

Mn Ore Reduction Technologies

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- Where does reduction fit into the EMM or EMD process flow?
- Main reduction reactions
- Overview of available technologies and equipment
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EMM and EMD production requires soluble manganese ore

- Hydrometallurgical process route to obtain high purity end product - needs ore that is soluble in sulphuric acid.
- The most stable oxidation state for manganese is +2, which has a pink to red colour. This is also the most soluble state.
- This oxidation state is seen in the mineral rhodochrosite, MnCO_3 , or manganese(II) carbonate. Ore containing this mineral can be leached as is.
- However, most ores of manganese don't contain manganese(II) but higher oxides, which are **not** soluble:

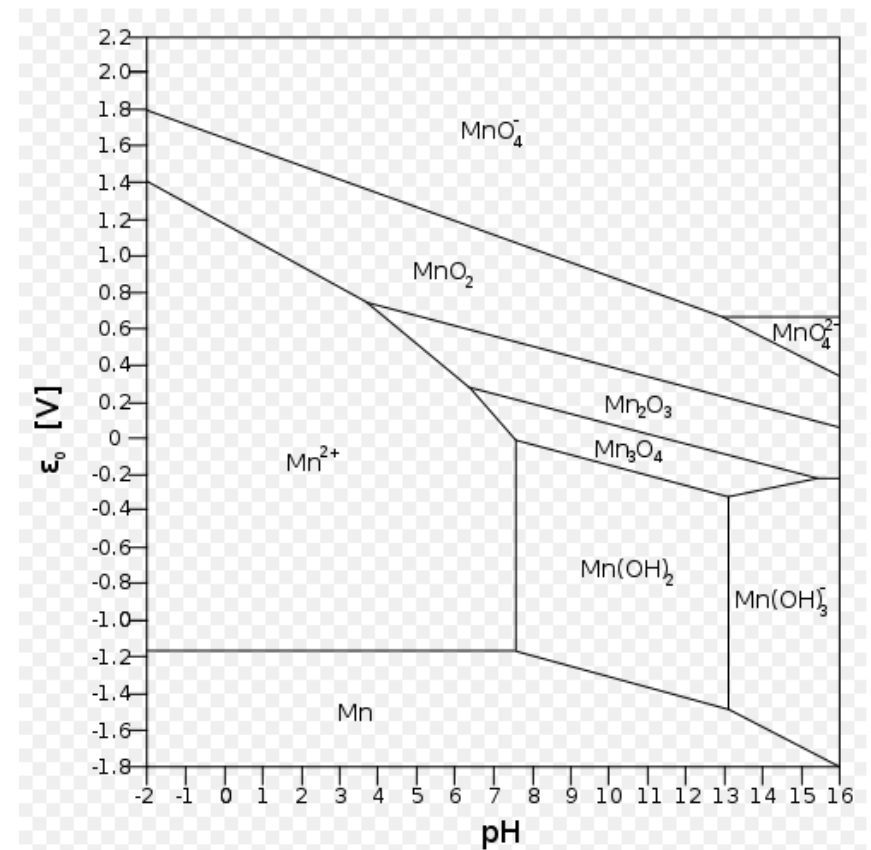
MnO_2 – pyrolusite – manganese (IV)

Mn_2O_3 – bixbyite – manganese (III)

Mn_3O_4 – hausmannite – manganese (II,III)


$\text{Mn}_7\text{SiO}_{12}$ – braunite – manganese (II,III)

[Braunite also contains Ca in some deposits]



Pourbaix diagram for Manganese: $c(\text{Mn}) = 1 \text{ mol/l}$, $T = 25 \text{ }^\circ\text{C}$

Oxide ore must be reduced before leaching: add heat and a reductant

- The higher oxidation states (IV) and (III) must be reduced to (II) by using a suitable reducing agent, being hydrogen or carbon or their compounds.
 - The temperature must be increased to over $\sim 850^{\circ}\text{C}$ before the reactions will take place.
 - Typical reductants are bituminous coal, heavy furnace oil, natural gas or liquefied petroleum gas. The reductant must be gaseous at the temperature of the reduction process. Higher hydrocarbons, e.g. kerosene, must first be cracked into lower chain molecules.
 - The amount of reductant used may vary widely, but must be above the stoichiometric amount necessary to reduce the manganese oxides to MnO. The reductant concentration may be controlled via various means, e.g. by monitoring the exit gas composition or the manganous content of the discharge solids.
 - **The sequence of reduction is $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$.** In each step another mole of oxygen is removed.
 - After the reduction, the ore must be cooled in a non-oxidizing atmosphere (inert or reducing), to prevent spontaneous re-oxidation of the MnO. The final discharge temperature must be 100°C or less.
 - Another term for reduction is roasting.
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Typical reduction reactions

