as a battery depolarizer (especially in high-performance alkaline cells) is a result of its unique solid state properties (which permit free transport of protons through the lattice) and the virtual absence of elements that promote the corrosion of zinc metal [19].

Production of EMD usually starts from manganese dioxide ore [13], [20, p. 385; 21, p. 637; 22] (Fig. 3), which is first reduced to  $\text{MnO}$  with either coal, heavy fuel oil, hydrogen, or natural gas. The  $\text{MnO}$  is then leached with sulfuric acid to form a manganese sulfate solution. Alternatively, if the rhodochrosite (manganese carbonate) is the starting material (as in Japan), only a leaching step with sulfuric acid is required. The acidic manganese sulfate solution is then purified by oxidation with  $\text{MnO}_2$  and neutralized with lime to a pH of 4–6. This treatment precipitates any heavy-metal ions present (Fe, Pb, Ni, Co). Hydrogen sulfide may be added for even more complete purification. After filtration and adjustment of concentrations to 75–160  $\text{g}/\text{L}$   $\text{MnSO}_4$  and 50–100  $\text{g}/\text{L}$   $\text{H}_2\text{SO}_4$ , the manganese sulfate solution is subjected to electrolysis, which can be represented in simplified form by the following reactions:



The electrolytic cells generally consist of open steel troughs equipped with an acid-resistant, electrically nonconductive lining (e.g., Hypalon, rubber, or ceramic). The anode is made from graphite, hard lead, or titanium. Anode current density is 70–120  $\text{A}/\text{m}^2$  at a cell voltage of 2.2–3.0 V. During the electrolysis, which is carried out at 90–98  $^\circ\text{C}$  (a paraffin layer is used to minimize evaporation), the concentration of  $\text{MnSO}_4$  decreases and that of  $\text{H}_2\text{SO}_4$  increases. Current yields range from 70% in older installations to > 90% in modern plants. In practically all commercial processes the EMD is deposited as a solid coating on the anode.

Electrolysis is terminated when the EMD deposit is 20–30 mm thick (requiring 14–20 d). The product is then mechanically removed from the anode, crushed, repeatedly washed with hot water, dried, and ground to the desired particle size (which depends upon the grade). The ground product is resuspended in water, adjusted to pH 6.5–7.0 with alkali, dried at 85  $^\circ\text{C}$  to a defined residual water content, and packaged.

Much of the recent progress toward economical production of high-quality EMD is related to technical advances in electrolytic cell (especially

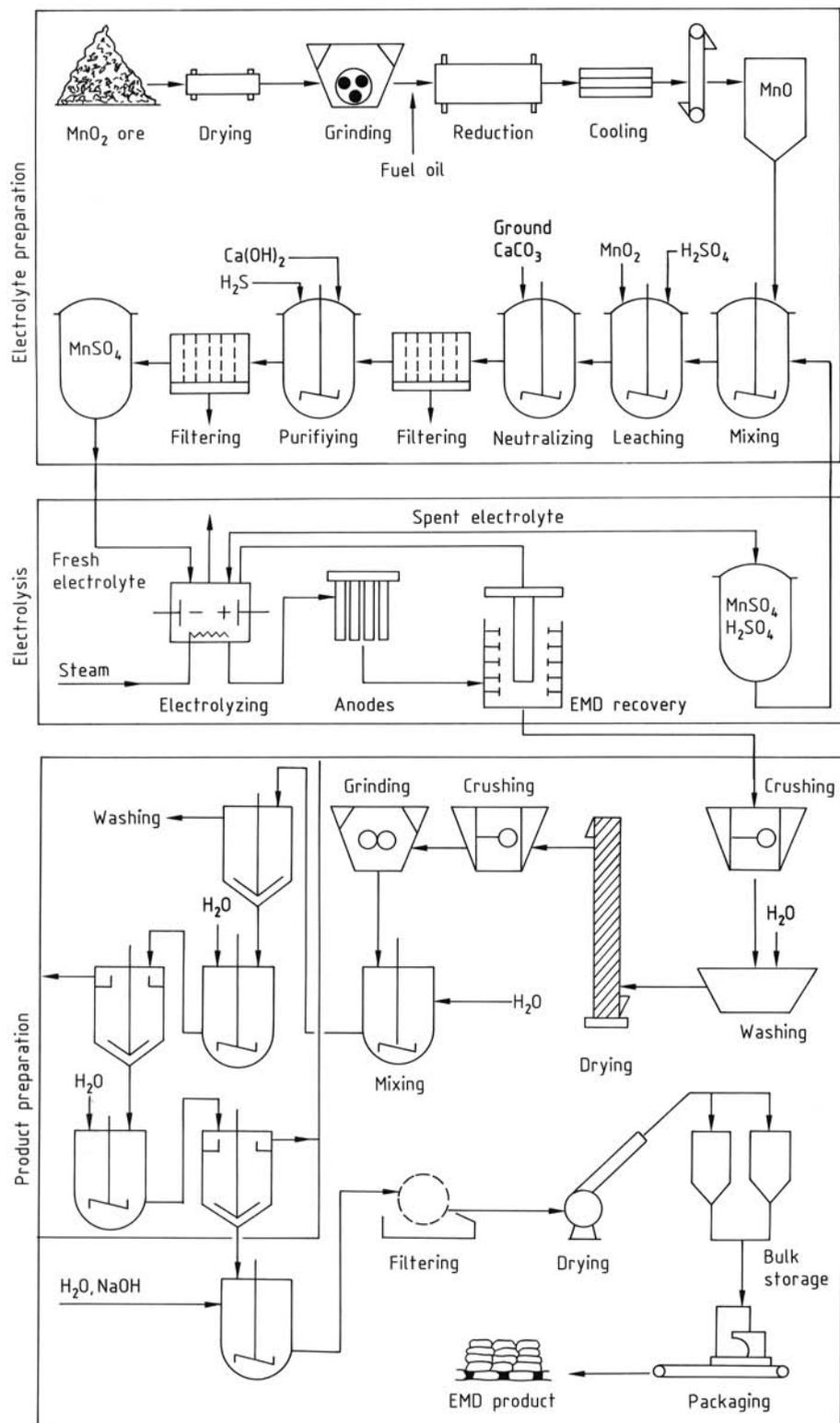


Figure 3. Production of electrolytic manganese dioxide (EMD) according to the process used by Tekkosha, Greece [13]

**Table 2.** Major producers of electrolytic manganese dioxide (EMD)

Country	Producer	Location	Production capacity, 10 <sup>3</sup> t/a*	Anode material [23]
Japan	Toyo Soda	Hyuga	24	Ti
Japan	Mitsui Mining and Smelting	Takehara	24	Ti
Japan	Dai-Ichi Carbon Company	Yokohama	6	C
Japan	Japan Metals and Chemicals Company	Takaoka	18	Ti
Greece	Tekkosha Hellas	Thessaloniki	15	C
Ireland	Mitsui Denman	Cork	12	Ti
United States	Kerr McGee	Henderson, NV	14.5	C
United States	Eveready Battery Co.	Marietta, OH	10	C
United States	ESB Materials Company	Covington, TN	3	C
United States	Chemetals, Inc.	New Johnsonville, TN	16	Ti
Spain	Cegasa	Odate	5	Pb
Soviet Union	state	Rustavi	5	Pb
People's Republic of China	state		8	C
India	Union Carbide	Thaha	5	C
India	T.K. Chemical	Trivandrum	1	C
Brazil	Union Carbide	Itaperceira	4	C
South Africa	Delta	Nelspruit	12	Pb
Total world capacity			194.5	

\* Compiled by Hoechst AG, 1987.[86]

electrode) technology. Nevertheless, many EMD producers still use graphite and lead anodes (Table 2). The main disadvantage of graphite anodes lies in their relatively short life; lead anodes lead to undesirable product contamination. The modern trend is toward titanium anodes, which are mechanically and chemically stable and do not cause product contamination. One of the apparent limitations of titanium anodes is the formation of a passivated layer on the electrode surface at current densities  $> 80\text{--}90\text{ A/m}^2$ , but this problem has been overcome by the addition of a mixture of finely ground manganese oxides ( $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ) to the electrolyte [24]. Cells are now operated at current densities  $\geq 150\text{ A/m}^2$ , resulting in a substantial increase in productivity.

