MANGANESE, MANGANESE DIOXIDE, FERROMANGANESE, AND SILICOMANGANESE

A. Commodity Summary

Approximately 95 percent of all manganese ore is consumed in the manufacture of steel, primarily as ferromanganese and silicomanganese, and other minor alloy-related industries. The other five percent is used by the non-alloying industries, including the chemical, paint, fertilizer, and battery industries, and in the production of manganese metal. Manganese ore was consumed mainly by about 20 firms with plants principally in the Eastern and Midwestern United States. Metallic manganese is often too brittle and unworkable to be widely used. However, leading identifiable end uses of manganese were construction, machinery, and transportation, which were estimated to be 14 percent, 9 percent, and 9 percent of total manganese demand, respectively. The other end uses include a variety of iron and steel applications.

Manganese ore containing 35 percent or more manganese was not produced domestically in 1993. The manganese industry in the United States relies almost entirely on foreign ores containing 35 to 55 percent manganese. The small amount of manganese ore produced in the United States is generally used as a pigment in the manufacture of brick.

As of 1992, there were four companies that produced manganese, manganese oxide, ferromanganese or silicon manganese in six plants in the United States. Exhibit 1 presents the names, locations, products and types of processes used by the facilities involved in the production of manganese, manganese oxide, ferromanganese, and silicomanganese.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Almost all of the ore processed in the United States is imported as a concentrate. Nonetheless, typical operations used to produce concentrates include crushing, screening, washing, jiggling, and tabling, as well as flotation, heavy-media, and high-intensity magnetic separation. Ferromanganese is made by smelting ore (which contains both iron and manganese) with coke and limestone, and silicomanganese is produced by smelting the slag from standard ferromanganese with additional ore and coke. Manganese metal is frequently produced by preparing a solution of manganous sulfate from ore that has been reduction roasted, and electrolyzing this solution. Manganese dioxide is prepared either chemically or electrolytically. Each of these processes is described in greater detail below.

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4 Ibid.


EXHIBIT 1

**SUMMARY OF MANGANESE, MANGANESE DIOXIDE, FERROMANGANESE, AND SILICOMANGANESE PRODUCERS**

<table>
<thead>
<tr>
<th>Facility Name</th>
<th>Location</th>
<th>Products</th>
<th>Type of Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemetals Inc.</td>
<td>Baltimore, MD</td>
<td>MnO₂</td>
<td>Chemical</td>
</tr>
<tr>
<td>Chemetals Inc.</td>
<td>New Johnsonville, TN</td>
<td>MnO₂</td>
<td>Electrolytic</td>
</tr>
<tr>
<td>Elkem Metals Co.</td>
<td>Marietta, OH</td>
<td>FeMn, SiMn, Mn</td>
<td>Electric Furnace and Electrolytic</td>
</tr>
<tr>
<td>Kerr McGee Chemical Corp.</td>
<td>Hamilton, MS</td>
<td>Mn</td>
<td>Electrolytic</td>
</tr>
<tr>
<td>Kerr McGee Chemical Corp.</td>
<td>Henderson, NV</td>
<td>MnO₂</td>
<td>Electrolytic</td>
</tr>
<tr>
<td>Everready Battery Co.</td>
<td>Marietta, OH</td>
<td>MnO₂</td>
<td>Electrolytic</td>
</tr>
</tbody>
</table>


2. **Generalized Process Flow Diagram**

**Ferromanganese and Silicomanganese**

In the United States, electrothermy is the predominant method of manufacturing manganese ferroalloys, using the submerged-arc furnace process. Standard or high-grade ferromanganese is the principal intermediate form into which manganese concentrates and other ore products are processed. Exhibit 2 shows a typical ferromanganese production process. Typically, a charge of ore, coke, and limestone is smelted in a submerged-arc furnace. In the manufacture of silicomanganese, an ore with a relatively high silica content, such as quartz or slag from standard ferromanganese, is included in the charge introduced into the submerged-arc furnace. Smelting economics favor an integrated standard ferromanganese-silicomanganese electric-furnace operation, in which the high manganese slag from ferromanganese production is used as part of the charge to the silicomanganese furnace, along with ore and coke. If silicomanganese is not co-produced, ore containing lower concentrations of manganese or higher concentrations of base oxides may be used, and the resulting slag is discarded.

