锰矿还原技术

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- 哪种还原技术适合电解锰或电解二氧化工艺流程?
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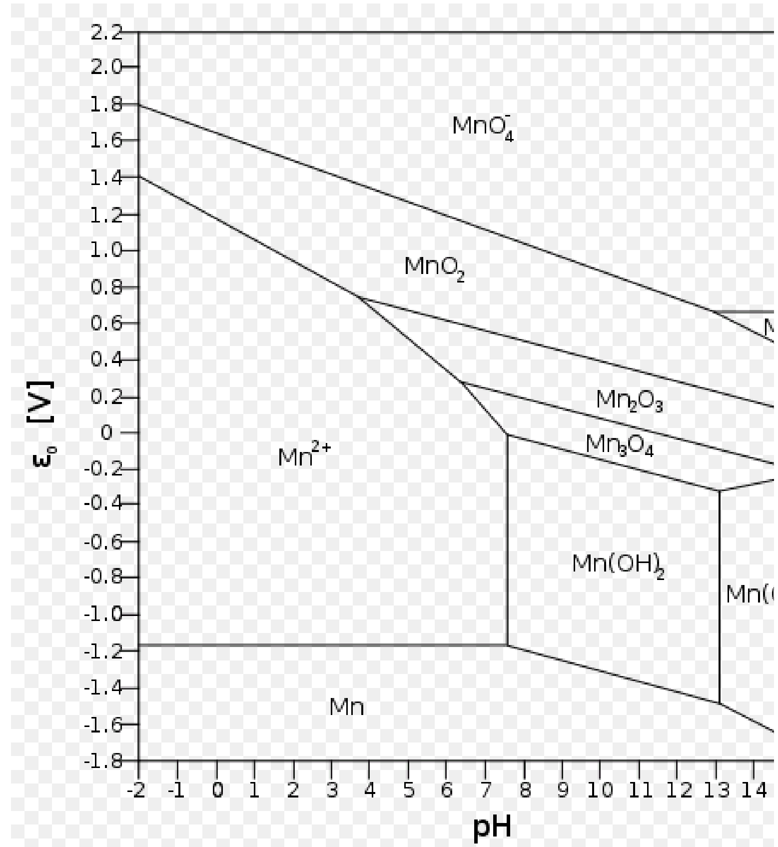
- 摘要

EMM and EMD production requires soluble manganese ore电解金属锰和电解二氧化锰生产需要可溶性锰矿

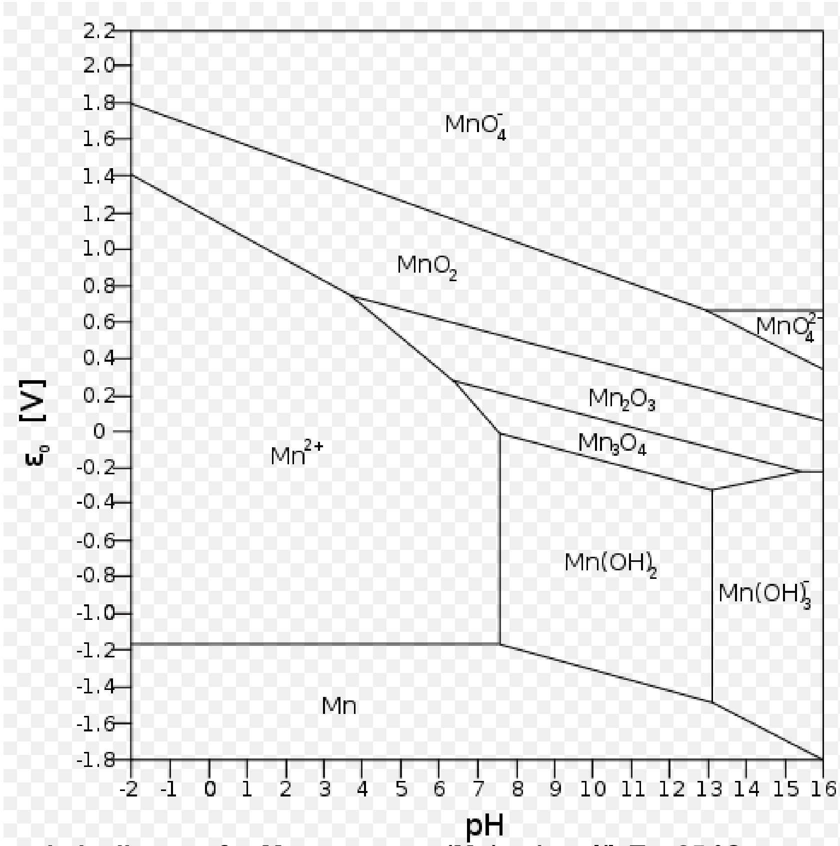
- Hydrometallurgical process route to obtain high purity end product - needs ore that is soluble in sulphuric acid.
- 湿法工艺生产工艺，以获得高纯度的产品 - 需要矿石在硫酸中溶解。
- The most stable oxidation state for manganese is +2, which has a pink to red colour. This is also the most soluble state.
- 锰最稳定的氧化态是+2，呈粉红色或红色，这也是最可溶性的状态。



Pourbaix diagram for Manganese: c(Mn) = 1 mol/l, T = 25 °C

EMM and EMD production requires soluble manganese ore电解金属锰和电解二氧化锰生产需要可溶性锰矿

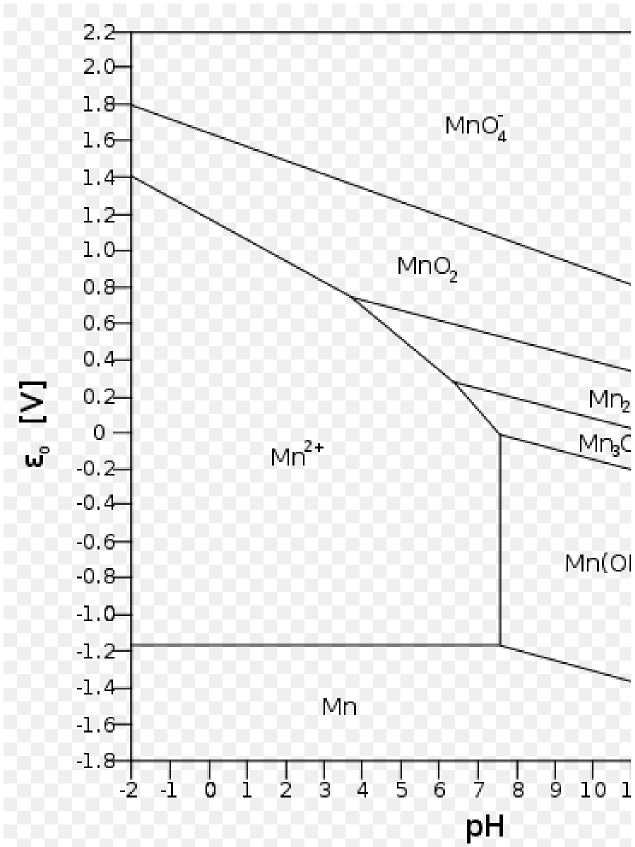
- This oxidation state is seen in the mineral rhodochrosite, $MnCO_3$, or manganese(II) carbonate. Ore containing this mineral can be leached as is.
- 二价氧化状态的锰矿，即碳酸锰矿石方可作为矿物浸出。 However, most ores of manganese don’t contain manganese(II) but higher oxides, which are **not** soluble:
- 然而，大多数二价锰矿石不含在高品位矿中，这种锰矿不溶于酸:



Pourbaix diagram for Manganese: c(Mn) = 1 mol/l, T = 25 °C

EMM and EMD production requires soluble manganese ore 电解金属锰和电解二氧化锰生产需要可溶性锰矿

MnO_2 – pyrolusite – manganese (IV)
Mn_2O_3 – bixbyite – manganese (III)
Mn_3O_4 – hausmannite – manganese (II,III)
Mn_7SiO_{12} – braunite – manganese (II,III)
[Braunite also contains Ca in some deposits]
MnO_2 –软锰矿 –四价锰
Mn_2O_3 –铁锰矿 – 三价锰
Mn_3O_4 –hausmannite –二、三价锰
Mn_7SiO_{12} – braunite –二、三价锰
[Braunite含钙]



Pourbaix diagram for Manganese: c(Mn) = 1 mol/l, T = 25 °C

氧化矿浸出前必须还原：加热和添加还原剂Oxide ore mus be reduced before leaching: add heat and a reductant

1. 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. 1. 较高的氧化态（四价和三价）的锰矿，必须使用合适的还原剂 - 氢、碳或其化合物还原成二价。

2. The temperature must be increased to over ~850˚C before the reactions will take place. 2. 温度必须提高到了～850˚C反应才会发生。

3. 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. 典型的还原剂是烟煤，重燃料油，天然气或液化石油气。该气体还原剂必须在还原温度下反应。较高级的是碳氢化合物，例如：煤油。但首先必须找到了破解低链分子。

氧化矿浸出前必须还原：加热和添加还原剂

4. 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.