**Economic Aspects.** World capacity for CMD is estimated to be ca. 40 000 t/a. This includes the Sedema Division of Sadacem in Belgium, Chemetals Corporation in the United States, and several plants in the former Soviet Union. Actual consumption is about 25 000 t/a [25]. Even though CMD has its own established niches in the battery industry, it also competes increasingly with EMD as a depolarizer in high-performance cells.

Electrochemical manganese dioxide is now the most important fastest growing synthetic

manganese product due to the high growth rate of the dry-cell battery and electronic component markets. World production capacity for EMD is approximately 183 000 t/a (Table 2) and growing. The EMD capacities in Japan and the United States are 73 000 and 32 000 t/a, respectively. Additionally, two Japanese companies operate EMD plants in Ireland and Greece, with a combined capacity of ca. 25 000 t/a.

In view of the rapid growth of the EMD market in the 1980s (averaging about 10%/a), considerable interest has been stimulated in establishing new EMD production plants. Thus, announcements regarding the construction of new facilities were recently made by BHP in Australia (15 000 t/a), Metalman in Brazil (12 000 t/a), and CIA Minera Autlan in Mexico (13 200 t/a).

According to [26], the 1986 world demand for EMD was about 128 000 t/a, and current production is said to be 165 000 t/a [25]. Serious EMD oversupply and fierce competition among producers is already evident, and is expected to intensify in the future.

## 2.2. Other Manganese Oxides

**Manganese(II) Oxide.** Manganese(II) oxide [1344-43-0], manganese monoxide,  $\text{MnO}$ ,  $M_T$

70.94, green,  $\rho$  5.37 g/cm<sup>3</sup>, *mp* 1945 °C, is practically insoluble in water and occurs in nature as manganosite. It dissolves readily in most acids. Synthetic manganese monoxide is obtained by reduction of manganese dioxide or by thermal decomposition of Mn(II) carbonate under the exclusion of air. Depending on particle size (a function of the method of preparation), MnO reacts at varying rates with atmospheric oxygen even at room temperature, thereby forming Mn<sub>3</sub>O<sub>4</sub>.

Manganese monoxide has major significance as an intermediate in the manufacture of Mn(II) compounds (especially manganese sulfate and sequential products) from MnO<sub>2</sub> ores. Reducing agents for MnO<sub>2</sub> in the large-scale manufacture of manganese monoxide include finely powdered coal, hydrogen, carbon monoxide, natural gas, and heavy fuel oils. The reaction is carried out at 400–800 °C in a rotary kiln or shaft furnace. The freshly formed manganese oxide must be allowed to cool in a reducing atmosphere in order to ensure room-temperature stability with respect to atmospheric oxygen.

Manganese monoxide (in contrast to manganese dioxide) is readily assimilated by most plants. This fact accounts for its widespread use as a fertilizer for manganese-deficient soils (→ Fertilizers, 1. General, → Fertilizers, 2. Types, Section 2.3.1.).

The consumption of manganese monoxide in the United States for fertilizer applications (alone or in combination with MnSO<sub>4</sub>) is about 20 000 t/a. A similar amount is used as an animal feed additive (→ Foods, 1. Survey, Section 3.5., → Foods, 1. Survey, Section 6.3.). Fertilizer/feed grade manganese monoxide (containing 77 wt% MnO) is made by direct reduction of manganese ore.

High-purity manganese monoxide (obtained, for example, by reduction of 99.5% MnO<sub>2</sub>) is used in the production of specialty ceramics and glasses for electronic applications, in ferrites and thermistors, and for making welding rod fluxes and high-purity manganese chemicals.

**Manganese(III) Oxide.** Manganese(III) oxide [1317-34-6], Mn<sub>2</sub>O<sub>3</sub>, *M<sub>r</sub>* 157.86, *decomp.* > 900 °C,  $\rho$  4.89 g/cm<sup>3</sup>, exists in  $\alpha$ - (rhombohedral or cubic) and  $\gamma$ - (tetragonal) modifications. The hydrate Mn<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O [1332-63-4] occurs as the mineral manganite and forms steel-gray, shiny, rhombic crystals. Manganese(III) oxide is made

industrially from manganese dioxide by calcination at 600–800 °C, or by thermal decomposition and controlled air oxidation of manganese carbonate. Primary uses are the preparation of such electronic materials as ceramic magnets and semiconductors. It is a small-volume product, a few hundred tonnes are consumed annually.

**Manganese(II, III) Oxide.** Manganese(II, III) oxide [1317-35-7], Mn<sub>3</sub>O<sub>4</sub>, *M<sub>r</sub>* 228.79, *mp* 1562 °C, occurs naturally as hausmannite and crystallizes tetragonally ( $\rho$  4.84 g/cm<sup>3</sup>). It may be obtained from the other manganese oxides by heating above 950 °C in the presence of air. According to [27], high-purity Mn<sub>3</sub>O<sub>4</sub> can also be made from an aqueous suspension of finely divided manganese metal by air oxidation at 30–100 °C in the presence of ammonium salts. The compound forms black crystals, but finely dispersed it appears as a red powder. Highly purified Mn<sub>3</sub>O<sub>4</sub> is used in the manufacture of semiconductors and ceramic magnets. World production is estimated at ca. 2000 t/a.

**Other Manganese Oxides.** Oxides with penta-, hexa-, or heptavalent manganese have no industrial significance. Indeed, the hypothetical oxides Mn<sub>2</sub>O<sub>5</sub> and MnO<sub>3</sub> have never been prepared. The anhydride of permanganic acid, Mn<sub>2</sub>O<sub>7</sub>, forms readily from KMnO<sub>4</sub> and concentrated sulfuric acid. It is an unstable, highly explosive, green-black liquid.

### 3. Manganese(II) Salts

**Manganese Acetate** [15243-27-3], Mn(CH<sub>3</sub>COO)<sub>2</sub>·4 H<sub>2</sub>O, *M<sub>r</sub>* 245.08,  $\rho$  1.589 g/cm<sup>3</sup>, forms pink crystals that are soluble in water, methanol, and ethanol. The compound dehydrates between 80 °C and 130 °C, and decomposes at 350 °C to Mn<sub>2</sub>O<sub>3</sub>. It is made industrially from acetic acid and either manganese carbonate, manganese(II) oxide, or electrolytic manganese metal. Its main use is as a catalyst (either alone or in combination with cobalt) in the liquid-phase air oxidation of hydrocarbons to carboxylic acids.

**Manganese Borate** [12228-91-0], MnB<sub>4</sub>O<sub>7</sub>·8 H<sub>2</sub>O, *M<sub>r</sub>* 354.34, is a white to pale reddish-white solid. It is insoluble in water and ethanol, but

soluble in dilute acids. The compound is precipitated from aqueous solutions of manganese chloride and sodium borate, and is used as a siccative.