Low carbon silicomanganese (or ferromanganese-silicon) is produced in a manner similar to standard silicomanganese, using standard silicomanganese, quartz, and coke or coal as the charge. Both standard ferromanganese and silicomanganese produce a slag and an off-gas containing CO₂. Low carbon silicomanganese manufacture is a slagless process, where the quartz is reduced to silicon and displaces the carbon in the remelted silicomanganese. The gases are filtered through either wet scrubbers or baghouses. Ore fines are often sintered into bulkier particles before charging them to the furnace to lower the CO₂ concentration in the off-gas, and reduce energy consumption.


9 Ibid., p. 832.
EXHIBIT 2
FERROMANGANESE AND SILICOMANGANESE PRODUCTION

Graphic Not Available.
Medium and low carbon ferromanganese are called refined ferromanganese. Silicon in silicomanganese or low carbon silicomanganese reacts with manganese ore and lime to produce refined ferromanganese.\textsuperscript{10} Exhibits 3-5 illustrate three variations of this process.

**Manganese Metal**

Manganese metal is frequently produced by preparing a solution of manganous sulfate from ore that has been reduction roasted, and electrolyzing this solution. Exhibit 6 depicts a typical production process of manganese metal from ore. Manganese ore is reduced to the higher oxides to manganese (II) oxide. Slag from the production of high carbon ferromanganese may also supply manganese (II) oxide. The reduced ore or slag is leached with sulfuric acid to produce manganese (II) sulfate. Impurities, such as iron and aluminum, are precipitated and filtered. Other metal impurities are removed as sulfides, by introducing hydrogen sulfide gas. Either ferrous or ammonium sulfide and air are added to remove colloidal sulfur, colloidal metallic sulfides, and organic matter. The purified liquid is put into a diaphragm cell, and electrolyzed. The manganese metal deposits on the cathode in a thin layer, which is brittle and extremely pure.\textsuperscript{11} Manganese metal can also be made electrolytically by fused-salt electrolysis (not shown.) Manganese ore that has been reduced to the manganese(II) level is charged to an electrolytic cell which contains molten calcium fluoride and lime. Fused electrolyte is periodically removed, as the volume of fused electrolyte increases.\textsuperscript{12}

**Manganese Dioxide**

Manganese dioxide is prepared either chemically or electrolytically. Exhibit 7 illustrates the electrolytic production of manganese dioxide, which is similar to the electrolytic production of manganese metal. Manganese ore and coke are reacted in kilns at 600°C. The mixture is cooled and leached with a solution containing 50 grams per liter of manganese sulfate and 67 grams per liter of sulfuric acid at 90°C. After leaching, the solutions are filtered to remove the insoluble ore residues, which are discarded as a waste. The filtered solution is treated with hydrogen sulfide to precipitate iron salts and sulfides. These solids are removed by filtration and the purified solutions are fed to electrolytic cells. The cells used are generally lead lined with graphite cathodes and anodes. During electrolysis, manganese dioxide builds up a coating on the anodes as thick as 6 mm before it is removed. The manganese dioxide is periodically stripped from the electrodes, recovered from the cells, crushed, washed, first with dilute soda ash solutions and then with pure water, dried, pulverized and packaged. The hydrogen co-product from the electrolysis is flared, and the spent process liquor containing mostly sulfuric acid is recycled to the ore leaching step.

Manganese dioxide also may be prepared chemically, either by chemical reduction of permanganate (Type I) or by thermally decomposing manganese salts, such as MnCO\textsubscript{3} or Mn(NO\textsubscript{3})\textsubscript{2} under oxidizing conditions (Type II).\textsuperscript{13} To produce Type I chemical manganese dioxide (not shown), the byproduct manganese dioxide from the oxidation of organics using potassium permanganate, is treated with hydrochloric or sulfuric acid, followed by MnSO\textsubscript{4}. This treatment removes the excessive quantities of adherent and bound alkali. KMnO\textsubscript{4} is added to convert the ion exchanged divalent Mn into MnO\textsubscript{2}. The product is washed and dried at low temperature, so as to avoid the undesirable loss of water of hydration.\textsuperscript{14}

\textsuperscript{10} Ibid., pp. 834-837.
\textsuperscript{11} Ibid., pp. 835-836.
\textsuperscript{12} Ibid., p. 837.
\textsuperscript{13} Ibid., p. 863.
\textsuperscript{14} Ibid.
EXHIBIT 3

Refined Ferromanganese Production

Graphic Not Available.

EXHIBIT 4

REFINED FERROMANGANESE PRODUCTION

Graphic Not Available.

EXHIBIT 5

REFINED FERROMANGANESE PRODUCTION

Graphic Not Available.