4. 还原剂的使用可能大不相同，但首先必须计量和配额，以还原成二氧化锰。还原剂浓度可通过多种途径控制，如通过监测出口气体成分或排放固体锰含量等方法。

5. The sequence of reduction is $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$. In each step another mole of oxygen is removed.

5. 还原的顺序是 $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$。在每个步骤中氧被逐一去除。

氧化矿浸出前必须还原：加热和添加还原剂

6. 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.

6. 还原后的矿石必须在非氧化性气氛（惰性）下冷却，以防止MnO重新二次氧化。最后的排放的温度必须在100˚C以下或更低。

7. Another term for reduction is roasting.

7. 还原的另一个术语是焙[bèi]烧。

典型的还原反应Typical reduction reactions

Reductant: hydrogen

$2MnO_{2(s)} + H_{2(g)} \rightarrow Mn_2O_{3(s)} + H_2O_{(g)}$

$3Mn_2O_{3(s)} + H_{2(g)} \rightarrow 2Mn_3O_{4(s)} + H_2O_{(g)}$

$Mn_3O_{4(s)} + H_{2(g)} \rightarrow 3MnO_{(s)} + H_2O_{(g)}$

Reductant: carbon monoxide

$4MnO_{2(s)} + 2CO_{(g)} \rightarrow 2Mn_2O_{3(s)} + 2CO_{2(g)}$

$3Mn_2O_{3(s)} + CO_{(g)} \rightarrow 2Mn_3O_{4(s)} + CO_{2(g)}$

$Mn_3O_{4(s)} + CO_{(g)} \rightarrow 3MnO_{(s)} + CO_{2(g)}$

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.

还原剂：氢

$2MnO_{2(s)} + H_{2(g)} \rightarrow Mn_2O_{3(s)} + H_2O_{(g)}$

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还原剂：一氧化碳

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$Mn_3O_{4(s)} + CO_{(g)} \rightarrow 3MnO_{(s)} + CO_{2(g)}$

还原反应的大部分是放热，上述反应通常是从800˚c开始。

典型的还原反应Typical reduction reactions

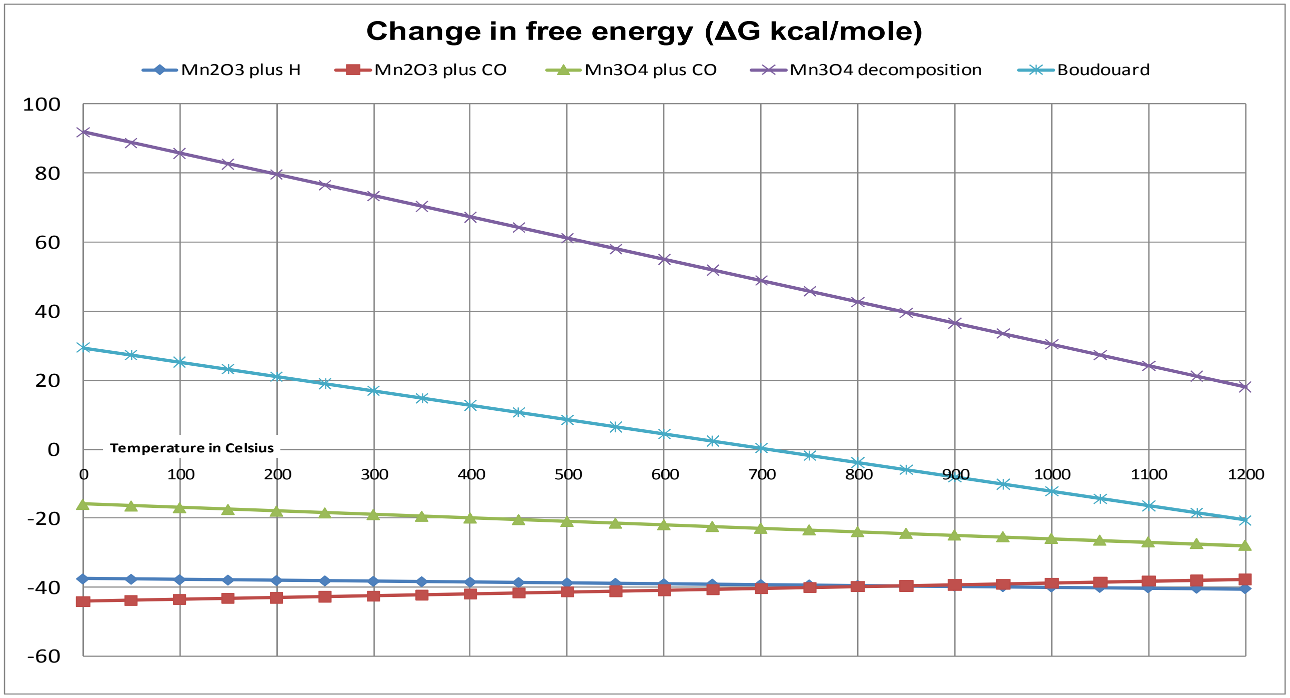
- Other typical reactions during ore reduction:
  - ❖ The *Boudouard* reaction: $CO_{2(g)} + C_{(s)} \leftrightarrow 2CO_{(g)}$
  - ❖ The water gas formation reaction $H_2O_{(g)} + C_{(s)} \leftrightarrow CO_{(g)} + H_{2(g)}$
  - ❖ These will convert solid reductant into gaseous reductant or vice versa.
  - ❖ 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.

- 其他典型的还原反应：
  1. 布德瓦反应: $CO_{2(g)} + C_{(s)} \leftrightarrow 2CO_{(g)}$
  2. 水气生成反应 $H_2O_{(g)} + C_{(s)} \leftrightarrow CO_{(g)} + H_{2(g)}$
  3. 固体还原剂将转化为气态。
  4. 另外，MnOOH转化成Mn_2O_3但不会消耗任何还原剂。
  5. 较高的碳氢化合物裂解不消耗还原剂或氧气。

典型的还原反应Typical reduction reactions

- 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.
- 如果还原剂是天然气，由于矿石粒度非常小，矿石和天然气良好的表面之间的接触能有效的提高还原反应。所有试剂必须在启动温度下反应，如温度较低则需要更长的还原时间。

锰矿热力学还原Thermodynamics of Mn ore reduction



1. 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. 反应发生的前提是他们导致全部反应物和产品自由能量的降低。自由能量是温度的一个作用，且对每一个反应都是独特的。

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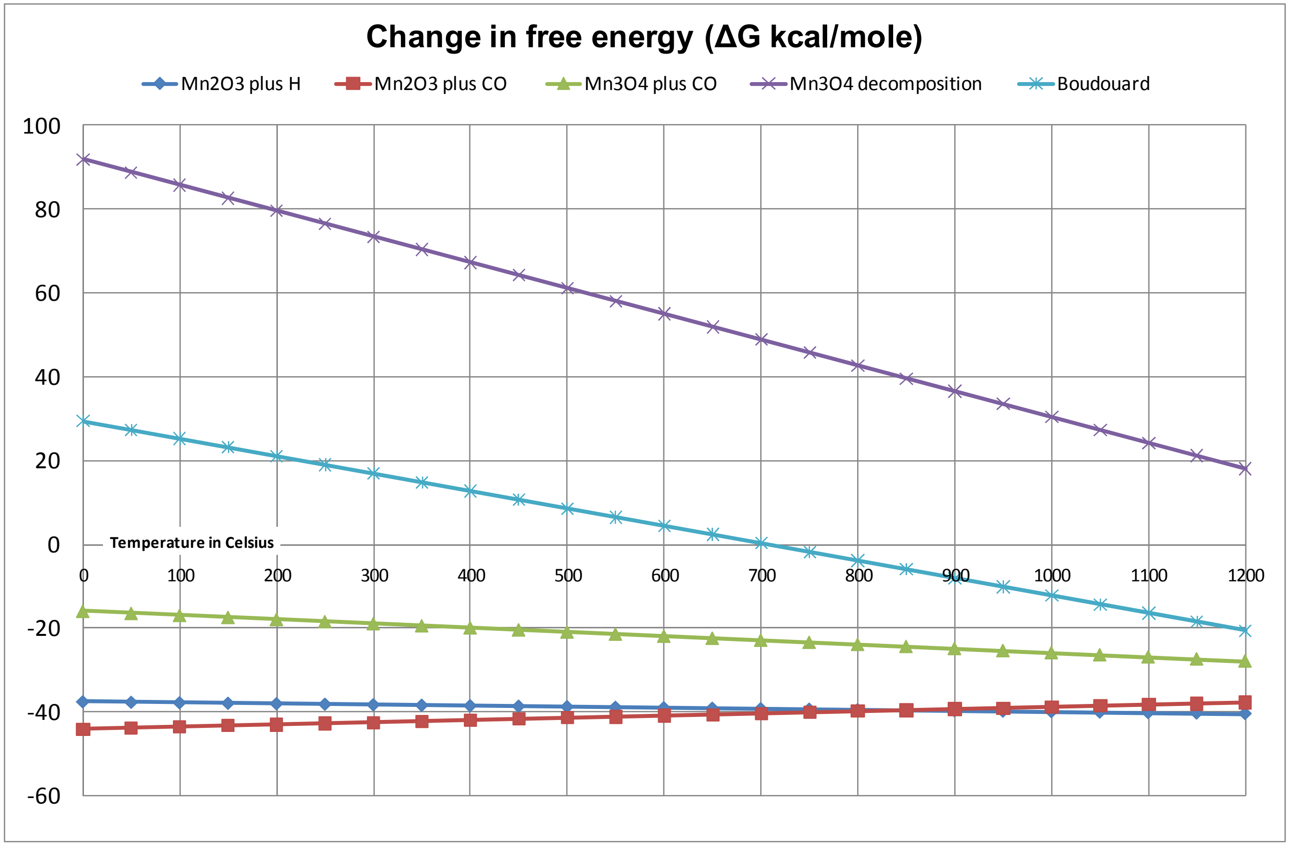


2. The activation energy for each reaction must also be overcome before the reaction starts to take place, even if it is an exothermic reaction.