**Manganese(II) Carbonate** [598-62-9],  $\text{MnCO}_3$ ,  $M_r$  114.94, light pink, decomp.  $> 200^\circ\text{C}$ ,  $\rho$   $3.125\text{ g/cm}^3$ , occurs naturally as rhodochrosite. It is sparingly soluble in water (solubility product at  $25^\circ\text{C}$ :  $8.8 \times 10^{-11}$ ) but readily soluble in acids. It is produced commercially from manganese sulfate by precipitation with alkali-metal carbonates or hydrogen carbonates. If the presence of alkali-metal ions must be avoided in the product (as in the manufacture of ferrites), ammonium hydrogen carbonate may be used as the precipitating agent. According to a GDR patent [28], the use of ferromanganese as a starting material results in manganese carbonate of especially high purity. The precipitated  $\text{MnCO}_3$  is filtered, washed, and dried at  $110 - 120^\circ\text{C}$ . Heating above  $200^\circ\text{C}$  causes decomposition to  $\text{MnO}$  and  $\text{CO}_2$ .

Manganese carbonate is used in the synthesis of other manganese(II) salts (by reaction with the corresponding acids) and also in the production of battery-active, chemical manganese dioxide (CMD) (see Chemical Manganese Dioxide). Manganese carbonate is also important in the preparation of high-quality manganese-zinc ferrites for the television and computer industries [4, p. 180]. World production of  $\text{MnCO}_3$  is estimated to be about 9000–10 000 t/a.

**Manganese(II) Chloride** [7773-01-5],  $\text{MnCl}_2$ ,  $M_r$  125.84,  $\rho$   $2.977\text{ g/cm}^3$ ,  $mp$   $690^\circ\text{C}$ ,  $bp$   $1190^\circ\text{C}$ , is readily soluble in water and exists in the anhydrous form and as di-, tetra-, and hexahydrates. Unless precautions are taken (see below), thermal dehydration of the hydrates to the anhydrous form may result in some hydrolytic decomposition, with formation of gaseous  $\text{HCl}$  and manganese oxychloride.

Industrial preparation of manganese chloride is based either on the reaction of aqueous hydrochloric acid with  $\text{MnO}_2$  ore,  $\text{MnO}$ ,  $\text{MnCO}_3$  (rhodochrosite), or on direct chlorination of manganese metal or ferromanganese. The process formerly employed in Bitterfeld (GDR) started from manganese ore ( $\text{MnO}_2$ ). Chlorine gas is generated



and is absorbed in a suspension of hydrated lime [6, p. 739]. An alternative process used by Chemetals avoids the formation of chlorine by pre-reduction of the  $\text{MnO}_2$  to  $\text{MnO}$ .

The  $\text{MnCl}_2$  solution thus obtained is purified by neutralization with  $\text{MnCO}_3$ , causing iron and aluminum impurities to precipitate. After filtration and evaporation, the tetrahydrate crystallizes from the cooled solution in plate-like crystals. This material, which is itself a commercial product, requires very careful drying because it melts at  $58^\circ\text{C}$  in its own water of crystallization. Dehydration requires a temperature above  $200^\circ\text{C}$ . Fusion in the oven is avoided by addition of previously dehydrated product. The drying process may be carried out in the presence of excess dry  $\text{HCl}$  gas if anhydrous manganese chloride free of oxychlorides is required.

Uses of manganese(II) chloride include dry cell manufacture, preparation of hard and corrosion-resistant magnesium alloys, synthesis of methylcyclopentadienylmanganese tricarbonyl (Chap. 5) and brick coloring [4, p. 182].

**Manganese(II) Nitrate** [10377-66-9],  $\text{Mn}(\text{NO}_3)_2$ ,  $M_r$  169.02, decomp.  $> 140^\circ\text{C}$ , exists in the anhydrous form and as mono-, tri-, tetra-, and hexahydrates. The commercial product is the tetrahydrate [20694-39-7], which is readily soluble in water. Manganese nitrate is prepared by nitric acid treatment of manganese carbonate or  $\text{MnO}$ , or by reaction of  $\text{MnO}_2$  with nitric oxides. The compound is an important intermediate in the production of high-purity manganese oxides and is also used in the preparation of colorants for the ceramics industry.

**Manganese(II) Phosphates.** The most important manganese phosphate is the water-soluble  $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  [18718-07-5], which is prepared by dissolving manganese carbonate, manganese(II) oxide, or manganese metal in phosphoric acid. This phosphate finds wide application in the phosphatizing of ferrous metals and is also used as a light stabilizer for polyamide fibers.

**Manganese(II) Sulfate** [7785-87-7],  $\text{MnSO}_4$ ,  $M_r$  151.01,  $\rho$   $3.25\text{ g/cm}^3$ ,  $mp$   $700^\circ\text{C}$ ,  $bp$   $850^\circ\text{C}$  (decomp.), is almost pure white in the

anhydrous state; the corresponding mono-, tetra-, penta-, and heptahydrates are pink. Manganese (II) sulfate is readily soluble in water, but has a strongly negative solubility coefficient at temperatures  $> 24\text{ }^{\circ}\text{C}$ . The solids content of a manganese sulfate solution saturated at  $24\text{ }^{\circ}\text{C}$  is 39.3 wt%; at  $100\text{ }^{\circ}\text{C}$  the solids content drops to 26.2 wt%.

The customary commercial product (technical grade) is the monohydrate, containing 99 wt%  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ . Manganese sulfate is produced either directly by reaction of manganese(II) oxide (or manganese carbonate) with sulfuric acid or as a byproduct from organic oxidations with manganese dioxide.

Until recently the manufacture of hydroquinone (by oxidation of aniline with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ ) was a major source of fertilizer-grade manganese sulfate, containing 78 wt%  $\text{MnSO}_4$  [29], but modern hydroquinone processes are based on either diisopropylbenzene/ $\text{O}_2$  or phenol and  $\text{H}_2\text{O}_2$  ( $\rightarrow$  Hydroquinone).

Before 1977 Tennessee Eastman, a major U.S. hydroquinone producer, operated with a byproduct manganese sulfate capacity of about 35 000 t/a. Eastman's manufacturing technology has since been changed, and manganese sulfate is no longer produced. Other organic oxidations are still carried out with  $\text{MnO}_2$  as the oxidant (e.g., the manufacture of 4-*tert*-butylbenzaldehyde and *p*-anisaldehyde), but the output of manganese sulfate from these processes is no more than a few thousand tonnes per year, so the majority of U.S. manganese sulfate is now derived directly from  $\text{MnO}$  or  $\text{MnCO}_3$ .

Manganese sulfate is commercially one of the most important manganese products. It is the starting material for electrolytic manganese metal, electrolytic manganese dioxide, fungicides such as Maneb ( $\rightarrow$  Fungicides, Agricultural, 2. Individual Fungicides), and other manganese compounds including manganese carbonate, manganese soaps (naphthenate, linolate, and resinate, all used as siccatives), and certain inorganic pigments. Manganese sulfate is also used in textile printing and glass making. Very significant in terms of volume is the use of manganese sulfate as a fertilizer for manganese-deficient soils, for example, in the vegetable- and citrus-growing areas of Florida. It is also valuable as a micronutrient additive for animal feeds [4, p. 187].

World production of commercial manganese sulfate is estimated to be about 120 000–130 000 t/a. Production in the United States is ca. 8000 t/a, with a demand of approximately 14 000–14 500 t/a. The deficit is covered by imports from Europe and the People's Republic of China.

Major producers of manganese sulfate include: Eagle Picher (USA), production capacity 6000 t/a; Sulfamex (Mexico) 21 000 t/a (start-up delayed); and Sedema (Belgium) 22 000 t/a. For more economic information on manganese sulfate, see [30].