EXHIBIT 6

MANGANESE METAL PRODUCTION

Graphic Not Available.


PRODUCTION OF ELECTROLYTIC MANGANESE DIOXIDE
EXHIBIT 7

Graphic Not Available.
To make Type II chemical manganese dioxide, as shown in Exhibit 8, manganese ore is reacted with coke in kilns at 600°C, then cooled and leached with 10 percent nitric acid at 85°C to generate a neutral manganese nitrate solution. This solution is filtered to remove insoluble materials, treated with sulfides to precipitate iron impurities and refiltered. The ore residues and iron sulfides are discarded as waste. The purified manganese nitrate solution is evaporated to about half the original volume. Manganese nitrate crystals separate at this point and are recovered by centrifugation. The mother liquor is recycled to the evaporators and the recovered crystals are heated to 200°C to produce manganese dioxide and nitrogen dioxide, which is absorbed as nitric acid for reuse. The manganese dioxide is recovered and packaged.

Type II chemical manganese dioxide can also be made from finely ground manganese dioxide ore that has been reduced with H₂—CO to manganese (II) oxide (not shown). This substance is leached with sulfuric acid and the manganese sulfate solution neutralized to pH 4-6 to precipitate iron, aluminum, nickel, cobalt, and other impurities. The solution is filtered to remove the precipitates, and (NH₄)₂CO₃ is added to precipitate manganese carbonate. The MnCO₃ is filtered, dried, and roasted in air to produce manganese dioxide (MnO₂) and carbon dioxide (CO₂).¹⁵

Other Manganese Products

Both manganese sulfate and manganese carbonate can also be prepared from ore. Manganese sulfate is used primarily as an agricultural chemical, while manganese carbonate is used to prepare other manganese compounds for specialty purposes. Both the sulfate and the carbonate production use less than five percent of total manganese ore demand. Manganese sulfate can be prepared by either the hydroquinone process or the ore-coke process.¹⁶

In the hydroquinone process, as shown in Exhibit 9, manganese ore, aniline, and sulfuric acid are reacted to produce manganese sulfate, quinone and ammonium sulfate. The reacted mixture is steam distilled to separate quinone, which is collected and processed on-site to hydroquinone. The remaining materials are filtered, and gangue solids are removed as a waste material. The filtrate is partially evaporated and manganese sulfate crystallized from solution is recovered as a solid. The spent liquor containing ammonium sulfate is sent to waste treatment and the recovered manganese sulfate is dried and packaged. The ore-coke process for manufacturing manganese sulfate is shown in Exhibit 10. Manganese ore and coke are reacted in a kiln and the product is leached with sulfuric acid. The resulting slurry is evaporated to dryness to recover a 30 percent product for agricultural purposes. The insoluble residues are left with the product.¹⁷

¹⁵ Ibid.


¹⁷ Ibid., pp. 6-2 - 6-8.
To produce manganese carbonate, as shown in Exhibit 11, manganese sulfate and soda ash are reacted in solution to form the carbonate, which precipitates from solution and is recovered by filtration, dried and packaged. The spent solutions containing by-product sodium sulfate are normally wasted.\textsuperscript{18}

\textsuperscript{18} Ibid., pp. 6-8 - 6-9.
EXHIBIT 8

Production of Chemical Manganese Dioxide (Type II)

Graphic Not Available.
EXHIBIT 9
EXHIBIT 10

PRODUCTION OF MANGANESE CARBONATE

Graphic Not Available.

Exhibit 11

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

Researchers are investigating how to increase recovery of manganese from refractory ores and steel slag.¹⁹,²⁰,²¹

4. Beneficiation/Processing Boundaries

EPA established the criteria for determining which wastes arising from the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in Section B.

**Ferromanganese and Silicomanganese**

EPA determined that for ferromanganese and silicomanganese, processing begins with smelting in a submerged arc furnace because the ore undergoes physical/chemical reactions which significantly alter the physical/chemical structure. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they

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involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

Since production of low carbon silicomanganese uses standard silicomanganese, all of the wastes generated during silicomanganese production are mineral processing wastes.

**Manganese Metal**

EPA determined that for this specific mineral commodity, the beneficiation/processing line occurs between reduction roasting and leaching because the ore (manganese (II) oxide) is converted to manganese (II) sulfate. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

**Manganese Dioxide**

**Electrolytic Production**

EPA determined that for manganese dioxide, mineral processing begins in the kiln because the ore reacts with coal to produce manganese dioxide. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

**Chemical (Type I) Production**

Since this process begins with byproduct manganese dioxide, all of the wastes generated during the process are mineral processing wastes.