- 每一个反应的激活能量必须在反应开始发生时被客服，即便是放热反应。

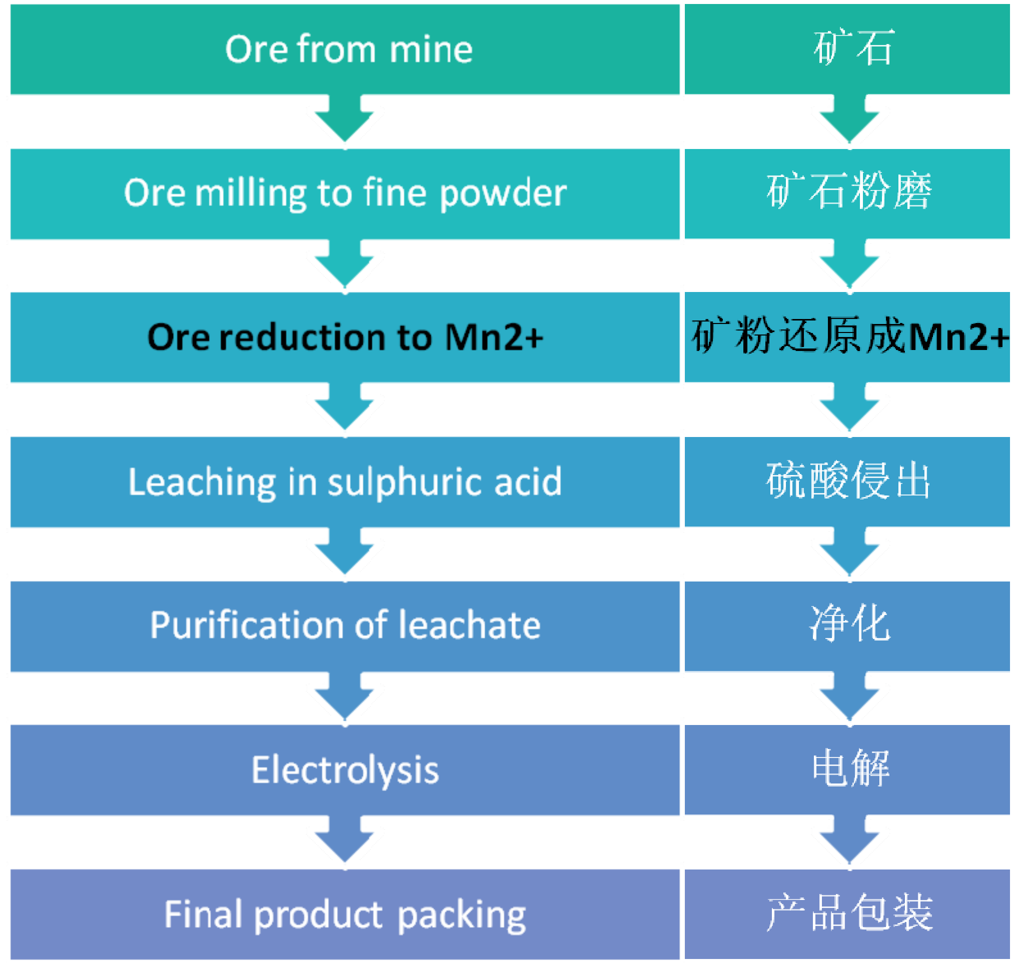
增加的工艺流程Additional step in process flow

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

- 实现矿石还原工艺的不同技术：
  - 反射炉
  - 煅烧
  - 微波炉
  - 堆还原
  - 竖炉
  - 单个或多个平炉
  - 流化床反应器
  - 以上技术定制设计/组合Different

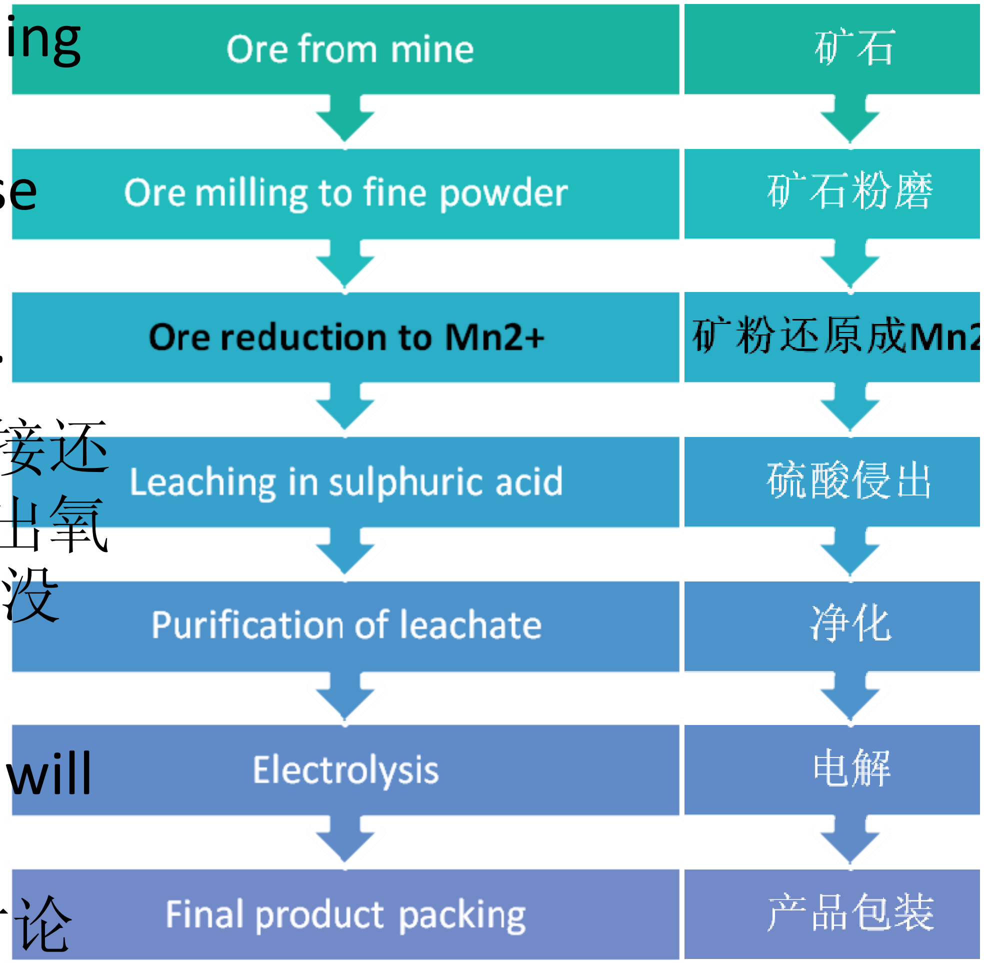
典型的电解锰或电解二氧化锰生产工艺流程



增加的工艺流程Additional step in process flow

- 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.
- 另一种可能性是使用氧化矿直接还原浸出（即直接从高品位矿浸出氧化态为2 +）。在这种情况下，没有额外的还原处理步骤。
- The balance of this presentation will briefly touch on some of these technologies.此文稿将概括地讨论一些技术。

