

Extraction of Mg

Extraction of Non-Ferrous Metals



Department of MME

Details about of Mg

Atomic Number: 12

Atomic Weight: 24 amu

Density: 1.738 gm/cm³

Melting Point: 650⁰ C

Boiling Point: 1107⁰ C

Common Minerals of Mg

Dolomite – $\text{MgCO}_3 \cdot \text{CaCO}_3$

Magnesite – MgCO_3

MgCl_2 and MgSO_4 present in sea water

Brucite- $[\text{Mg}(\text{OH})_2]$

Carnallite- $(\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O})$

Olivine- $(\text{Mg}_2\text{SiO}_4)$

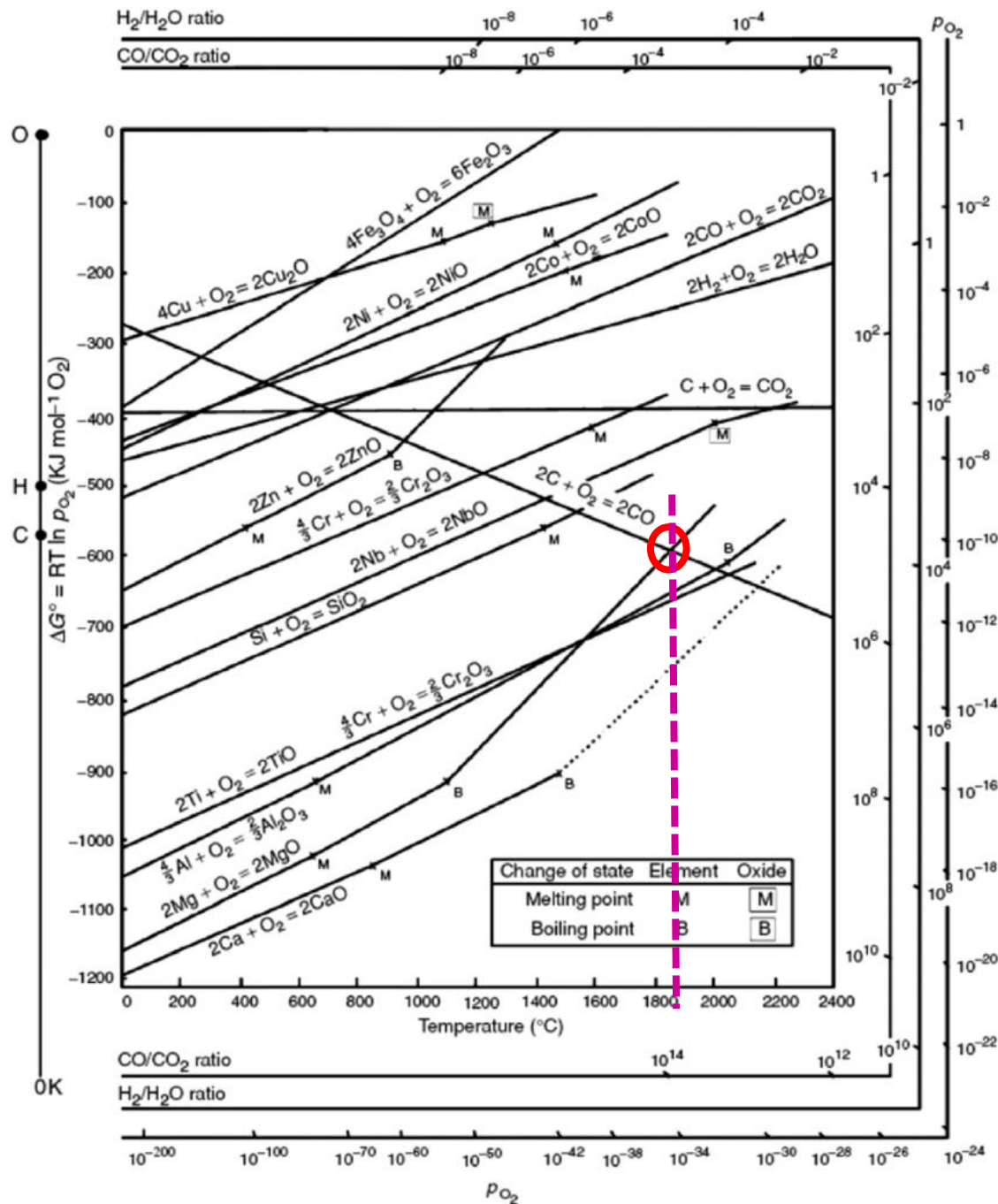
Serpentine- $(\text{Mg}_3\text{Si}_2\text{O}_7)$