Reductant: hydrogen



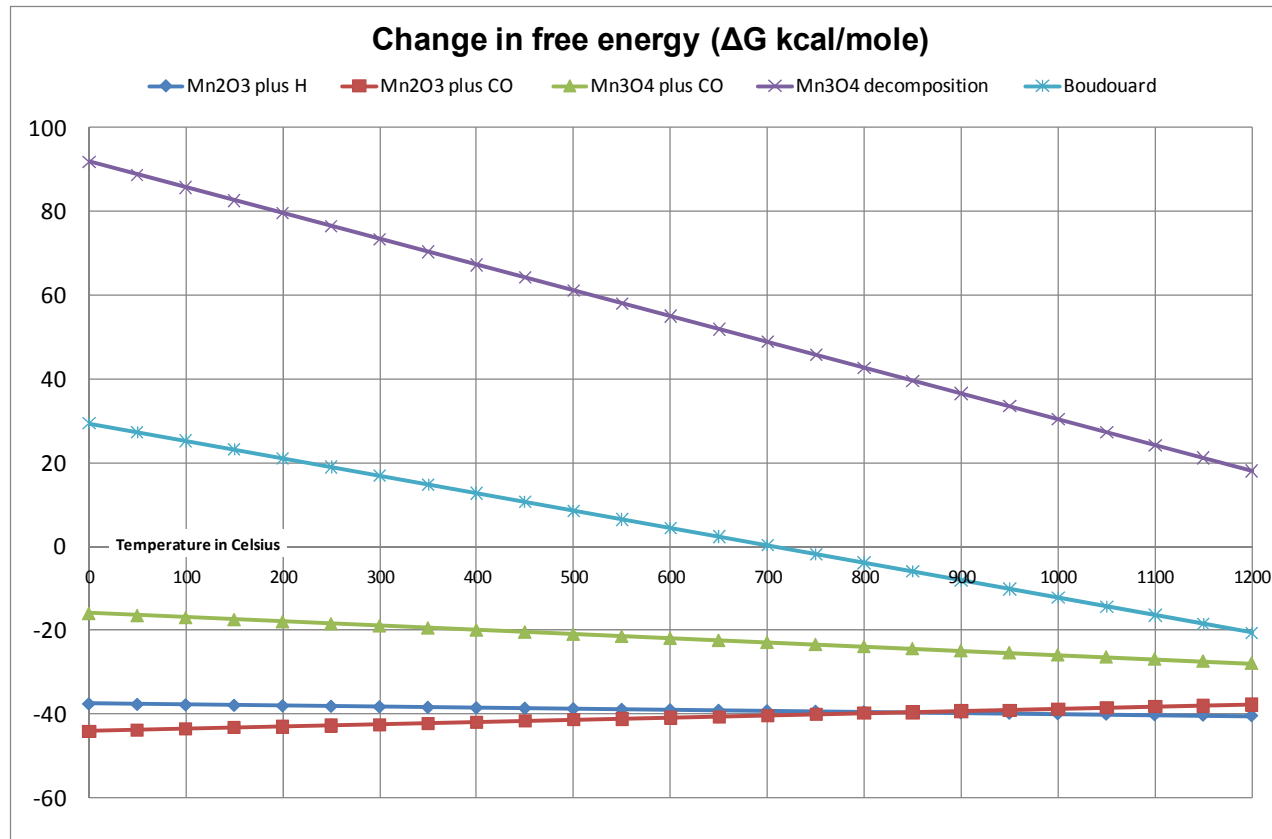
Reductant: carbon monoxide



Most of the reduction reactions are exothermic, but they have fairly high activation energy that must be overcome first. Reactions typically start above 800°C only.

- Other typical reactions during ore reduction:
 - ❖ The *Boudouard* reaction: $\text{CO}_{2(g)} + \text{C}_{(s)} \leftrightarrow 2\text{CO}_{(g)}$
 - ❖ The water gas formation reaction $\text{H}_2\text{O}_{(g)} + \text{C}_{(s)} \leftrightarrow \text{CO}_{(g)} + \text{H}_{2(g)}$
 - ❖ These will convert solid reductant into gaseous reductant or vice versa.
 - ❖ Also, decomposition of MnOOH to Mn_2O_3 will take place without consuming any reductant.
 - ❖ Cracking of higher hydrocarbons don't consume reductant or oxygen.
- The **efficiency** of the reduction reactions are improved if the reductant is a gas, the ore particle size is very small and good surface contact is ensured between ore and gas. All reagents must be at the temperature required for the reactions to start. At lower temperatures a long retention time is needed.