典型的电解锰或电解二氧化锰生产工艺流程



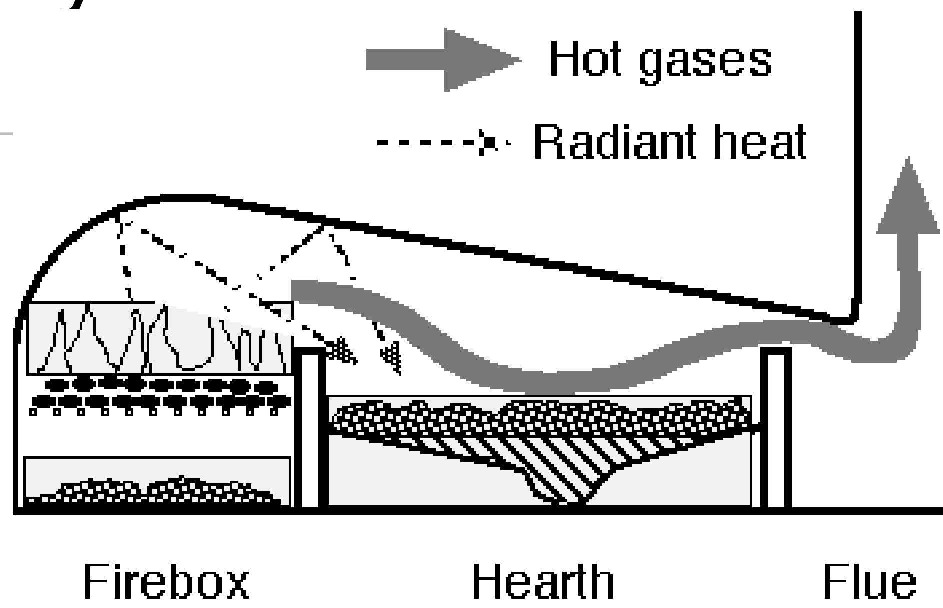
反射炉Reverberatory furnace

1. The ore is separated from the fuel but is in contact with the combustion gases. Bituminous coal is a typical fuel.

1. 矿石与被燃料是分开的，但与燃烧气体接触。典型的燃料是烟煤。

2. 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.

2. 这是一种旧技术。中世纪用于铜或铅工业。18世纪在日本用于铁，后被高炉取代。



缺点:Disadvantages:

1. Difficult to maximise heat transfer due to the spatial separation of the burning fuel and the ore.1. 由于燃料和矿石空间分离，难以最大限度地传热。
2. Exhaust gas chemistry must be controlled to maintain a reducing mixture in the chamber.2. 废气排放必须控制以保证在炉内的还原混合。
3. Poor contact between ore and reductants due to ore being a stationary bed.

3. 矿石和还原剂的接触率低, 因为矿石位置固定， 。

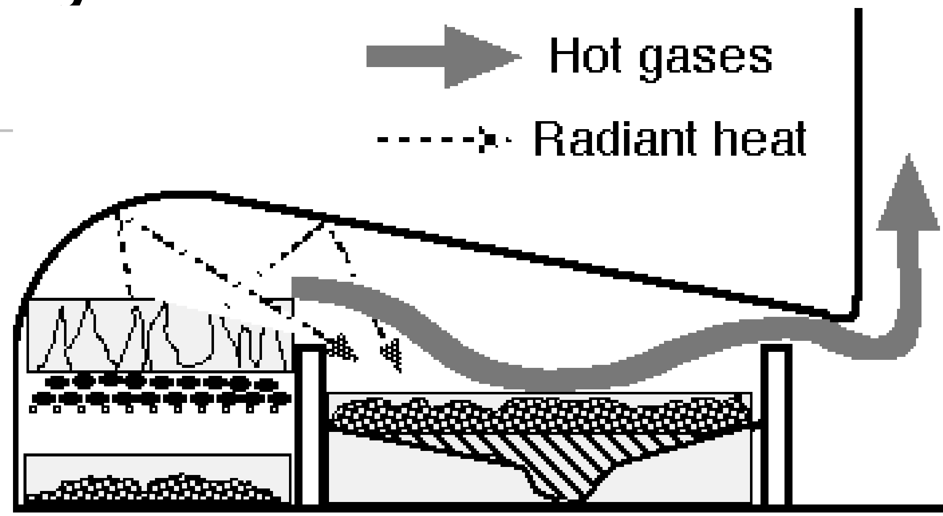
反射炉Reverberatory furnace

3. Currently used mostly in secondary aluminium (scrap) industry, for smelting before die-casting. 目前主要用于铝（废料）压铸前冶炼。

4. Used in China at a number of ElMn factories to reduce Mn oxide ore.

在中国一些电解锰厂用于氧化锰矿石还原。

5. If the exhaust gas is not collected and combusted fully, this process is potentially highly polluting.如果废气的收集和燃烧不充分，这个工艺是潜在的高污染。



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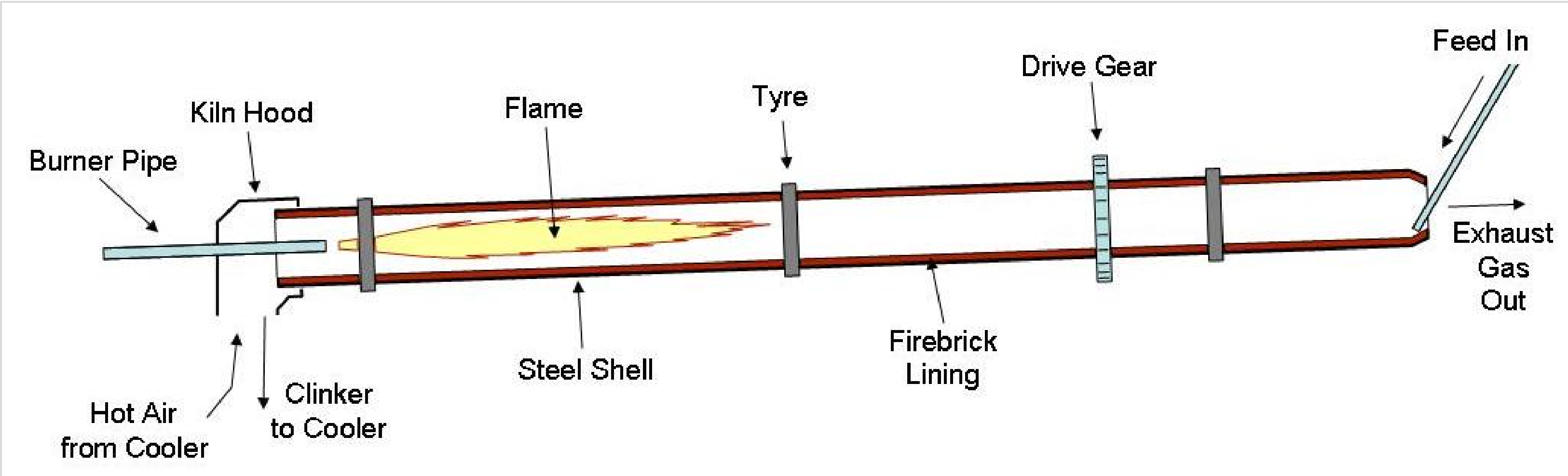
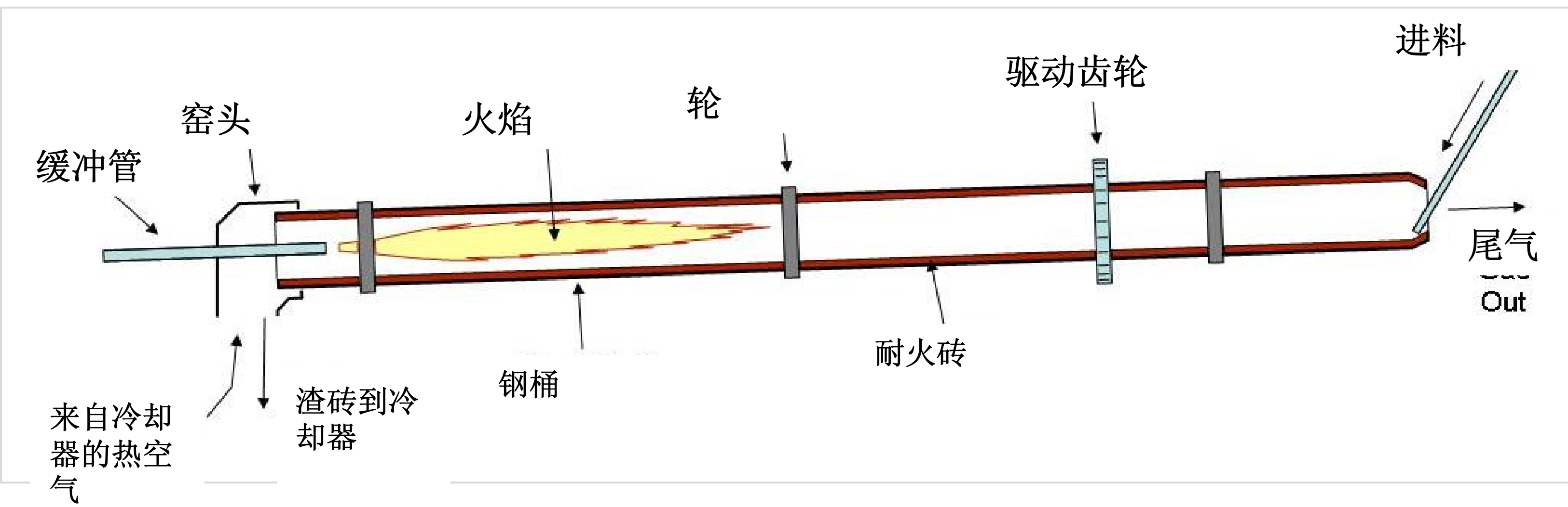
煅烧Calcining