Asbestos – $(\text{CaSiO}_3 \cdot 3\text{MgSiO}_3)$

Kainite- $(\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O})$

- ☐ Dolomite and magnesite are *commercial* minerals.
- ☐ Magnesium hydroxide derived from sea water have sufficiently high Mg content sand *do not require* upgradation before subsequent extraction.

Problems encountered during the extraction of Mg by Pyrometallurgical process



MgO is very stable oxide and requires $T > 1800^\circ\text{C}$ for carbothermic reduction.

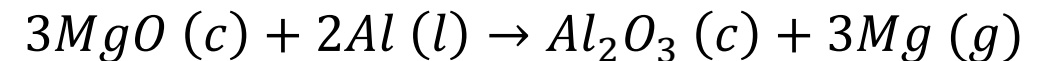
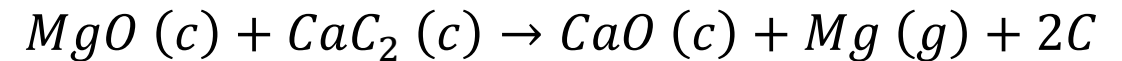
Such high temp. is not practicable with external heating.

Reduction temp. can be reduce by using vacuum to distil off the Mg and to drive the reduction reaction in forward direction.



However, it is very difficult to prevent the backward reaction, and hence carbothermic reduction is *not* commercially accepted.

Reduction of MgO by other reductants like CaC_2 and Al at 1200°C under vacuum is feasible, but not commercially attractive.



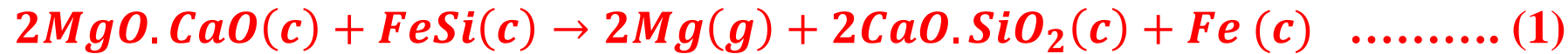
Problems encountered in Electrometallurgy viz. direct electrolysis from aqueous medium

- Mg requires 2.3V more than H_2 for deposition and the hydrogen overvoltage is not sufficiently high to overcome this voltage → hydrogen is evolved *before* magnesium can be deposited.
- To generate sufficiently high hydrogen overvoltage, *amalgam cathode* can be employed. It can serve two (2) purposes:
 1. Because of its extremely smooth surface, hydrogen overvoltage is rendered difficult.
 2. The low activity of Mg in amalgam cathode lowers the Mg deposition potential.
- However, amalgam cathode has *not* found commercially acceptable.

Extraction of Mg by Pyrometallurgical process

PIDGEON Process

- Thermodynamically pure Si can not reduce MgO when both reactant and products are in their standard state. Therefore, the Pidgeon process reduces pressure to remove the Mg vapor and drive the reduction process. In this process, calcined dolomite is briquetted with powered ferrosilicon (75% Si), and the reduction is carried out under vacuum of 0.1 mm Hg at 1100-1200°C in an externally heated retort.