## 4. Higher Oxidation-State Manganates

### 4.1. Potassium Manganates(V) and (VI)

**Potassium Manganate(V)** [12142-41-5],  $\text{K}_3\text{MnO}_4$ ,  $M_r$  236.24,  $\rho$  2.78  $\text{g/cm}^3$ , decomp.  $> 1000\text{ }^{\circ}\text{C}$ , occurs as fine blue-green to turquoise crystals. In the presence of water it is readily hydrolyzed, disproportionating to  $\text{K}_2\text{MnO}_4$ ,  $\text{KMnO}_4$ , and  $\text{MnO}_2$ . Solutions of  $\text{K}_3\text{MnO}_4$  in 40% potassium hydroxide have limited stability even below  $-10\text{ }^{\circ}\text{C}$ ; however, in the presence of 75% KOH and under nitrogen, potassium manganate(V) is stable up to  $240\text{ }^{\circ}\text{C}$ . Pure potassium manganate(V) can be heated to over  $900\text{ }^{\circ}\text{C}$  without decomposition. It is an important intermediate in the production of potassium permanganate.

**Potassium Manganate(VI)** [10294-64-1],  $\text{K}_2\text{MnO}_4$ ,  $M_r$  197.14,  $\rho$  2.703  $\text{g/cm}^3$ , decomp.  $640\text{--}680\text{ }^{\circ}\text{C}$ , exists in the pure state as brilliantly green, rhombic crystals. Upon aging, the color changes to black-green due to the formation of a surface film of  $\text{KMnO}_4$ . The compound is less prone to decomposition than  $\text{K}_3\text{MnO}_4$ ; the deep green solutions in 15–20% potassium hydroxide (for solubilities in KOH see [31]) are quite stable even at  $50\text{--}60\text{ }^{\circ}\text{C}$ . In more dilute solutions, and especially in the presence of acid,  $\text{K}_2\text{MnO}_4$  disproportionates to  $\text{KMnO}_4$  and  $\text{MnO}_2$ . Pure potassium manganate(VI) is stable up to ca.  $600\text{ }^{\circ}\text{C}$ ; at higher temperatures it loses oxygen to form  $\text{K}_3\text{MnO}_4$  and  $\text{Mn}_2\text{O}_3$ . By far the largest

part of the  $K_2MnO_4$  produced industrially is converted to potassium permanganate; smaller quantities are used in the surface treatment of magnesium metal [32] and as a chemical oxidant [5, p. 175].

## 4.2. Potassium Permanganate

The best known of the manganates, potassium manganate(VII) (potassium permanganate) was introduced as a commercial product in 1862 [33]. It soon became a very important chemical [34] not only industrially but also in the eyes of many generations of academic and industrial researchers. The former concerned themselves with the chemistry of  $KMnO_4$  and its precursors, while the latter devised new and improved methods for its production. Unraveling the chemistry of the higher valence states of manganese (generally referred to as manganates) proved to be a major challenge. Since 1954 the roles of the various manganates [especially manganate(V)] in the industrial production of  $KMnO_4$  have been fully clarified [35]. For more detailed historical information, see [36].

### 4.2.1. Properties

Potassium manganate(VII) [7722-64-7],  $KMnO_4$ ,  $M_r$  158.03,  $\rho$  2.703 g/cm<sup>3</sup>, decomp. > 200 °C, gives dark purple to bronze-colored rhombic crystals. Its solutions are faint pink to deep violet, depending on concentration. The solids content of a saturated aqueous solution at 20 °C is ca. 6 wt%  $KMnO_4$  (11 wt% at 40 °C and 20 wt% at 65 °C). Permanganate solutions are most stable in the neutral or near-neutral pH region; acidic or alkaline solutions decompose with loss of oxygen. For solubilities in aqueous KOH see [31]. Potassium permanganate is also soluble in several organic solvents, including acetone, glacial acetic acid, methanol, and sulfolane (tetrahydrothiophene-1,1-dioxide). Such solutions usually have limited stability because the permanganate ion slowly attacks the solvent.

When dry potassium permanganate is heated to 200–300 °C, an exothermic, autocatalytic decomposition takes place with the evolution

of oxygen. Contact with combustibles, especially water-soluble organic substances (such as polyhydroxy compounds), can lead to spontaneous ignition and potentially violent combustion.

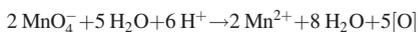
The usefulness of permanganate as an oxidant is a result of several unique properties. One is the compound's ability to function as an oxidant at all pHs. Also interesting is the fact that permanganate oxidations can be carried out in both aqueous and several nonaqueous solvents. Phase-transfer catalysis greatly extends the range of usable solvents [37].

Permanganate oxidizes a wide variety of inorganic and organic compounds ( $\rightarrow$  Oxidation). It is often regarded as the oxidant of choice for olefins and aromatic side chains even though it can also interact with other functional groups [5, pp. 183–288], [38]. Permanganate oxidations can be used not only for specific modification of organic molecules but also to destroy such materials as in pollution abatement applications.

In moderately alkaline, neutral, or slightly acidic media,  $KMnO_4$  donates active oxygen according to the following equation:



Only under substantially more acidic conditions, and with particular substrates, does permanganate oxidation follow an alternative course:



### 4.2.2. Production [6, pp. 741–762]

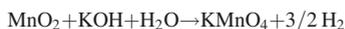
Most permanganate is made from  $MnO_2$ -containing ore by fusion followed by electrolysis. However, all-electrolytic methods also exist. One such method, practiced in the Soviet Union since the late 1950s, involves direct single-step anodic oxidation of ferromanganese to permanganate [39]:



This process is not generally considered economical because of high energy consumption (about 15 kWh/kg), the high cost of preparing cast ferromanganese anodes, and the cost of cooling the electrolyte to the required operating temperature (20 °C).

In another patented all-electrolytic process [40] a 10–25 wt% suspension of precipitated

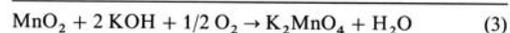
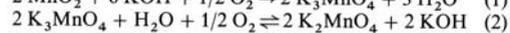
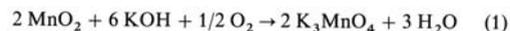
manganese dioxide in aqueous KOH is electrolyzed at  $\geq 60\text{ }^\circ\text{C}$ :



It is not clear whether this process is, or has been, used commercially.

#### 4.2.2.1. Fusion Processes [41]

The industrial preparation of potassium permanganate and its precursors ( $\text{K}_3\text{MnO}_4$  and  $\text{K}_2\text{MnO}_4$ ) begins with a finely ground  $\text{MnO}_2$  ore which is subjected to alkaline oxidative fusion:

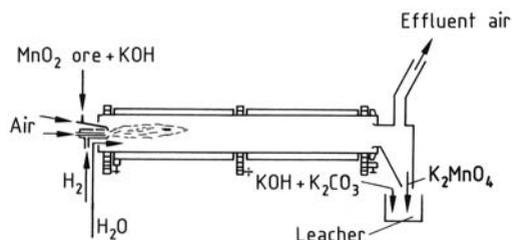


In a separate step, potassium manganate(VI) is subsequently converted to potassium permanganate, usually by anodic oxidation (see Section 4.2.2.2).

Several continuous or batch-type fusion processes are in current use, but they may be categorized in two groups:

1. *Roasting processes* that employ a  $\text{MnO}_2$ :KOH molar ratio of 1 : 2 to 1 : 3 (the reaction mixture is a solid).
2. *Liquid-phase processes* with a  $\text{MnO}_2$ :KOH molar ratio  $\geq 1 : 5$ .