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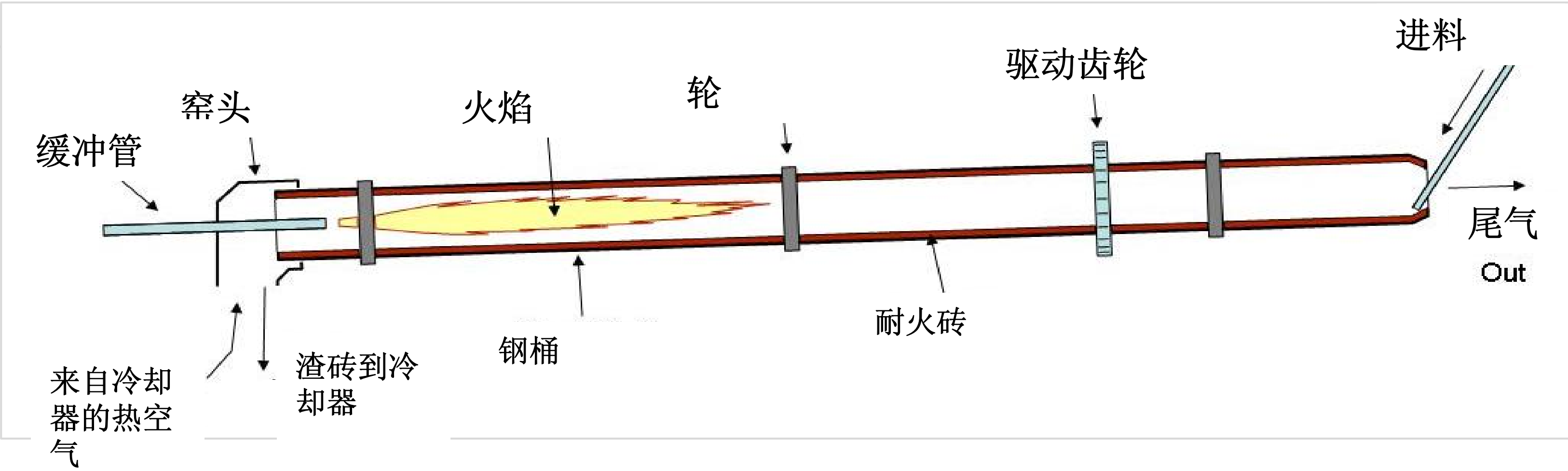
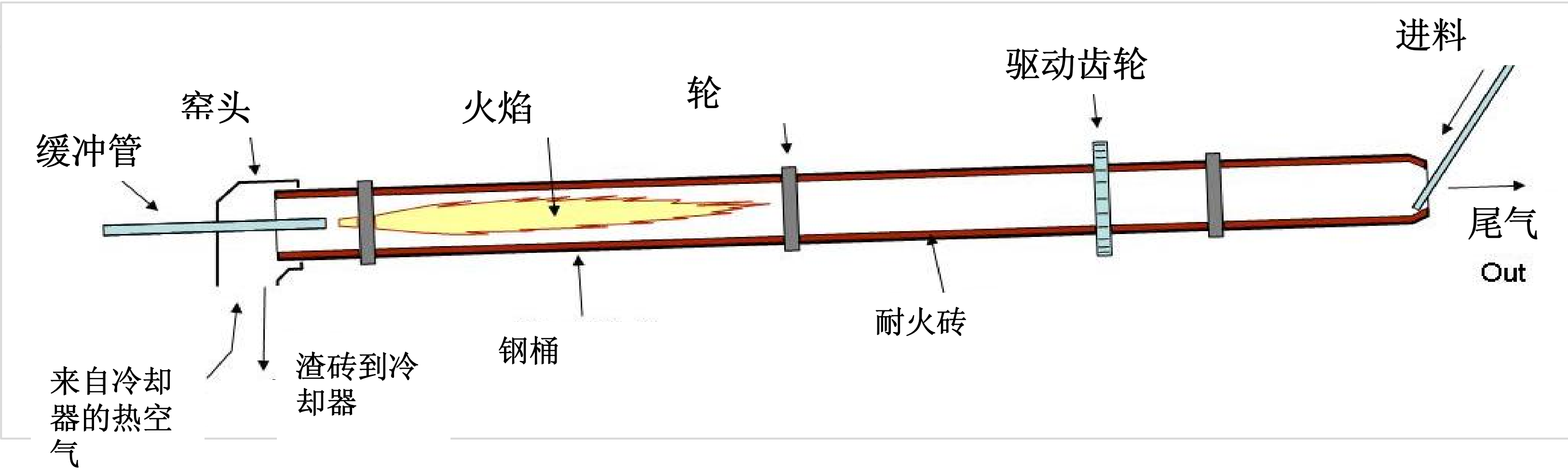


- 回转窑以一定的倾角工作，窑内锰矿和其它还原剂混合在一起。连续作业。典型还原剂为煤和重炉油。
- 窑内的料的加热可以直接通过内部火焰或间接通过管外的电力来实现。
- 控制窑内的空气非常重要，以避免还原剂燃烧。温度和氧气的水平应该只将还原剂破裂。

- 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.

煅烧Calcining



- 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.

- 煤气和料可以是同向的，也可以是反向，取决于还原剂和加热方式。尾气可以收集预热炉料。
- 由于旋转可实现良好的热传导和炉料和煤气的良好接触。矿石的还原从而发生。

缺点: **1.** Expensive to install and drive system require good maintenacnce安装费用高，驱动系统需要良好维护

- Electricity requirment are high电力要求高-如不使9用火，需要驱动系统和加热元素

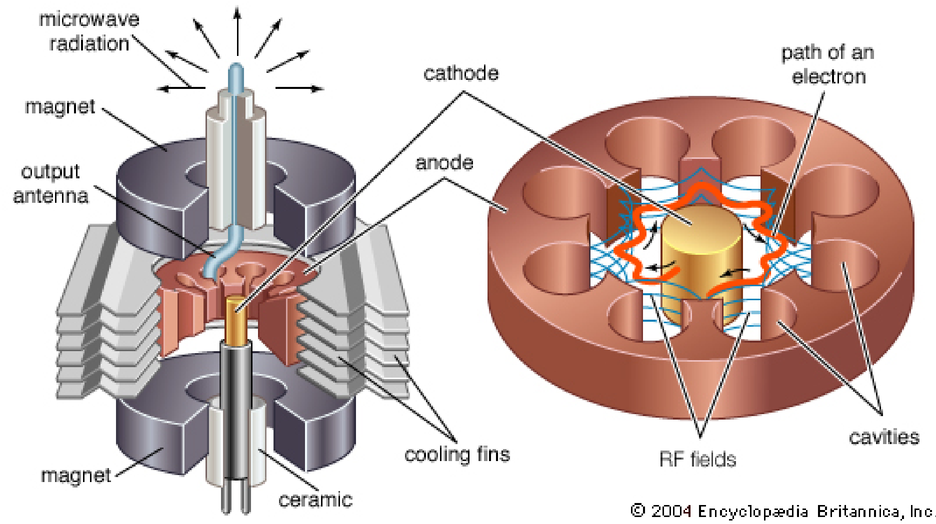
微波炉Microwave furnace

1. 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.

1. 和煅烧一样的院里和设置，但热源是微波。还原剂（煤或油）需要和矿一块加入到旋转管中。

2. 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.

2 效率取决于磁电管的设计和基座的好坏-一种暴露在微波下就会加热的材料。石墨是一种好的基座。空气必须和煅烧一样加以控制。



磁电管内部– 与国内或工业设备设计相同

缺点:

- 新工艺，需要证明对锰行业工业化生产是可行的。
- 还原剂的选择有限，因为需要基座且不要热气流。

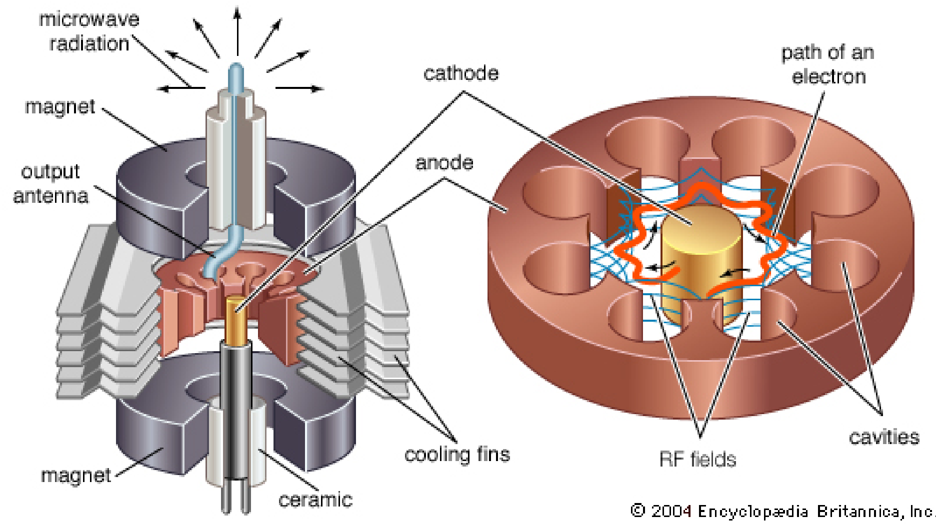
微波炉Microwave furnace

3. Microwaves heat only the substance being reduced and not the atmosphere around it or the furnace walls. This makes is highly energy efficient.