Thermodynamics of Mn ore reduction

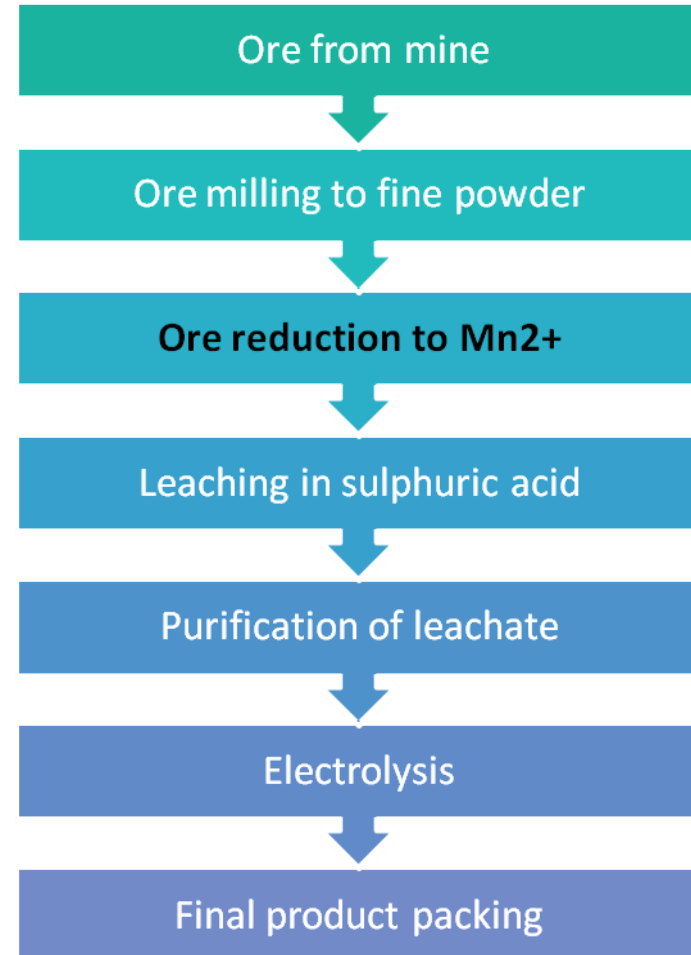


- Reactions will only take place if they result in a lowering of the total free energy (ΔG) of the reagents and products. Free energy is a function of temperature and is unique for every reaction.
- The activation energy for each reaction must also be overcome before the reaction starts to take place, even if it is an exothermic reaction.

Additional step in process flow

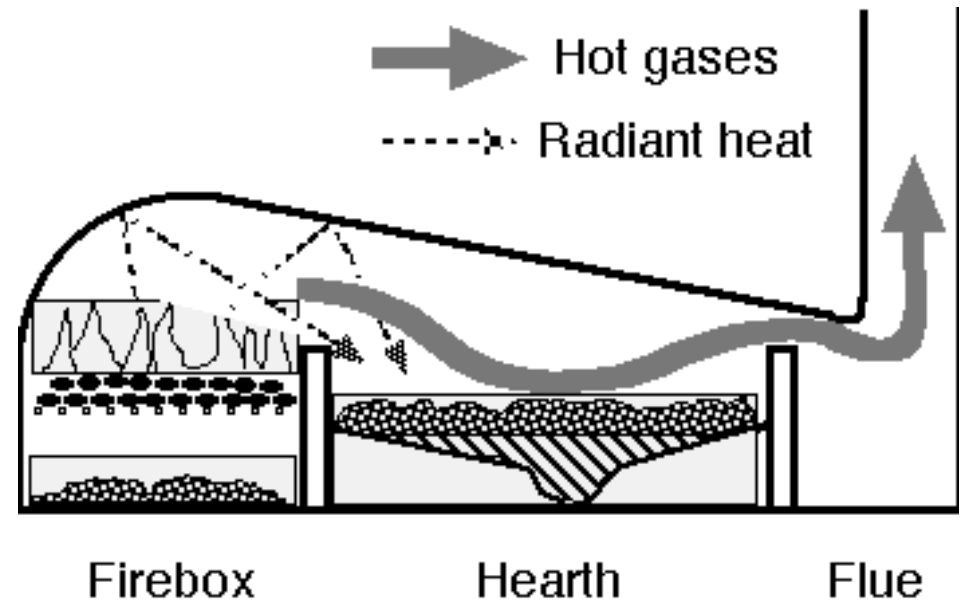
- Different technologies can be used to achieve the ore reduction step:
 - Reverberatory furnace
 - Calcining
 - Microwave furnace
 - Heap reduction
 - Shaft furnace
 - Single or multiple hearth furnace
 - Fluidized bed reactor
 - Custom designs / combinations of above
- Another possibility for using oxide ore is to perform reductive leaching (i.e. leach directly from higher oxidation state to 2+). In this case no additional process step is required, i.e. no furnace needed.
- The balance of this presentation will briefly touch on some of these technologies.