**Roasting Processes.** usually involve two steps, with reactions (1) and (2) carried out sequentially. In the primary step, finely ground manganese dioxide is mixed with 50% KOH (frequently in a highly dispersed form) and treated with air or oxygen at  $300\text{--}400\text{ }^\circ\text{C}$ . The KOH/ $\text{MnO}_2$  reaction mixture is usually introduced as a fine spray into internally or externally heated rotary kilns (see Fig. 4). Stationary spray drier-like reactors are also in use. Most of the water quickly evaporates, and the highly concentrated KOH reacts within a few minutes with  $\text{MnO}_2$  and oxygen to form  $\text{K}_3\text{MnO}_4$  (Eq. 1). The dry, blue-green reaction product is ground to increase its surface area and then subjected to secondary oxidation (Eq. 2), in which it is exposed to a moisture-laden air or oxygen stream at  $190\text{--}210\text{ }^\circ\text{C}$ . Several hours are required to effect nearly complete conversion to the black-green  $\text{K}_2\text{MnO}_4$ .



**Figure 4.** Rotary kiln with internal heating for the production of potassium manganate(VI)

Rotary kilns are commonly employed for this step, but other types of solid–gas contactor (e.g., specially designed “plate” reactors) are also utilized. The removal of hard crusts that form on the inner walls of the reactor can cause substantial downtime.

**Liquid-Phase Processes.** In liquid-phase processes (see Fig. 5) finely ground  $\text{MnO}_2$  ore is added to an excess of concentrated, molten potassium hydroxide (70–90 wt%) at  $200\text{--}350\text{ }^\circ\text{C}$ . The reaction mixture is agitated vigorously and a stream of finely dispersed air or oxygen is passed through the molten mass. The  $\text{MnO}_2$  is converted to  $\text{K}_2\text{MnO}_4$  in a single step (Eq. 3), although such an oxidation can also be effected in two stages [42–44]. Potassium manganate(VI) crystallizes from the melt, from which it must then be separated by suitable means (e.g., thickening, decantation, filtration, and centrifugation) [45, p. 870].

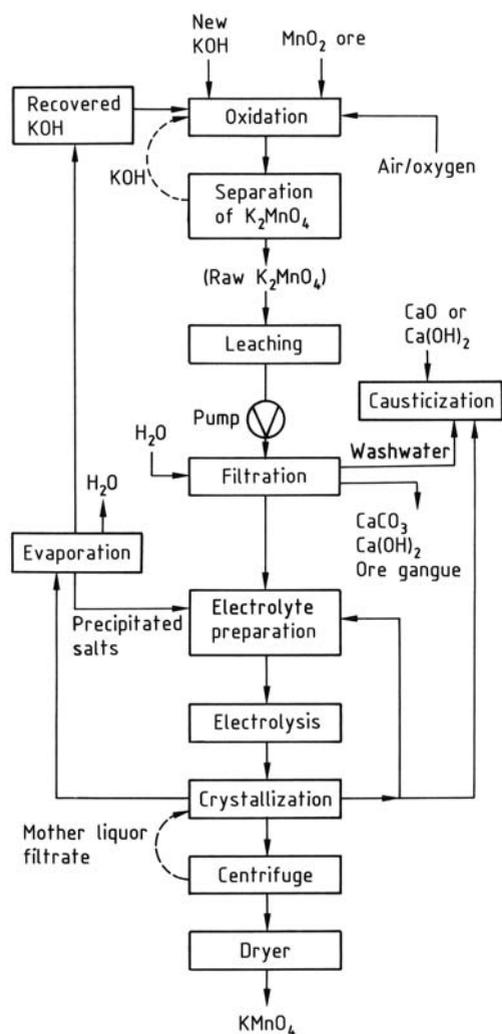
#### 4.2.2.2. Anodic Oxidation of Manganate(VI)

Oxidation of the manganate(VI) to permanganate is always accomplished by electrolysis:



Crude manganate from the fusion process is first leached in dilute potassium hydroxide (90–250 g KOH per liter, depending upon the nature of the subsequent electrolysis). The resulting leach solution is usually filtered to separate insolubles, originating from the gangue portion of the ore (see Fig. 5).

Effective control of key parameters is decisive for the overall success of the electrolysis, including the concentrations of  $\text{K}_2\text{MnO}_4$ ,  $\text{KMnO}_4$ , and KOH, as well as the temperature (usually ca.  $60\text{ }^\circ\text{C}$ ).

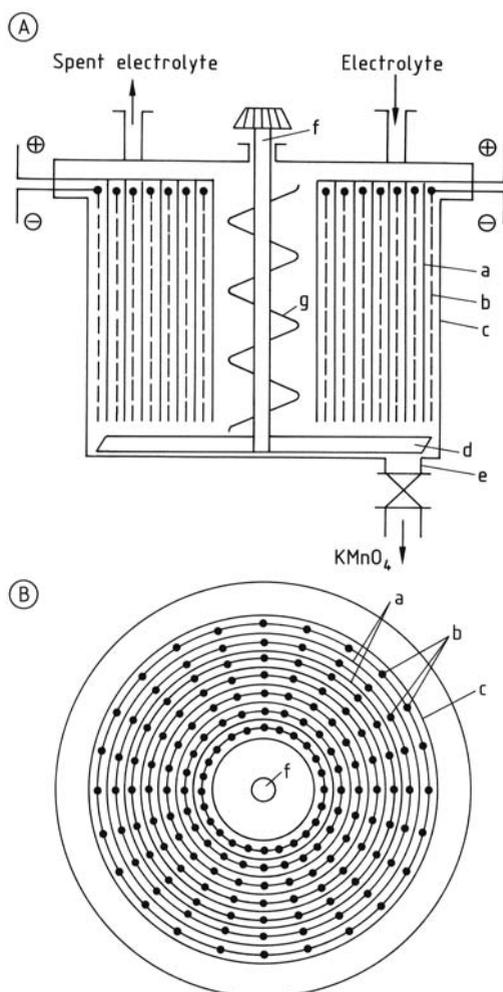


**Figure 5.** Production of potassium permanganate: liquid-phase oxidation process (overall flow schematic)

**Cell Design.** Typical electrolysis cells employ voltages of 2.3–3.8 V and anodic current densities of 50–1500 A/m<sup>2</sup>. Current yield depends on cell design and mode of operation, and ranges from 40–90%. Nickel or Monel Metal are the preferred materials for the anode, whereas iron is usually the metal of choice for the cathode.

Cells may be either monopolar or bipolar, rectangular or circular, and may be designed for either flow-through or batch operation.