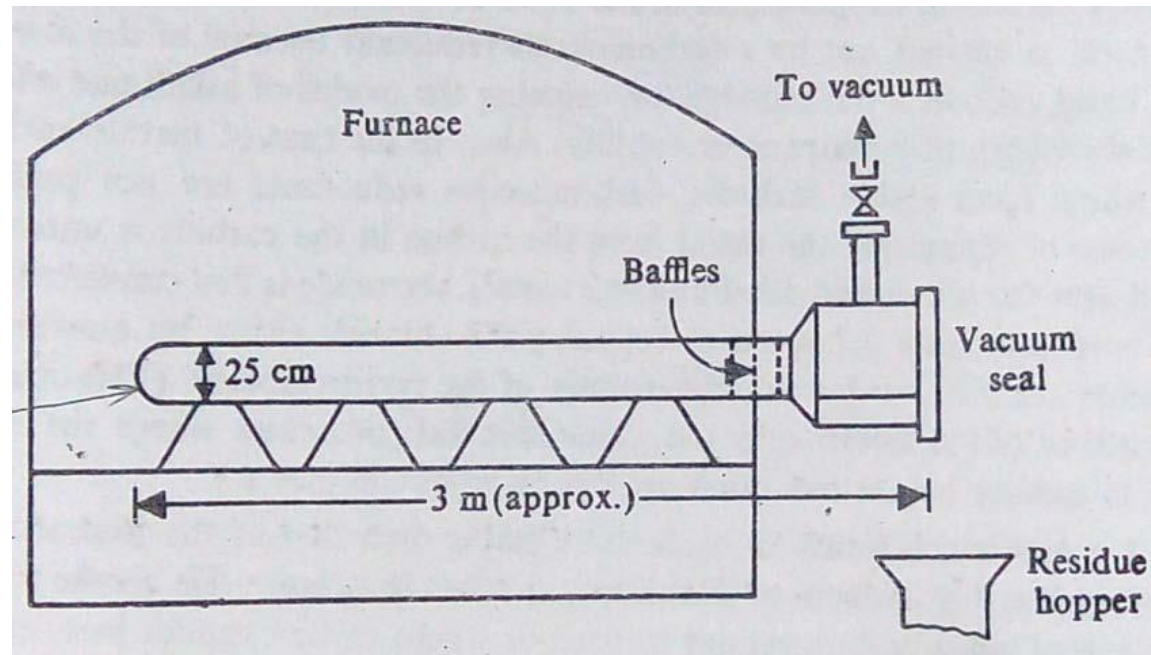
Since Mg is the only gaseous product, it can be easily removed from the reaction chamber to avoid possibility of backward reaction.

- Presence of CaO lowers the free energy of the reduction reaction. The free energies of the reactions at 1200°C:



- At 1200°C the equilibrium pressure of Mg for reaction (3) is 15 mm Hg, and to attain 1 atm. of Mg about 1700°C is required. Such high temp. is not practicable with external heating, therefore, Pidgeon process incorporates vacuum to drive the reaction (3) in forward direction.
- Reaction (3) is highly endothermic. Addition of CaF_2 and MgF_2 acts as catalyst and speeds up the evolution of Mg vapor.

PIDGEON Process (continue..)



PIDGEON Process (continue..)

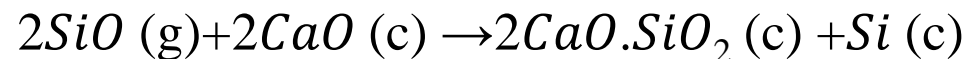
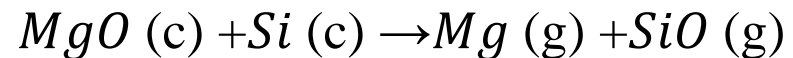
Reaction Mechanism:

The reaction occurs through *transient liquid phase* at some intermediate stages.

Distinct stages of Pidgeon process are:

- (1) The initial reaction between CaO and Fe-Si produce liquid Ca-Si-Fe alloy, which permeates the briquette and forms a metallic network. The reaction occurs at around 1000°C and mildly exothermic. The ternary alloy serves as the main reducing agent.
- (2) Mg vapors produce by reduction of MgO by Ca-Si-Fe alloy. At this stage, pressure increases rapidly and slows down the rate of reaction. The subsequent reaction rate is governed by the rate at which Mg can escape from the briquettes.

Kinetics of the reaction controlled by the presence of SiO vapor in Pidgeon process as:



N.B. Energy required in Pidgeon process (39.43×10^6 kcal/ton) is ~46% of Dow process. Because it uses high quality raw materials, no heat required to evaporate solution and no energy requirement for fused chloride electrolysis.