Typical process flow for EIMn or EMD production



Reverberatory furnace

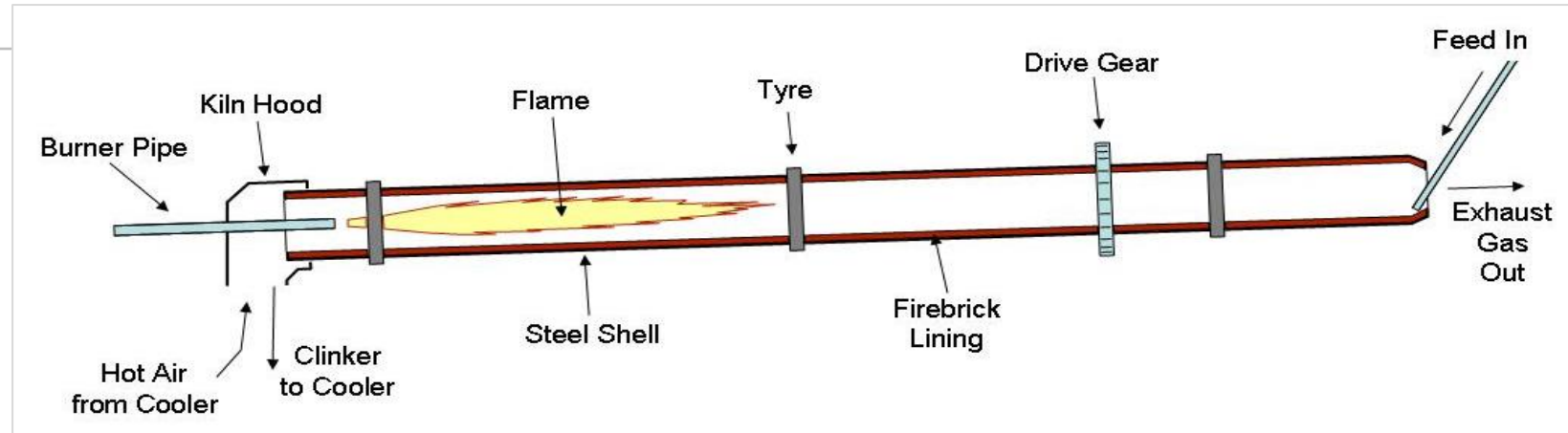
- The ore is separated from the fuel but is in contact with the combustion gases. Bituminous coal is a typical fuel.
- Old technology. Used for copper or lead in middle ages. Used in Japan for iron making in 18th century, was replaced by the blast furnace.
- Currently used mostly in secondary aluminium (scrap) industry, for smelting before die-casting.
- Used in China at a number of EIMn factories to reduce Mn oxide ore.
- If the exhaust gas is not collected and combusted fully, this process is potentially highly polluting.



Disadvantages:

- Difficult to maximise heat transfer due to the spatial separation of the burning fuel and the ore.
- Exhaust gas chemistry must be controlled to maintain a reducing mixture in the chamber.
- Poor contact between ore and reductants due to ore being a stationary bed.