3. 微波炉只加热需还原的物质，并不加热周围的空气或炉壁。这使得它非常节能。

4. With a smaller physical footprint and a substantially smaller carbon footprint, microwave furnaces offer far lower operating costs than calciners or reverberatory furnaces.

4.体积较小，碳需求少，微波炉比煅烧炉或反射炉运行成本低很多。



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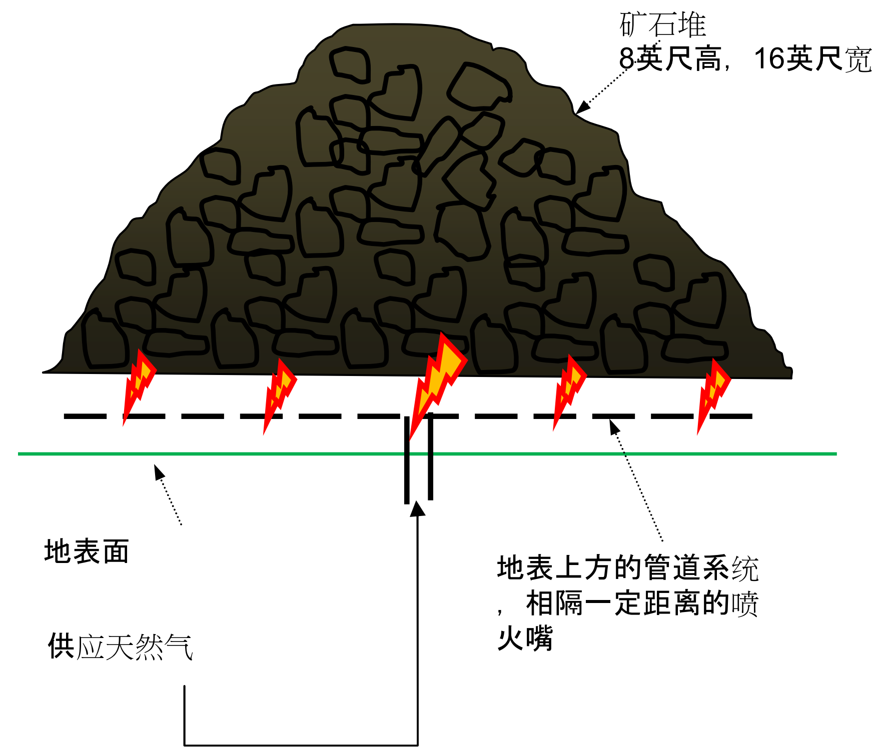
Heap reduction (also called pile roasting)
堆法还原 (也称堆式焙烧)

1. Simplest method of reduction available – no significant equipment installation required, only gas piping system.

1. 这是目前最简单的还原方法-不需要太多设备安装，只有燃气管道系统。

2. This method was used at Kerr-McGee's EMM factory in USA (closed in 2001).

2. 这种方法在美国的Kerr-McGee的电解锰厂使用过（2001年关闭）



缺点：
- 污染控制几乎不可能实现
- 受恶劣天气影响
- 1-2天的保留时间
- 不能用粉矿
- 较热地方形成熔块

Heap reduction (also called pile roasting)
堆法还原 (也称堆式焙烧)

3. Natural gas is the source of heat and the reductant. Sub-stoichiometric combustion of the gas provides heat and leaves hydrocarbons available for reduction.

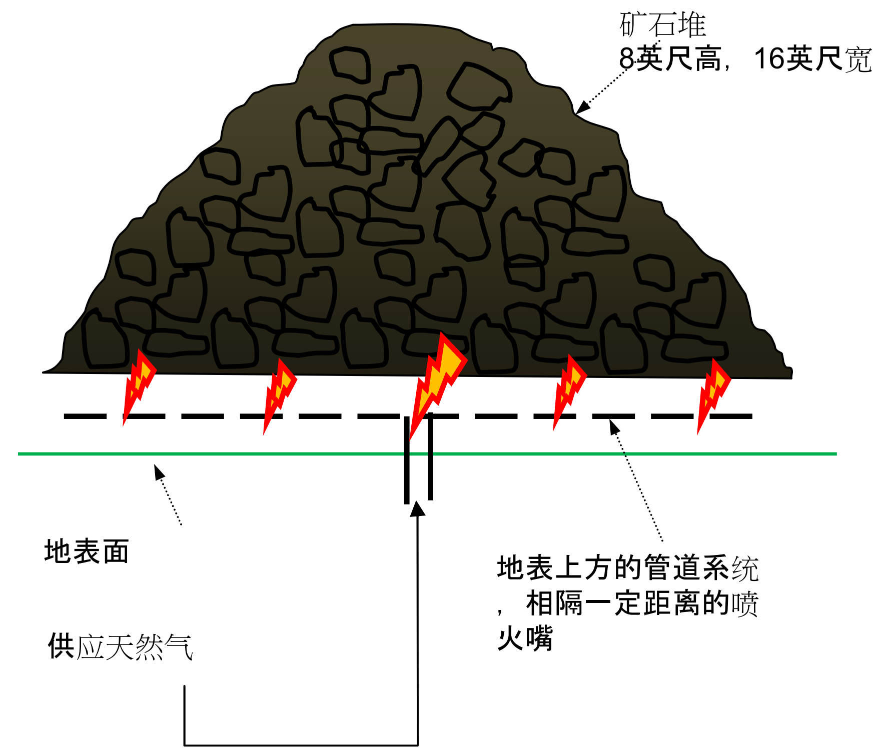
3. 天然气为热源和还原剂。天然气的亚燃烧提供热量并使碳氢化合物还原。

4. Temperature inside pile must be in the 700° to 900°C range. Most suitable for high grade ore – exothermic reactions.

4. 矿石堆内的温度必须在700-900摄氏度之间。最适合高品位锰矿-放热反应。

5. Batch process, usually followed by polishing step in vertical bins.

5. 批次过程，通常之后是磨料步骤



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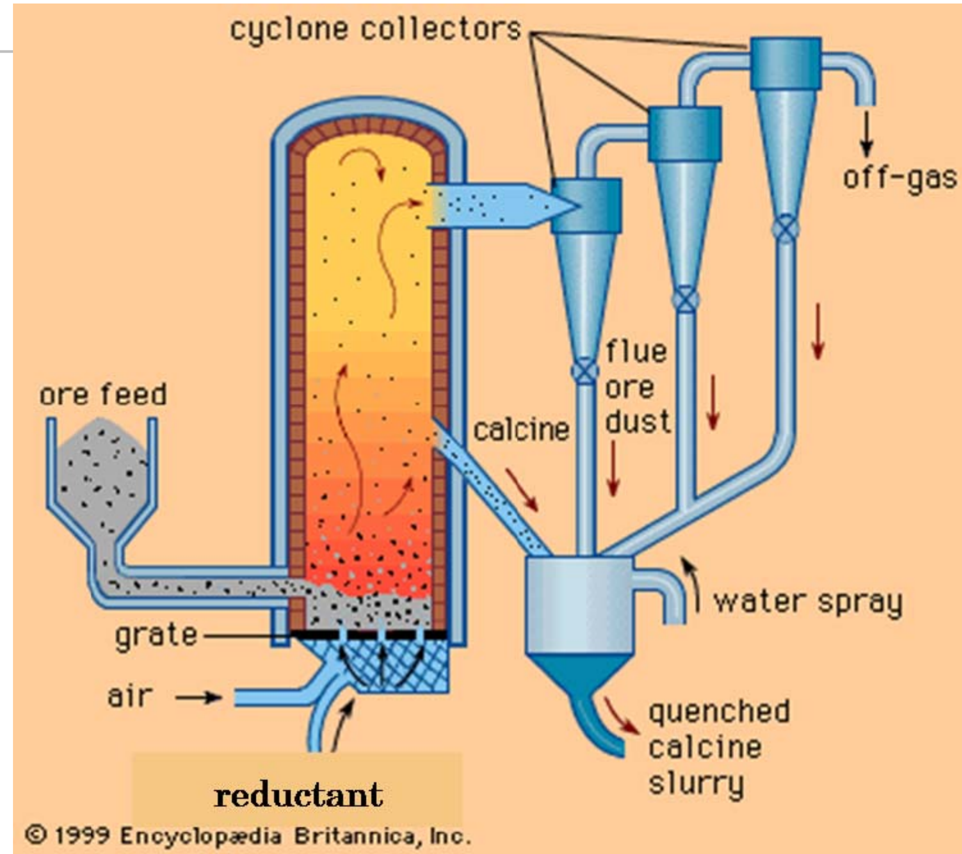
流化床反应器Fluidized bed reactor

1. Air stream is passed through a perforated plate at the bottom of a vertical reaction chamber, into which ore is fed on continuous basis.