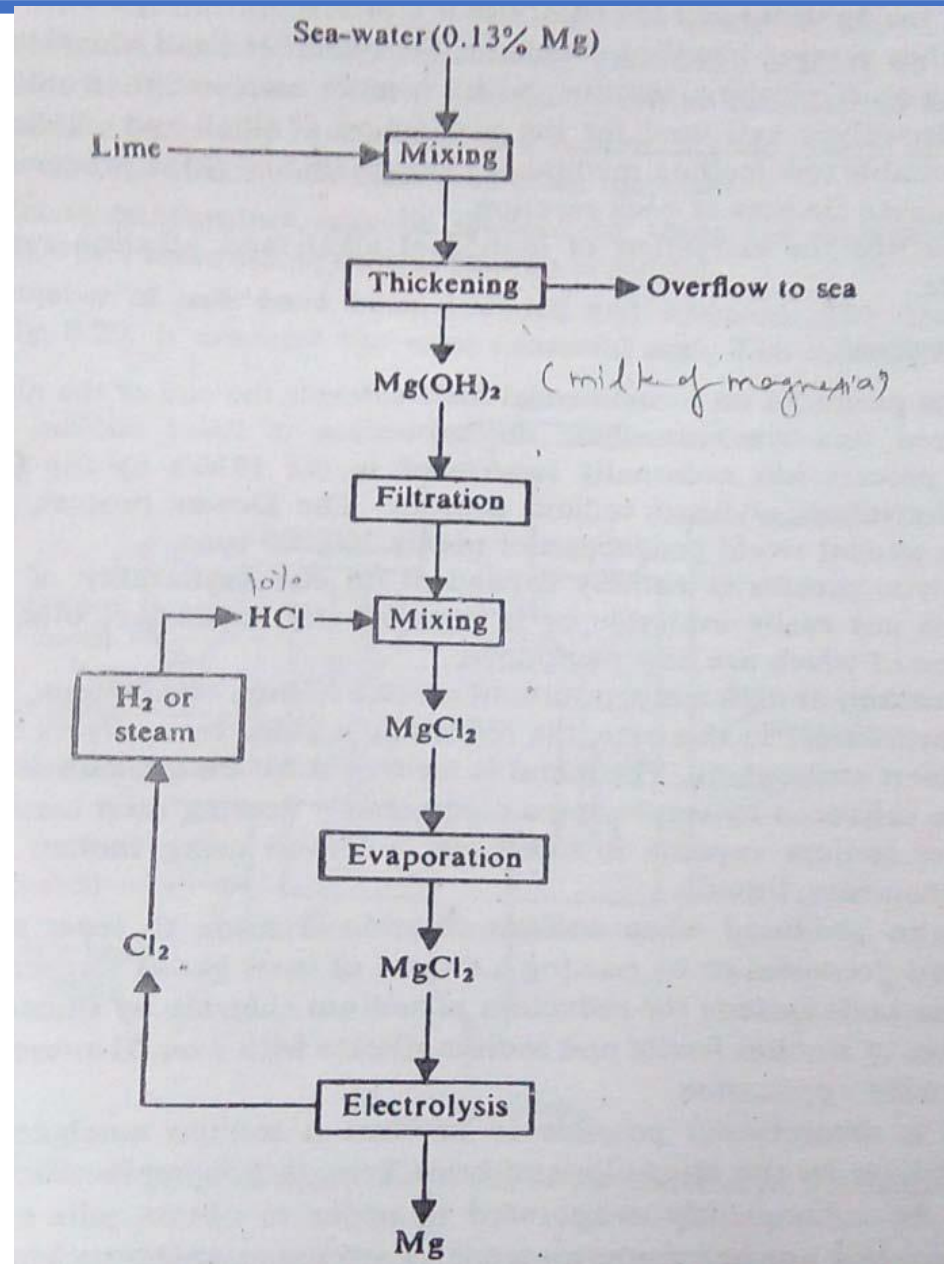
MAGNETOTHERM Process

It is essentially a ferrosilicon reduction process carried out at 1500°C and the bath is maintained in molten state by the addition of aluminum to form a molten slag.