Calcining



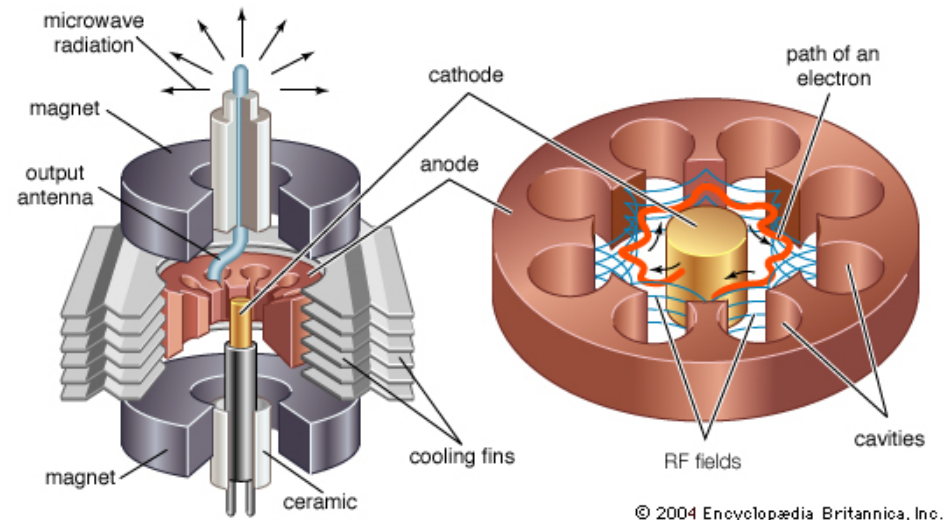
- Rotary kiln operating at an incline, in which the ore and the reductant are added together. Continuous operation. Typical reductants are bituminous coal or heavy furnace oil.
- The content of the kiln can be heated either directly via an internal flame, or indirectly with electrical elements from outside the tube.
- Control of the atmosphere inside the kiln is very important to avoid combustion of the reductant. The temperature and oxygen levels should be controlled only to 'crack' the reductant.
- The flow of gas and solids can be co-current or counter-current, depending the type of reductant and method of heating. Exhaust gas can be utilised to pre-heat the feed.
- Good heat transfer can be established and good contact between solids and gas due to rotation. Homogenous reduction of ore takes place.

Disadvantages:

- Expensive to install and drive system requires good maintenance.
- Electricity requirements are high – drive system and heating elements if not using flame.

Microwave furnace

- Same principal and layout as calcining, but the source of heat is microwaves . The reductant (coal or oil) is still added with the ore into the rotating tube.
- Efficiency of the process depends on the design of the magnetron and the presence of a good susceptor – a material which heats up when exposed to microwaves. Graphite is a good susceptor. Atmosphere must be controlled similar to calcining.
- Microwaves heat only the substance being reduced and not the atmosphere around it or the furnace walls. This makes is highly energy efficient.
- With a smaller physical footprint and a substantially smaller carbon footprint, microwave furnaces offer far lower operating costs than calciners or reverberatory furnaces.



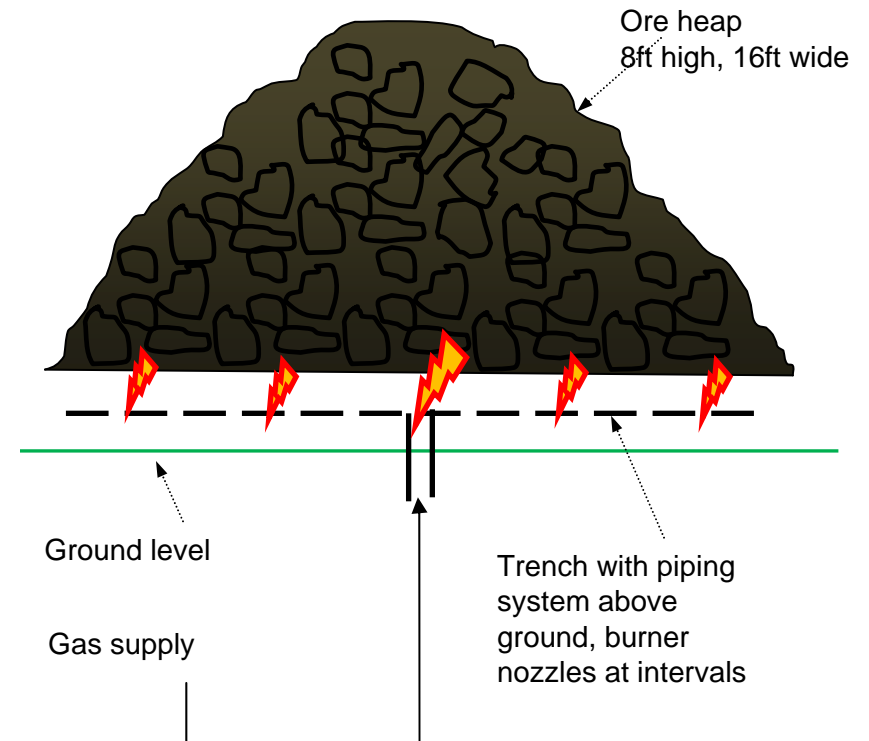
Internal parts of a magnetron – same design for domestic or industrial equipment

Disadvantages:

- This is fairly new technology that has not yet been proved on industrial scale for the manganese industry.
- Choice of reductant is limited due to need for a susceptor and absence of hot gas stream.