1. 空气从垂直反应室底部的一个冲孔板通过，进入放有矿石的炉内。

2. Fine particles suspended in hot gas stream allows complete reduction.

2. 细小颗粒在热气中悬浮可以达到完全还原。



Disadvantages:

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

缺点：

- 安装费用高，需要备用鼓风机
- 开机到稳定运行耽搁时间厂
- 控制粒度大小非常重要

流化床反应器Fluidized bed reactor

3. Quenched slurry can be pumped directly to leach tanks.

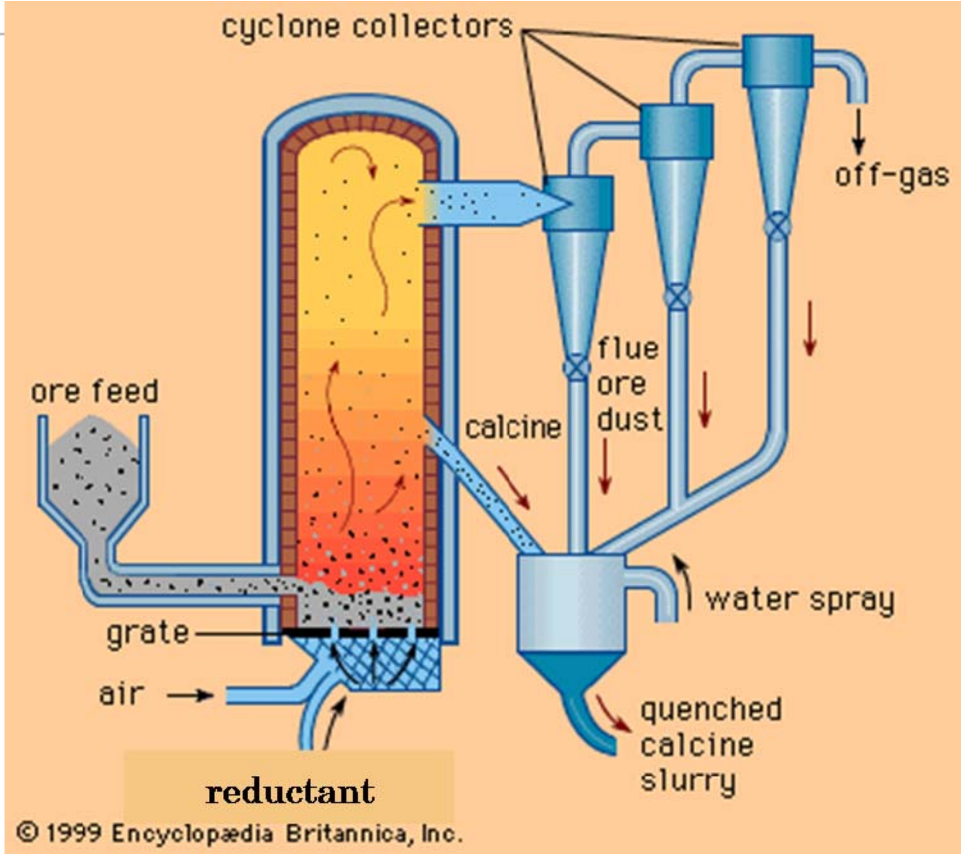
3. 焙烧的灰可以直接泵送到滤池中

4. Reductant can be gas or coal partially combusted in separate chamber.

4. 还原剂可以是煤气或另一个燃烧室里部分燃烧的煤炭。

5. Efficient use of reductant, recirculation.

5. 有效使用还原剂，再循环



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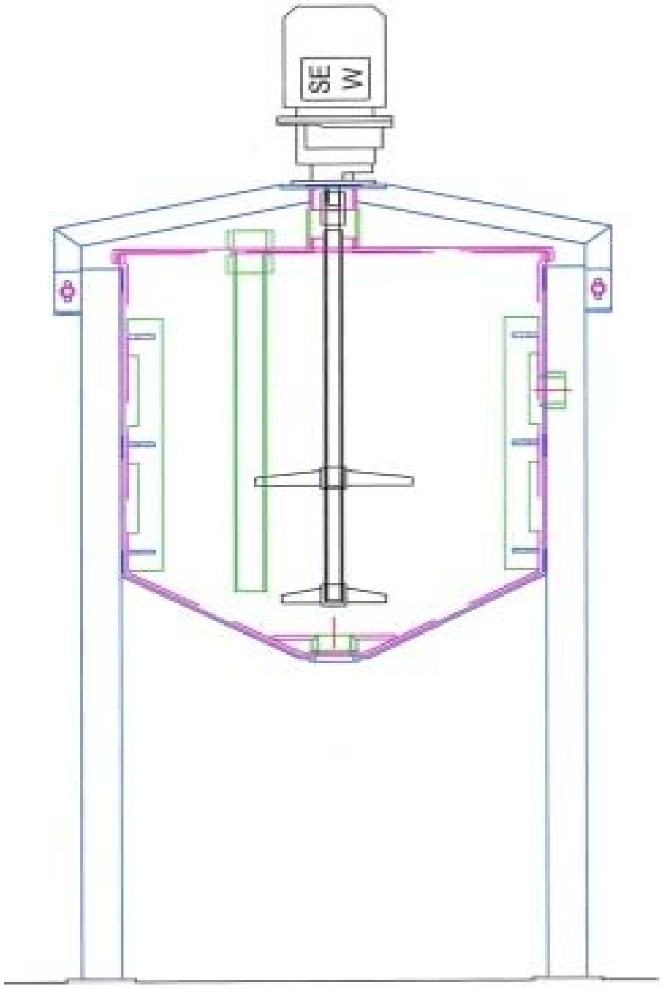
还原浸出Reductive leaching

1. Alternative to high temperature reductive roasting.

1. 替代高温还原焙烧。

2, 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.

2, 氧化锰矿石直接溶解在在加有还原剂的硫酸或盐酸。.



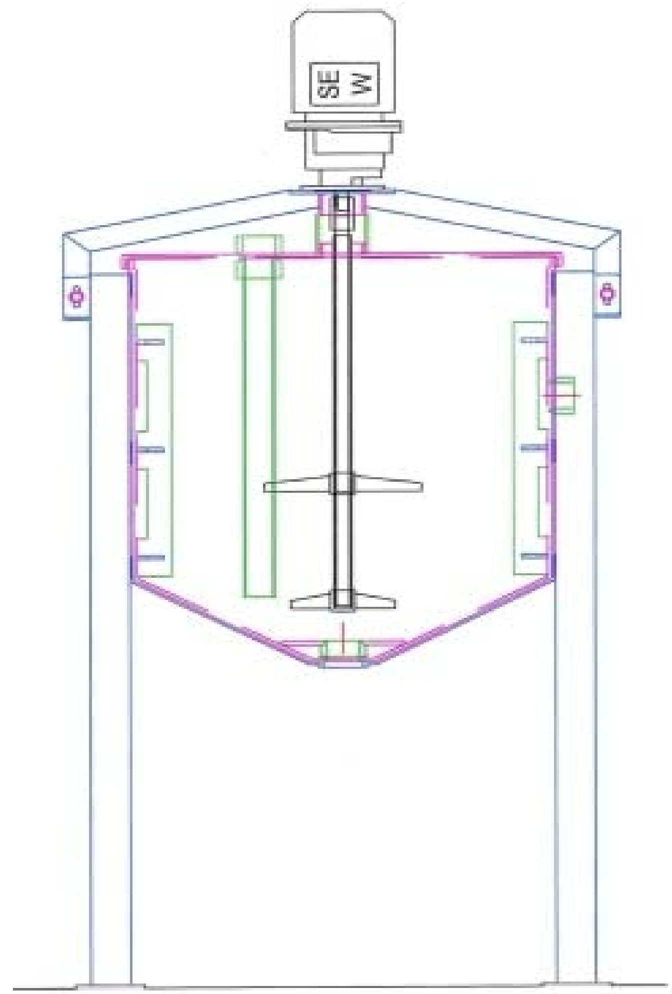
还原浸出Reductive leaching

3. Standard leach tank design with pre-wetter, agitator and ventilation.

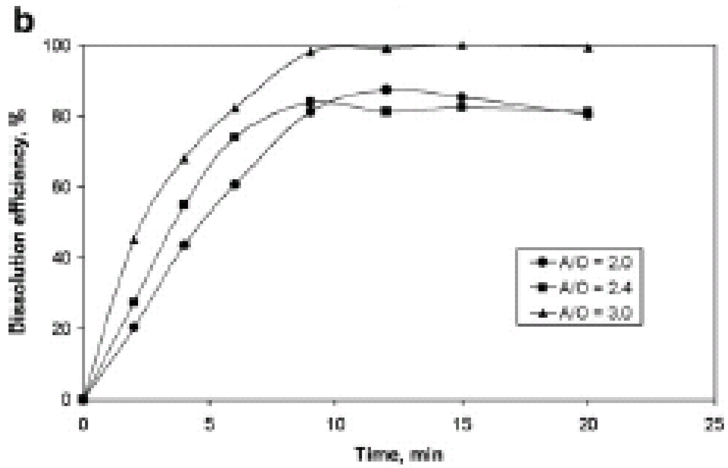
3. 标准的浸出池，装有预湿装置，搅拌器和通风装置。

4. Process efficiency is affected by temperature, particle size of ore, concentration of reducing agent, and concentration of acid.