It is in operation in France since 1964.

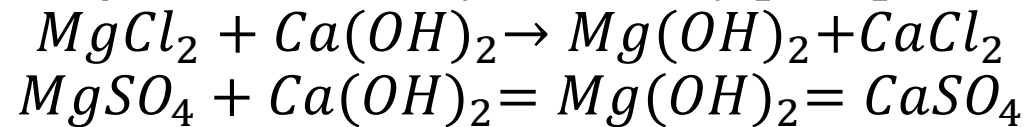
DOW Process: Extraction of Mg from Sea-Water

DOW Process: Flow Chart



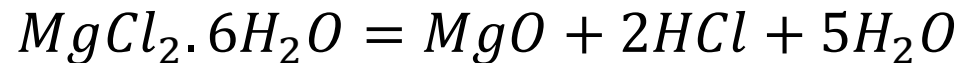
DOW Process: Flow Chart Explanation

- Developed by the Dow Chemical Company (U.S.A).
- It involves the collection of Mg as insoluble hydroxide by precipitation with lime as:



The suspension is distributed to thickeners, in which the hydroxide settle and the cleaner overflow pumped back to the sea.

- The milk of magnesia (slurry) underflow is pumped to filter tank, and subsequently agitated with 10% HCl, which converts it to a weak solution of chloride. This dilute solution is concentrated and filtered to recover the crystallized solids.
- The filtrate is then evaporated to recover remaining chloride. Evaporation is carefully controlled as the hydrous chloride is liable to lose hydrogen chloride, which results in oxide contamination in the final product. The reaction is:



DOW Process: Flow Chart Explanation

Electrolysis of Magnesium Chloride:

Principle:

Mg is reactive metal, has a high decomposition potential. Therefore, during aqueous electrolysis hydrogen evolution occurs before the decomposition of $\text{MgCl}_2 \rightarrow$ Not feasible

For electrolysis of MgCl_2 , the electrolyte is normally composed of 25-30% MgCl_2 , 15% CaCl_2 and 50-60% NaCl . A large amount of flux is necessary to maintain fluidity and to increase the density of the bath so that the liberated metal at cathode floats on the surface of the electrolyte. The theoretical decomposition voltage of dissolved MgCl_2 is 3.3, but the resistance of the bath raises the voltage to 6.6. A current of 30,000-50,000 A is employed and the temperature of the electrolytic cell is maintained at 670-730°C.

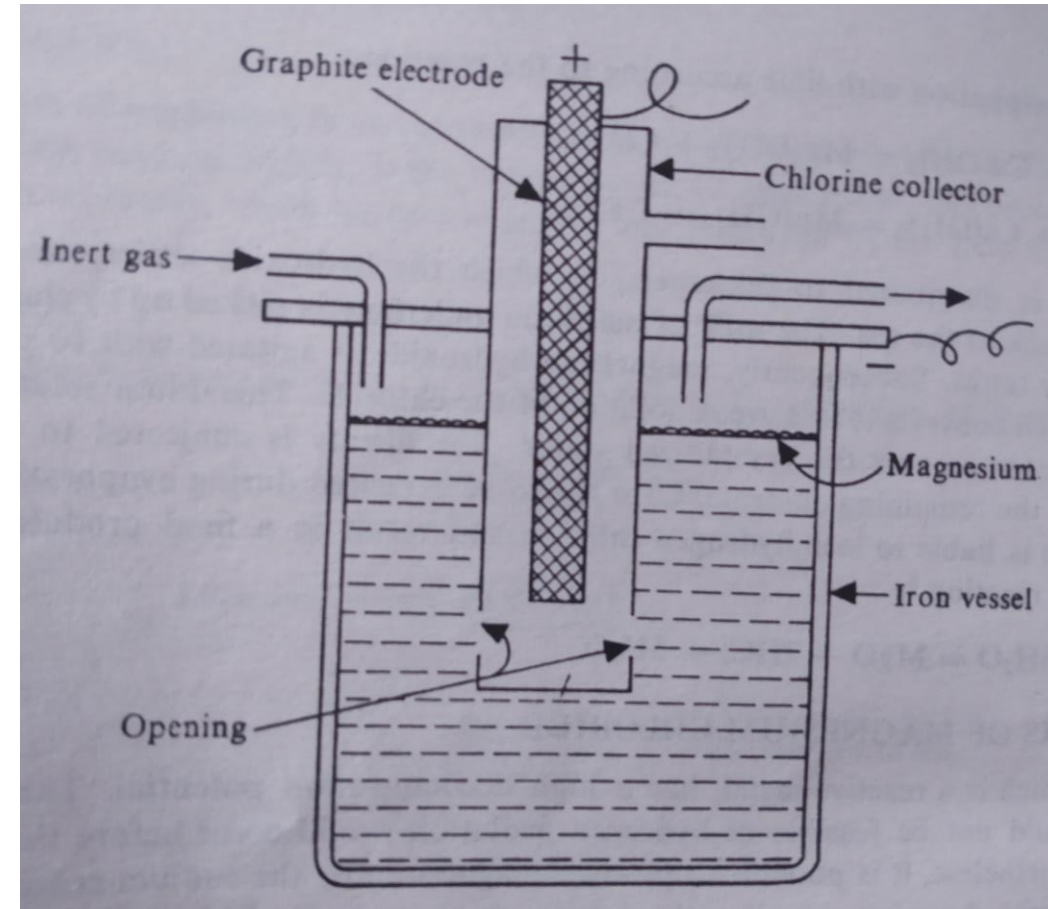
Cell design:

The electrolytic cell for Mg extraction may be divided into two (2) categories: lined and unlined. Lined cell must be provided with separate cathodes, usually made of steel, whereas in case of unlined cell, the steel wall of the cell itself may be used as cathode.

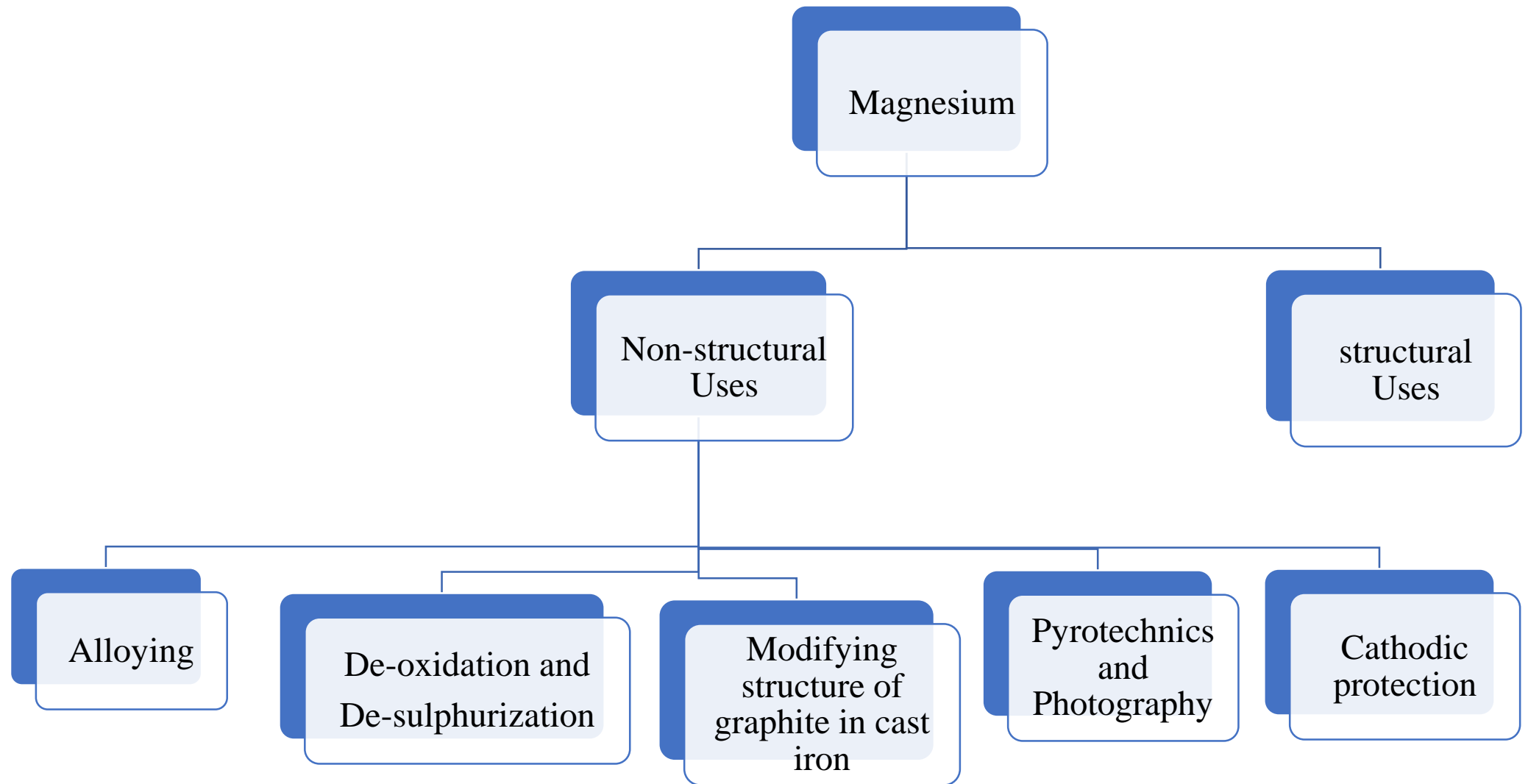
Graphite anode is used for both cell. The anodes are inert, therefore, not consumed. The cell operate in an inert atmosphere.