Heap reduction (also called pile roasting)

- Simplest method of reduction available – no significant equipment installation required, only gas piping system.
- This method was used at Kerr-McGee's EMM factory in USA (closed in 2001).
- Natural gas is the source of heat and the reductant. Sub-stoichiometric combustion of the gas provides heat and leaves hydrocarbons available for reduction.
- Temperature inside pile must be in the 700° to 900°C range. Most suitable for high grade ore – exothermic reactions.
- Batch process, usually followed by polishing step in vertical bins.



Disadvantages:

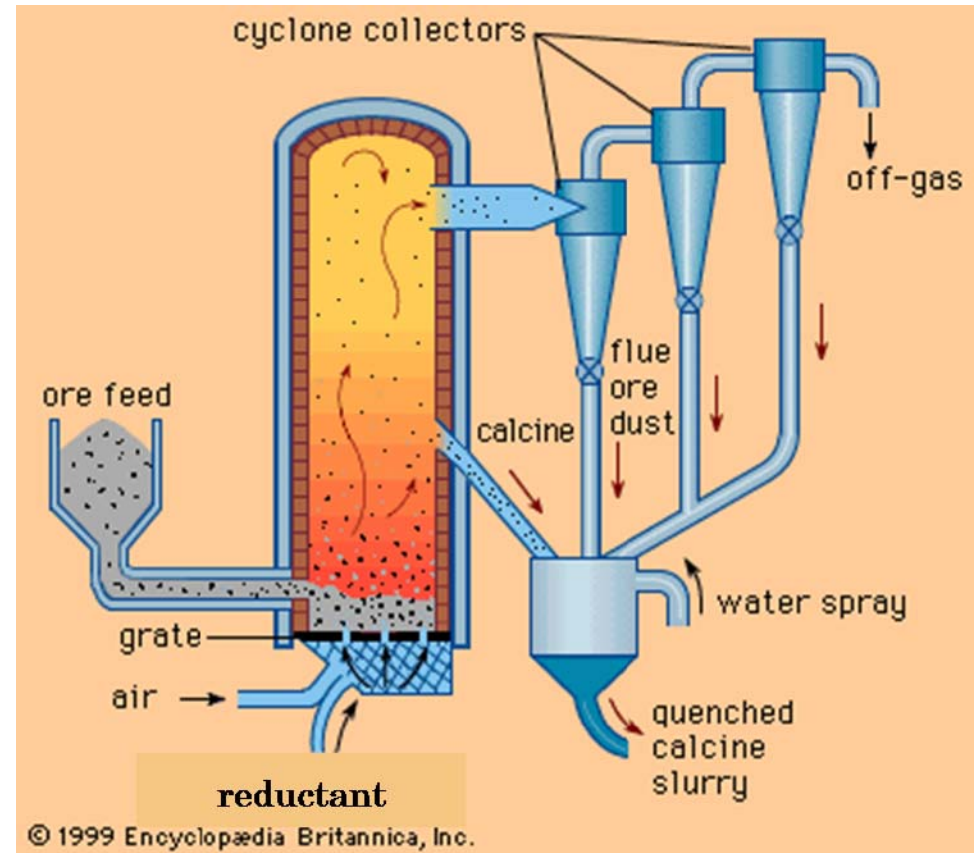
- Pollution control is almost impossible
- Affected by inclement weather
- Long retention time of 1 to 2 days
- Cannot use fines
- Clunker formation at hot spots

Fluidized bed reactor

- Air stream is passed through a perforated plate at the bottom of a vertical reaction chamber, into which ore is fed on continuous basis.
- Fine particles suspended in hot gas stream allows complete reduction.
- Quenched slurry can be pumped directly to leach tanks.
- Reductant can be gas or coal partially combusted in separate chamber.
- Efficient use of reductant, recirculation.