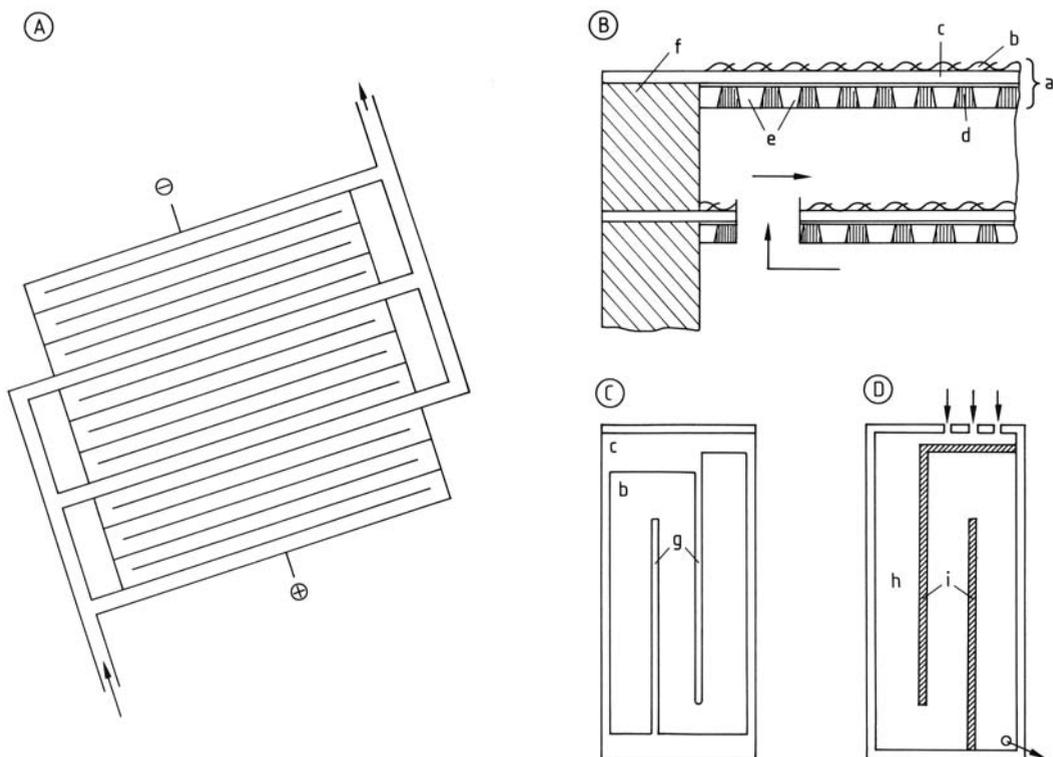
Cells used by the Chemiekombinat Bitterfeld in the German Democratic Republic [6, p. 749]



**Figure 6.** Electrolytic cell used in the Bitterfeld (GDR) process for the production of potassium permanganate  
A) Vertical section; B) Cross section a) Anode; b) Cathode; c) Rubber-lined cell trough; d) Agitator; e) Bottom discharge valve; f) Agitator shaft; g) Spiral agitator

(see Fig. 6), for example, have a volume of about 4 m<sup>3</sup>, are circular in shape, and are equipped with a built-in mechanical agitator. The electrode system is monopolar. These batch-operated cells use unfiltered electrolyte; the resulting KMnO<sub>4</sub> is allowed to crystallize within the cells and is drawn off periodically through a bottom valve. The crude product must be recrystallized to separate it from residual ore gangue.

In the cell developed by the Carus Chemical Company, numerous bipolar electrodes are combined in an arrangement resembling a filter press to form a closed, diaphragmless, flow-through



**Figure 7.** Carus Chemical electrolytic cell for the production of potassium permanganate from potassium manganate (VI) [47] A) Schematic overview of the cell bank; B) Side elevation of an individual cell section; C) Cross section of the anode side of a bipolar electrode; D) Cross section of the cathode side of a bipolar electrode a) Individual bipolar electrode; b) Anode (wire screen of Monel Metal); c) Base steel sheet; d) Steel cathode with perpendicular projections; e) Insulating plastic; f) Insulating spacer; g) Cutout for flow dividers; h) Cathode projections embedded in plastic; i) Flow dividers

electrolyzer (Fig. 7) [46–48]. The anodic side of each cell sheet consists of Monel Metal screens, while the effective cathode area consists of a multitude of small steel protrusions. The rest of the cathode is covered with a corrosion-resistant insulating material. A lower surface area for the cathode than for the anode maximizes the anodic oxidation of  $\text{MnO}_4^{2-}$  and minimizes undesirable cathodic reduction of both manganate and permanganate. The resulting potassium permanganate is crystallized outside the Carus cell in a continuous crystallizer system.

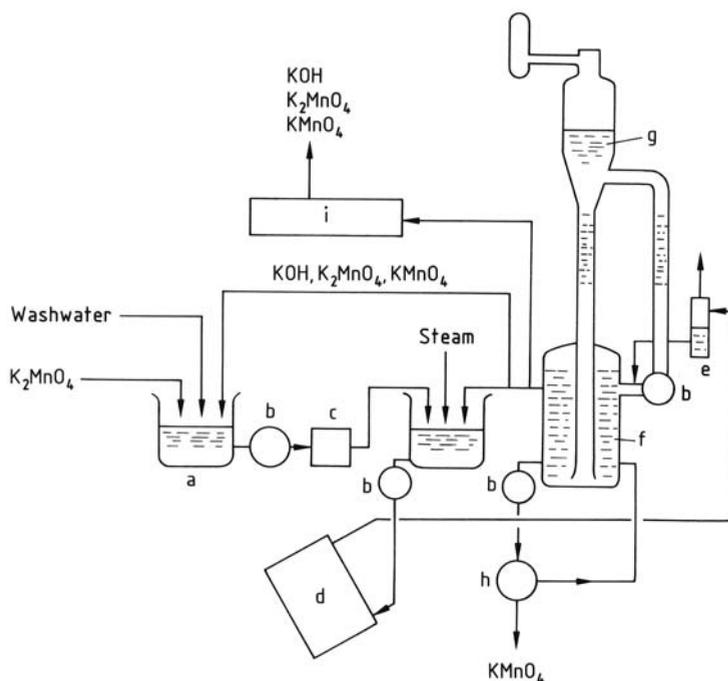
**Crystallization.** Crystallization of potassium permanganate is effected either directly in a specially designed electrolytic cell or in separate crystallizers. Modern installations use single- or multistage vacuum crystallizers, which produce a crystalline product directly from the mother liquor in such purity that only centrifugation

and drying are required before the  $\text{KMnO}_4$  is packaged and sold (see Fig. 8).

#### Removal of Impurities and Recycling.

When the crude manganate is leached with dilute KOH a solid residue remains. This is composed of the insoluble portion of the ore gangue (e.g., iron oxide hydrates, precipitated aluminum silicate), unreacted  $\text{MnO}_2$  ore, and some precipitated  $\text{MnO}_2$  (from disproportionation of  $\text{K}_2\text{MnO}_4$ ). These insoluble constituents are removed by the use of thickeners, vacuum filters, or filter presses. The Bitterfeld process operates with unfiltered electrolyte, but here the electrolyzers have been specially designed to cope with suspended matter.

In order to recycle potassium hydroxide generated in the electrolysis step (Eq. 4 in Section 4.2.2.2), the spent mother liquor is first concentrated by evaporation to a relative density



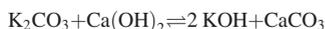
**Figure 8.** Production of potassium permanganate: continuous electrolyzing–crystallizing system a) Leach tank; b) Pump; c) Filter; d) Electrolysis cell; e) Gas separator; f) Crystallizer; g) Vacuum evaporator; h) Centrifuge; i) Evaporator

of ca. 1.575–1.585. This “recovered” caustic potash is then recycled to the front end of the process and added to either the roaster or the liquid-phase oxidizer. Alternatively, after removal of dissolved impurities, the recovered KOH can be treated with carbon dioxide to produce potassium carbonate. This method has the drawback that there is a limited market for the substantial quantities of potassium carbonate coproduct.

Dissolved impurities (in particular silicate and aluminate from the gangue portion of the ore) must be removed from the process liquors in order to avoid formation of rock-like deposits on pipeline and equipment walls. Equally undesirable is the buildup of carbonate in the process liquors due to reaction of atmospheric  $\text{CO}_2$  with KOH. Excessive carbonate concentrations in the recycle system reduce the rate of conversion of ore into manganates and can also cause low current efficiencies in the electrolytic cell.