4. 处理效率受温度、矿石粒度、还原剂浓度和硫酸浓度影响。

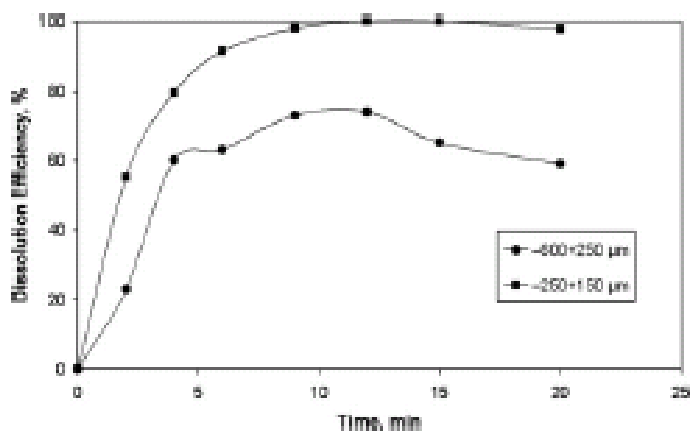


还原浸出 – 实验结果
Reductive leaching – test results example



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

酸对矿石**(A/O)**摩尔比率对 二氧化锰溶解效率的影响。 **20˚C,** 粒度 **-250+150** 微米**,** 铁对矿石摩尔比率 **(I/O) 0.8.**



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

矿石粒度对二氧化锰溶解效率的影响 **20˚C, A/o** 摩尔比率是**= 4.0, I/O**的摩尔比率 **=2.0.**

还原浸出 – 实验结果
Reductive leaching – test results example

Experimental Condition	Tests by Bafghi *et al*	Tests by Zakeri *et al*
Reductant used	Sponge iron powder	Ferrous ion
Temperature	20˚C	20˚C
Particle size of solids	-250+150 µm	-250+150 µm
H2SO4/MnO2 molar ratio	3.0	3.0
Fe/MnO2 molar ratio	0.8	2.4
Mn dissolution efficiency after 10mins	98%	80%
Maximum dissolution efficiency	100% (15mins)	92% (30mins)

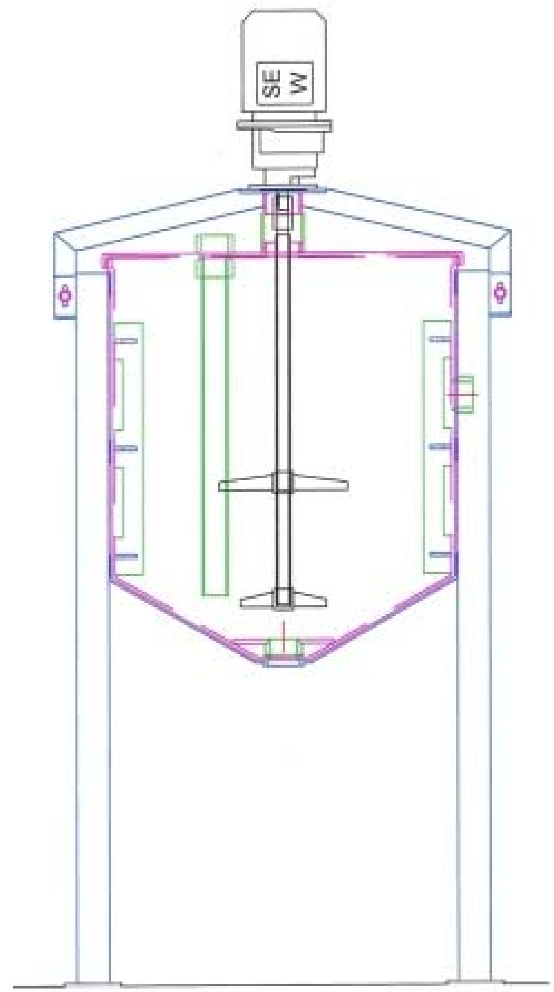
实验条件	由 Bafghi *et al测试*	由 Zakeri *et al测试*
使用的还原剂	海绵铁粉末	铁离子
温度	20˚C	20˚C
固体粒度	-250+150 µm	-250+150 µm
硫酸/二氧化锰 摩尔比率	3.0	3.0
铁/二氧化锰 摩尔比率	0.8	2.4
10分钟后锰溶解效率	98%	80%
最大溶解效率	100% (15分钟)	92% (30分钟)

来源: 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还原浸出

Disadvantages:

1. The relative low pH that is necessary to obtain dissolution of the Mn will leach out more impurities compared to conventional oxidative leaching.
1. 相比常规浸出，获取锰溶液的相对低PH值会浸出更多杂质。



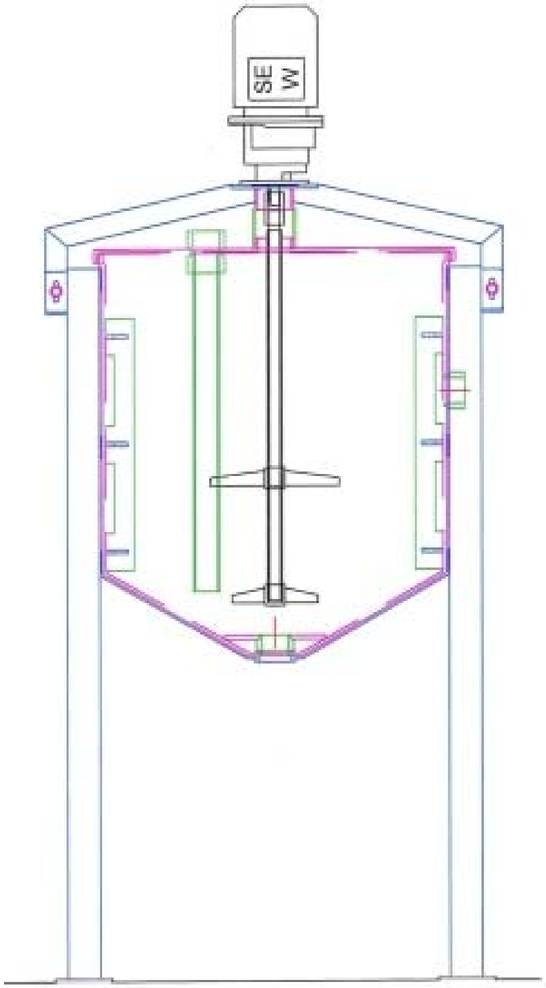
Reductive leaching还原浸出

Disadvantages:

2. The access to and cost of suitable reductants are key limitations to this process:

2.获取还原剂和其成本是这一工艺的主要限制：

- SO_2 results in need for a manganese sulphate bleed stream to manage the sulphate mass balance
- SO_2 导致需要锰盐流来控制硫酸盐平衡
- Fe^{2+} will precipitate when pH is lifted after leach, to recover the Fe^{2+} will require roasting of the hydroxide precipitate
- 二价铁在PH值升高时沉淀，回收二价铁需要对氢氧化物沉淀焙烧
- Scrap iron does not have sufficient surface area and atomised or sponge iron is expensive.
- 铁屑表面积不够，雾化铁粉或海绵铁成本太高



Summary总结

- 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.
- 世界大多数锰矿是氧化矿，由于较高的氧化态不能被溶解。这包括澳大利亚和南非的高品位矿（锰含量>40%）
- Ore choices for a producer of EMM or EMD:
- 电解锰和电解二氧化锰的矿石选择
  - Use low-grade carbonate ore without any need for reduction.
  - 使用不需要还原的低品位碳酸锰矿
  - Use high-grade oxide ore but add a reduction step before leaching.
  - 使用高品位氧化锰矿，但在浸出前增加还原步骤

Summary总结

- Various different technologies can be employed to achieve reduction of oxide ore, each has benefits and disadvantages.
- 采用不同的技术可以实现氧化锰矿还原，每一种都有优点和不足。
- Laboratory or pilot scale testing of an ore type is needed before the optimal technology choice can be made.
- 在选用一种工艺之前需要对矿石进行实验室或小规模实验
- Availability of accurate ore mineralogy data is sometimes limited.
- 准确的矿物学数据有时比较有限

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