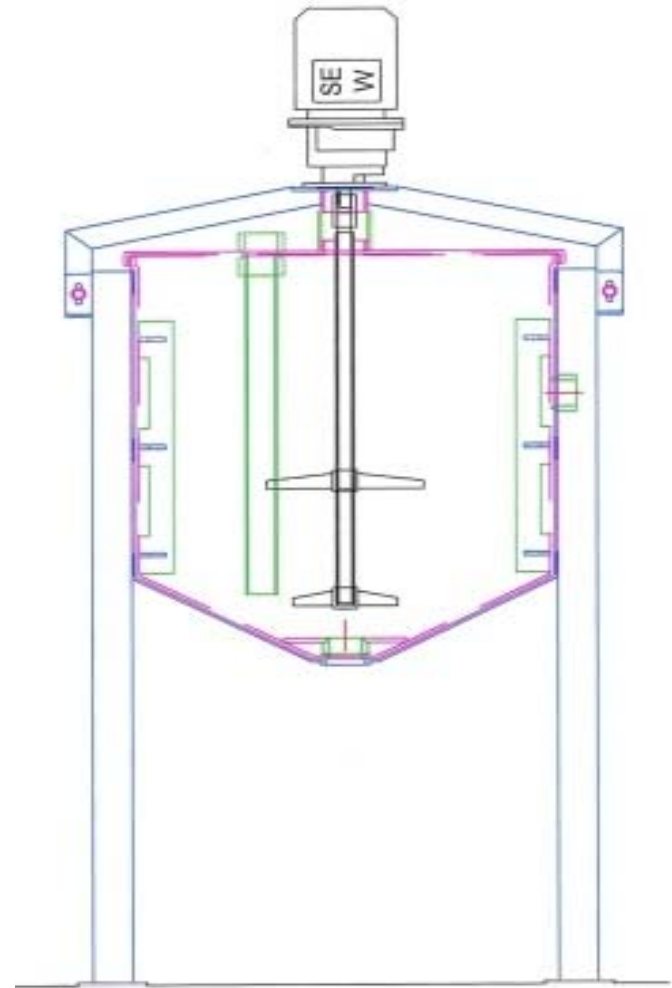
Disadvantages:

- Expensive to install. Need standby blower.
- Long delay between start-up and stable state operation.
- Control of particle size is critical.

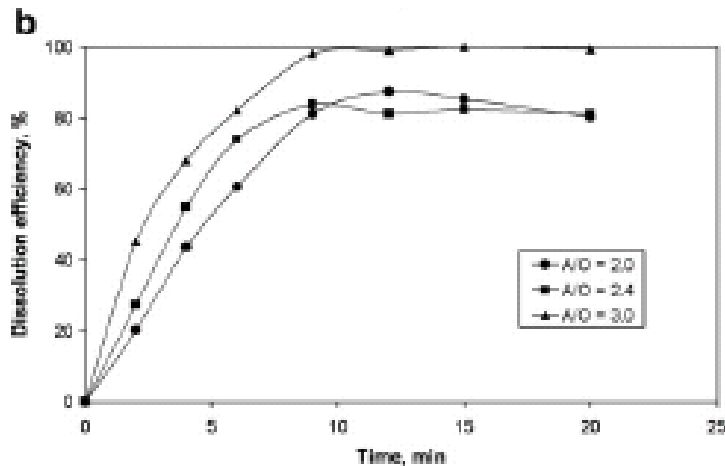


Reductive leaching

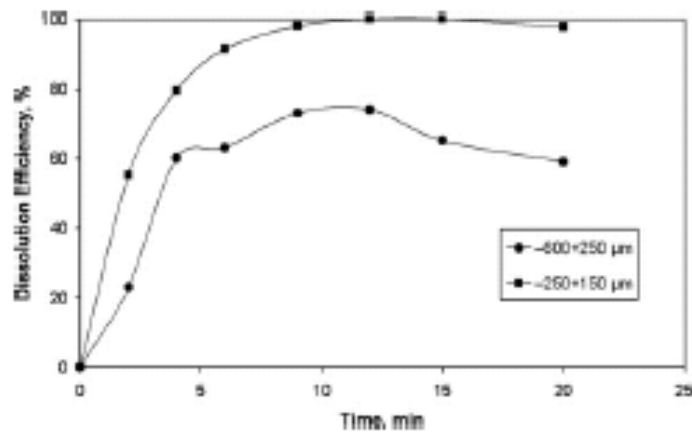
- Alternative to high temperature reductive roasting.
- MnO_2 ore is dissolved directly in dilute sulphuric or hydrochloric acid in the presence of a suitable reducing agent, e.g.: sulphur dioxide, ferrous sulphate or ferrous chloride, hydrogen peroxide, elemental iron, cane molasses, etc.
- Standard leach tank design with pre-wetter, agitator and ventilation.
- Process efficiency is affected by temperature, particle size of ore, concentration of reducing agent, and concentration of acid.