All three major impurities (Si, Al, and carbonate) can be removed together with such minor impurities as Cu, Pb, Ni, and Co by treatment with calcium hydroxide [49]. Effective

causticization of the potassium carbonate occurs according to



and requires that the potassium hydroxide concentration be kept  $\leq 80$  g/L. The process used by Nippon Chemical Industrial Company [50] entails addition of  $\text{Ca}(\text{OH})_2$  as early as the roasting step to prevent formation of soluble carbonate and the solubilization of other impurities.

**Waste Disposal.** The treatment and disposal of solid wastes from permanganate production is an ecological as well as an economic problem. The waste product contains not only unreacted ore but also some precipitated  $\text{MnO}_2$ . The main constituents are derived from the insoluble portion of the ore gangue (Fe, Si, Al compounds) but these are accompanied by significant quantities of potassium and calcium salts. One permanganate producer has proposed recovering most of the adsorbed and chemically-bound potassium by treatment with calcium hydroxide. After washing, the treated waste could then be deposited

in landfills [51]. The patent literature describes a number of potential uses for the waste from permanganate production, including extraction of residual manganese, or use of the waste as an absorbent for air pollutants [52], as a micronutrient additive for fertilizers [53], or in building materials [54].

#### 4.2.2.3. Production Plants

This section gives a brief review of production plants for potassium permanganate in eight countries. Most of the reported production capacities are estimates.

**India.** Permanganate production began in India after World War II. Only one plant remains, that of Curti Chemicals (Goa) built in 1970 with a capacity of less than 1000 t/a. It uses a roasting step followed by electrolytic oxidation.

**Spain.** The Spanish permanganate plant in Trubia was established in 1940 and modernized in 1977. The plant is operated by Asturquímica and capacity is 4000 t/a. A modified spray drier is used as the reactor in the first roasting step and a "plate" reactor for the second roasting step [55]. Electrolytic oxidation and vacuum crystallization occur continuously.

**Japan.** Nippon Chemical constructed a new, continuously operating plant in Aichi Prefecture in 1971 (capacity ca. 3000 t/a). An improved roasting process is employed for making the manganate intermediate, whereby the  $\text{MnO}_2$ -KOH reaction mixture containing hydrated lime is dewatered in a separate step before it is introduced into the two-stage roaster system [50]. The electrolysis cells are arranged in cascade fashion and overflow from the final stage is passed to a vacuum crystallizer.

**Former Soviet Union.** The Soviet Union operates three plants, built in the late 1950s and early 1960s. The plant in Rustavi has a capacity of 500 t/a and employs single-step anodic oxidation of ferromanganese [45, p. 875]. The second plant, in Saki, has a capacity of about 2500 t/a and uses technology similar to that of the Bitterfeld plant in the GDR. The third plant is also in Saki and has a capacity of about 3000 t/a. It uses discontinuous liquid-phase oxidation in the manganate step [45, p. 870], followed by batch electrolysis and crystallization.

**Former Czechoslovakia.** The Czech plant (Spolek pro Chimickou a Hutní Vyrobu n.p.,

Usti n.L.) was built in the 19th century. It uses a two-stage roasting process with rotary hearth furnaces for the manganate step. Conversion of each batch of  $\text{MnO}_2$  to  $\text{K}_2\text{MnO}_4$  requires ca. 48 h. The monopolar, continuously operating electrolytic cells contain asbestos diaphragms and electrodes. Plant capacity in 1981 was stated to be 2000 t/a [56].

**People's Republic of China.** China, with ten state-owned plants, has become a major factor in the world permanganate market, especially as an exporter. Estimates of production capacity range from 7000–15 000 t/a. The largest most modern installation (with production of ca. 3000 t/a), established in 1954 in Guangzhou, Canton, presumably uses a liquid-phase oxidation process in the manganate step. The other (smaller) plants are said to employ roasting methods.

**United States.** The Carus Chemical Company of La Salle, Illinois, has been a producer of potassium permanganate since 1915. New production technology was developed and installed during the late 1950s and early 1960s when patented processes included liquid-phase oxidation in the manganate step [42–44] and closed bipolar cells with continuous crystallization in the permanganate step [46–48]. Numerous improvements have since been introduced, and the current process is fully continuous, highly automated, and in full compliance with environmental regulations. Production capacity is ca. 15 000 t/a.

#### 4.2.3. Commercial Grades, Packaging, and Transportation

Potassium permanganate is offered in several standard grades, including technical, technical free-flowing, U.S.P., and reagent. Guaranteed assays for the various products range from 97%  $\text{KMnO}_4$  for the free-flowing grade (which contains an anticaking additive) to 98% for the technical grade and 99% for both U.S.P. and reagent grades (typical assays are usually approximately 0.5% above the guaranteed levels). In addition to assay requirements, reagent grade and U.S.P. grade potassium permanganate conform to specifications set forth in the U.S.P. [57] and the 7th Edition of Reagent Chemicals [58], respectively. Additional specialty grades are also available. Material intended

for drinking water treatment must conform, for example, to NSF Standard 60 [59] in the United States and to DIN 19 619 [60] in the Federal Republic of Germany. Packaging is in steel drums or, for large users, bulk containers, bulk cars, and trucks.

The following transportation regulations are applicable: IMDG code D 5187, class 5; RID/ADR class 5.1, number 9 c; UN no. 1490; CFR 49: 172.101 oxidizing material.

#### 4.2.4. Uses

The United States is the leading consumer (followed by Western Europe and Japan) of permanganate intended for environmental applications, such as drinking water treatment (removal of tastes, odors, iron, and manganese [61]; control of trihalomethanes [62]); wastewater treatment (destruction of hydrogen sulfide [63] and other toxic and/or corrosive compounds, including phenols [64] and plating wastes [65]); and air purification (degradation of malodorous or toxic constituents in industrial off-gases) [66].

In other parts of the world (particularly Eastern Europe and India), the principal use of potassium permanganate is in chemical processing, especially the manufacture of synthetic organics (e.g., saccharine, chloroamphenicol, ascorbic acid, isonicotinic acid, pyrazinoic acid). Even in the Western world, chemical processing applications are significant. Thus, numerous intermediates for pharmaceuticals and pesticides are made via permanganate oxidation, as are many fine organics, including flavoring. Significant tonnages are also consumed for the oxidative destruction or precipitation of undesirable impurities, often ones that impart unwanted colors or odors.  $\text{KMnO}_4$  is used in the purification of such chemicals as methanol, ethanol, acetic acid, caprolactam, adiponitrile, plasticizers, carbon dioxide for dry ice manufacture, zinc chloride, and hydrofluoric acid. In recent years,  $\text{KMnO}_4$  has played a major role in the bleaching of indigo and other dyes for cotton twill fashion garments. This involves processes known as "frosting", "icing", or "acid washing". Permanganate is also used for bleaching beeswax, natural sponges, jute fibers, and certain clays.

Other important uses include surface treatment of carbon steels and stainless steels

(descaling and desmutting, especially in wire manufacture), etching of rubber and plastics, and decontamination of nuclear reactors. Fish farmers utilize  $\text{KMnO}_4$  to prevent oxygen depletion and to control fish parasites.

#### 4.2.5. Economic Aspects

Even though potassium permanganate is not a large-volume chemical it is industrially very important. Especially in the manufacture of specific organic intermediates (Section 4.2.4)  $\text{KMnO}_4$  is an indispensable oxidant.

World production capacity for potassium permanganate is estimated to be 43 000–51 000 t/a, although actual demand is less than 30 000 t/a. Most of the idle capacity is to be found in countries with free market economies: the United States, Western Europe, and Japan. Two of the three West European permanganate plants have been shut down since 1975: Rhône Poulenc's installation in France and the Boots Company plant in the United Kingdom.