DOW Process: Flow Chart Explanation

- It is necessary to prevent chlorination of metallic product by gaseous chlorine evolved at the anode.
- Thus, the metal must be diverted away from the anode zone and recombination prevented by special design features.
- Cl₂ gas is collected in a special hood and the collection of the metal is facilitated by diverting to a pool.
- The chlorine set free at the anode is used to dry the incoming MgCl₂ and also to chlorinate Mg(OH)₂. However, complete drying is both expensive and difficult. Therefore, for electrolyzing a chloride that has been one and two moles of combined water have been evolved.



Uses or Applications of Mg



Uses or Applications of Mg

Nonstructural uses:

1. *Alloying:* Mg is widely used in alloying, especially in Al-Based alloys, to improve strength, hardness and corrosion resistance. It also improves mechanical properties of Pb-based alloys containing Ca, Sn and In.
2. *Deoxidation and desulphurization:* Mg has strong affinity for oxygen, effectively deoxidizes many molten metals. For production of iron and steel, the S content in the BF coke is rather high, and the pig iron contains a large quantity of S. To reduce the Sulphur level less than 0.01%, Mag-Coke or magnesium wire is injected into the hot metal.
3. *Modifying structure of graphite in cast iron:* Mg is effective nodulizer of graphite particles in cast iron for production of spheroidal graphite (S.G. iron). S.G. iron is stronger, tougher and more ductile than ordinary cast iron, and is widely used in automotive industry.
4. *Pyrotechnics and Photography:* Mg emits a brilliant light when ignited. This property is extensively used in pyrotechnics and photography. Flashlight powder consist of Mg powder mixed with chemicals which readily give off oxygen when heated, e.g. potassium chlorate, potassium permanganate and magnesium dioxide.

Uses or Applications of Mg (continue..)

Nonstructural uses (continue..):

5. Cathodic protection: For Pipelines, storage tank bases and lead-sheathed cables, 'sacrificial' Mg anode are placed in the soil and connected by means of insulated wire to the material that is to be protected against corrosion. In such an arrangement, the corrosion attack is directed preferentially against the magnesium, and the material is spared.

Structural uses:

Magnesium and aluminum alloys are important for properties like high specific strength, damping capacity, and resistance to corrosion by chemicals. Consequently, Mg alloys find structural use mainly in the aircraft industry and also land transportation and material handling.

Thank you