Reductive leaching – test results example



Effect of acid to ore (A/O) molar ratio on dissolution efficiency of manganese dioxide. 20°C, particle size - 250+150µm, iron to ore (I/O) molar ratio 0.8.



Effect of ore particle size on dissolution efficiency of manganese dioxide. 20°C, A/O = 4.0, I/O = 2.0.

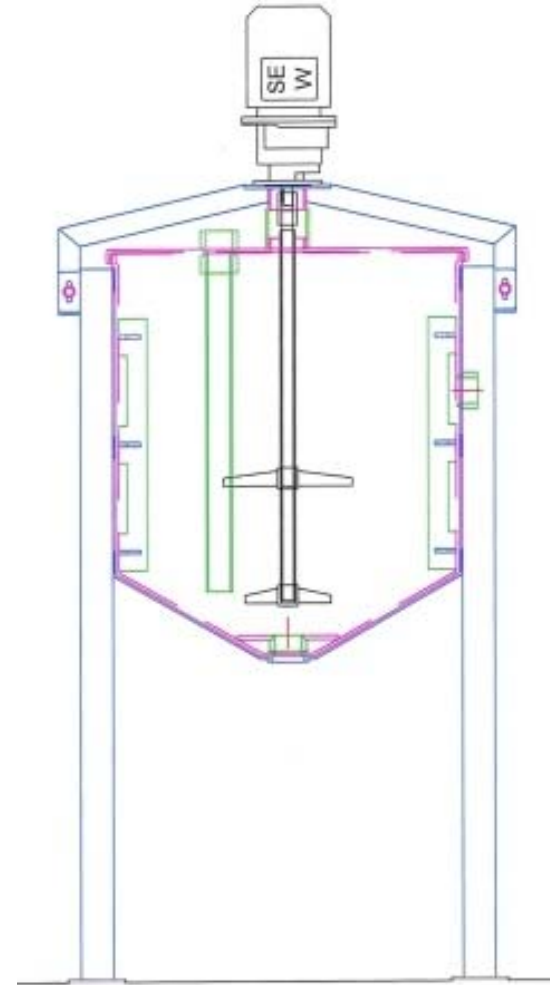
Experimental Condition	Tests by Bafghi <i>et al</i>	Tests by Zakeri <i>et al</i>
Reductant used	Sponge iron powder	Ferrous ion
Temperature	20°C	20°C
Particle size of solids	-250+150 µm	-250+150 µm
H ₂ SO ₄ /MnO ₂ molar ratio	3.0	3.0
Fe/MnO ₂ molar ratio	0.8	2.4
Mn dissolution efficiency after 10mins	98%	80%
Maximum dissolution efficiency	100% (15mins)	92% (30mins)

Source: Bafghi, M.S., Zakeri, A., Ghasemi, Z., Adeli, M., 2007. Reductive dissolution of manganese ore in sulphuric acid in the presence of iron metal. *Hydrometallurgy* 90 (2008), 207-212.


Reductive leaching

Disadvantages:

- The relative low pH that is necessary to obtain dissolution of the Mn will leach out more impurities compared to conventional oxidative leaching.
- The access to and cost of suitable reductants are key limitations to this process:
 - SO_2 results in need for a manganese sulphate bleed stream to manage the sulphate mass balance
 - Fe^{2+} will precipitate when pH is lifted after leach, to recover the Fe^{2+} will require roasting of the hydroxide precipitate
 - Scrap iron does not have sufficient surface area and atomised or sponge iron is expensive.



Summary

- Most of the manganese ores of the world are oxide minerals that are not soluble due to the higher oxidation state. This includes the high grade (>40% Mn) ore produced in Australia and South Africa.
 - Ore choices for a producer of EMM or EMD:
 - Use low-grade carbonate ore without any need for reduction.
 - Use high-grade oxide ore but add a reduction step before leaching.
 - Various different technologies can be employed to achieve reduction of oxide ore, each has benefits and disadvantages.
 - Laboratory or pilot scale testing of an ore type is needed before the optimal technology choice can be made.
 - Availability of accurate ore mineralogy data is sometimes limited.
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