**Chemical (Type II) Production**

EPA determined that for this specific process, mineral processing begins with the reaction of manganese ore with coke in kilns because the reaction alters the chemical structure of the ore. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

**Other Manganese Products**

Hydroquinone Process

EPA determined that for other manganese products produced via the hydroquinone process, mineral processing begins with reacting the ore, aniline, and sulfuric acid because the resulting chemical reaction alters the chemical structure of the ore. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

Ore-Coke Process

EPA determined that for other manganese products produced via the ore-coke process, mineral processing begins with the reaction of the ore and coke in kilns because the reaction alters the chemical structure of the ore. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

Manganese Carbonate

Since manganese carbonate is produced from manganese sulfate, all of the wastes generated during manganese carbonate production are mineral processing wastes.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

The following wastes may be generated by extraction and beneficiation operations: gangue, flotation tailings, spent flotation reagents, and wastewater.

2. Mineral Processing Wastes

Ferromanganese Production

Both Slag and APC Dust/Sludge are recycled where possible. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Electrolytic Manganese Dioxide and Metal

Waste Electrolyte. Available data do not indicate that waste electrolyte exhibits hazardous characteristics. Therefore, the Agency did not evaluate this material further.

Spent Graphite Anodes. The spent anodes are directly recovered from the process and landfilled. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Iron Sulfide Sludge. This waste is generated by solution purification prior to electrolysis and is landfilled. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

APC Water. Particulates generated during the calcination and product drying steps are collected by wet scrubbers. The scrubber waters are used as process make-up waters. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater. This waste is generated during product washing and in slurring ore residues to disposal lagoons, and may contain suspended ore residue and minor amounts of soda ash. Wastewater is treated with lime to precipitate manganese salts and then discharges to lined evaporation ponds. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Chemical Manganese Dioxide

APC Dust. Dry particulate collection methods are used to reduce ore calcination and product handling particulate emissions. Collected materials are recycled. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Ore residues. These wastes are generated in the leaching operations, which are acid insoluble material such as aluminates and silicates, and in the purification of the intermediate manganese nitrate. There is also some unrecovered manganese nitrate entrained in these wastes, which are slurried

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24. Ibid.

25. Ibid., p. 6-13.

26. Ibid.

27. Ibid., p. 6-17.

to treatment lagoons. Lime is added to the lagoons to precipitate any soluble manganese present.\textsuperscript{28} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater. This waste is generated by slurring the ore residues to the treatment lagoons. After treatment the slurry water is discharged.\textsuperscript{29} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Other Manganese Products - Manganese Sulfate (Hydroquinone Process)

APC Dust. This dust consists of particulates generated in the calcination and drying operations, which are captured and recycled.\textsuperscript{30} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Spent Process Liquor. This waste contains ammonium sulfate and unrecovered manganese sulfate. This waste, along with washings from the ore residues are lime treated to precipitate residual manganese, settled, and discharged.\textsuperscript{31} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater Treatment Solids. These solids formed by wastewater treatment (i.e., manganese oxides and calcium sulfate) are left in ponds. Solid ore residues wastes are washed free of soluble manganese and land disposed.\textsuperscript{32} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Other Manganese Products - Manganese Sulfate (Ore-Coke Process)

APC Dust. This dust consists of particulates generated in the calcination and drying operations, which are captured and recycled.\textsuperscript{33} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Other Manganese Products - Manganese Carbonate

\begin{flushleft}
\textsuperscript{28} Ibid., p. 6-17.
\textsuperscript{29} Ibid., p. 6-17.
\textsuperscript{30} Ibid., pp. 6-2 - 6-6.
\textsuperscript{31} Ibid.
\textsuperscript{32} Ibid., p. 6-6.
\textsuperscript{33} Ibid., p. 6-8.
\end{flushleft}

APC Dust. This dust consists of particulates generated in the drying operation, which are captured and recycled.\footnote{Ibid., pp. 6-8 - 6-10.} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Spent Process Liquor. This waste contains sodium sulfate and small amounts of unrecovered product. This waste is lime treated to precipitate residual manganese salts, settled, neutralized, and discharged.\footnote{Ibid., p. 6-10.} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater Treatment Solids. The solids formed by wastewater treatment (i.e., manganese oxides and calcium sulfate) are left in ponds.\footnote{Ibid.} Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents, tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors.

BIBLIOGRAPHY