Much of the permanganate output from countries with controlled economies enters Western markets at very low prices as a result of extremely low labor costs and virtually no environmental overhead. Government-imposed antidumping duties provide some relief, but not enough to ensure competition on a comparable-cost basis between the imported and domestic product.

#### 4.3. Sodium Permanganate

Many permanganates other than  $\text{KMnO}_4$  are known [44, pp. 859–860], but only sodium permanganate is currently of industrial significance.  $\text{NaMnO}_4 \cdot \text{H}_2\text{O}$  [10101-50-5],  $M_r$  195.93,  $\rho$  1.972 g/cm<sup>3</sup>,  $mp$  36.0 °C, can be made in several ways, including anodic oxidation of ferromanganese in  $\text{Na}_2\text{CO}_3$  solution [6, p. 759], via aluminum permanganate [67], or from  $\text{KMnO}_4$  by the hexafluorosilicate method [68]. The price of sodium permanganate is about 5 to 8 times that of  $\text{KMnO}_4$ . This is mainly due to the fact that  $\text{NaMnO}_4$  cannot be made in the same way as  $\text{KMnO}_4$ , because the oxidation of  $\text{MnO}_2$  in a  $\text{NaOH}$  melt does not lead to the required  $\text{Na}_2\text{MnO}_4$  (with hexavalent Mn) but only to  $\text{Na}_3\text{MnO}_4$  with pentavalent Mn. The latter is very

unstable in dilute NaOH solution (and therefore cannot be converted electrolytically to the desired  $\text{NaMnO}_4$ ). Even if electrolytic oxidation were possible, there would still be the difficult problem of isolating the extremely soluble  $\text{NaMnO}_4$  from the alkaline mother liquor.

Sodium permanganate is readily soluble in water (900 g/L at ambient temperature) and is preferred for applications requiring high concentrations of the  $\text{MnO}_4^-$  ion. Thus,  $\text{NaMnO}_4$  is used in the etching of plastic parts such as printed circuit boards [69], as well as in some special organic oxidation reactions, particularly if the presence of potassium ions is undesirable.

## 5. Miscellaneous Manganese Compounds

*Manganese(III) Fluoride* [7783-53-1],  $\text{MnF}_3$ ,  $M_r$  111.93,  $\rho$  3.54 g/cm<sup>3</sup>, is a red crystalline material, thermally stable to 600 °C, that is obtained by reacting Mn(II) halides with elemental fluorine at 200 °C. It decomposes in water and is used as a fluorinating agent for organic compounds.

*Manganese Hypophosphite* [10043-84-2],  $\text{Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ ,  $M_r$  202.91, is soluble in water, forms pink, odorless crystals, and decomposes spontaneously upon heating to flammable phosphine. It is prepared from calcium hypophosphite and manganese sulfate. The compound is used as a stabilizer to improve the heat and light resistance of certain man-made fibers and as a food additive and dietary supplement.

*Manganese(III) Acetylacetonate* [14284-89-0],  $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3$ ,  $mp$  172 °C, is a brown to black crystalline solid that is insoluble in water but soluble in organic solvents. In the dry state it is relatively stable. It is synthesized by reacting manganese(III) sulfate, acetylacetone, and ammonia in an aqueous medium, and is used industrially as a catalyst for organic reactions (e.g., in the polymerization of 2-hydroxyethyl methacrylate to a soluble polymer [70]).

*Manganese Ethylenebis(dithiocarbamate)* [12427-38-2], Maneb,  $(\text{CH}_2\text{NHCS}_2)_2\text{Mn}$ ,  $M_r$  265.3, is a yellow powder. It is prepared by the addition of an aqueous solution of ethylene

diamine and ammonia to carbon disulfide, followed by neutralization with acetic acid and precipitation with  $\text{MnSO}_4$  or  $\text{MnCl}_2$ . The compound is an important fungicide ( $\rightarrow$  Fungicides, Agricultural, 2. Individual Fungicides).

*Methylcyclopentadienylmanganese Tricarbonyl* [12108-13-3] (MMT),  $M_r$  218.08,  $\rho$  1.39 g/cm<sup>3</sup>,  $bp$  233 °C, is a yellow liquid that is insoluble in water but soluble in organic solvents. Several synthetic routes exist for this compound. For example, manganese(II) chloride may be allowed to react with cyclopentadienylmagnesium bromide,  $\text{C}_5\text{H}_4\text{MgBr}$ , to form biscyclopentadienylmanganese, an intermediate that reacts with carbon monoxide to give the tricarbonyl. This is then methylated in the presence of Friedel-Crafts catalysts. The product finds limited use as an antiknock additive in motor fuels and as a combustion aid in heating oils.

## 6. Occupational Health and Environmental Aspects

Manganese plays an important biochemical role in animal and plant life, and is regarded as an essential trace element [71]. It is added as a fertilizer (in the form of  $\text{MnO}$  or  $\text{MnSO}_4$ ) to manganese-deficient soils and is also a constituent in dietary supplements for animals and humans.

The United States Food and Drug Administration has given GRAS (Generally recognized as safe) clearance to manganese chloride, manganese citrate, manganese gluconate, and manganese sulfate as direct human food ingredients [72]. Nevertheless, excessive intake and long-term exposure, especially to airborne manganese, can lead to toxic effects [73–76]. Acute poisoning with manganese compounds in humans is very rare, but a few cases involving potassium permanganate are mentioned in the literature, either in connection with its attempted use as an aborticide (abortifacient) or in cases of attempted suicide. The human LDLo for  $\text{KMnO}_4$  is reported to be 143 mg/kg, with a TDLo for women of 2400 mg kg<sup>-1</sup> d<sup>-1</sup> [77].

Chronic manganese poisoning is of much greater concern [78]. Inhalation of manganese in the form of oxidic dust or as vaporized metal over extended periods of time (3 months to

several years) increases susceptibility of the respiratory organs to infection (manganese pneumonia). Manganese can also cause permanent damage to the central nervous system (manganism). The hazard of chronic manganese poisoning affects not only workers in manganese mines and manganese ore crushing/grinding facilities but also those employed in various manganese-consuming industries (e.g., the production and use of ferro- and silicomanganese in steelmaking, welding with manganese-containing welding rods, dry cell manufacture, and production of manganese chemicals) [79, 80]. The early symptoms of manganism are classed as psychological disturbances: fatigue, loss of appetite, incoordination, speech disorders, and psychotic behavior. Manganism at this stage is reversible provided exposure ceases. Continued exposure causes the disease to enter a second stage, in which permanent injury is inflicted on the central nervous system. Symptoms include severe rigidity of the limbs with jerky movements, gait problems, tremors, and excessive salivation and perspiration. There is some similarity between the symptoms of manganism and those of Parkinson's disease.

In the United States, the Federal Republic of Germany, Switzerland, and Japan a general ceiling value (MAK) has been set for manganese in air at 0.5 mg/m<sup>3</sup>/BAT-Wert: 20 mg/l [87]. The ceiling value for Mn<sub>3</sub>O<sub>4</sub> is 1 mg/m<sup>3</sup> [81]. OSHA has proposed lowering the "Permissible Exposure Limit" to manganese at the workplace to 1 mg/m<sup>3</sup> [82]. On the other hand, the United States Environmental Protection Agency decided not to designate manganese as a hazardous air pollutant under the Clean Air Act, mainly because public exposure to manganese is far below levels associated with serious noncarcinogenic health effects, and available data do not indicate that manganese is carcinogenic [83].

Detailed information about the location of major manganese air emission sources in the United States can be found in [84]. At current exposure levels, manganese does not constitute a general environmental risk [81]. The limit for manganese in drinking water in the United States and most West European countries is 0.05 ppm. This low value is based largely on aesthetic rather than toxicological considerations [85].

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