Thermodynamics Principle and Application of Matte Smelting and Converting

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Smelting:-

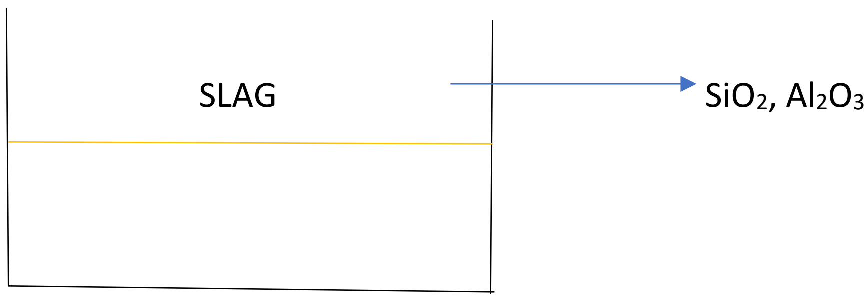
- The process in which a metal is obtained either as element or simple compound, form its ore heating beyond melting point either in presence of oxidizing agent such as air or reducing agent such as coke.

- In smelting we extract a base metal by applying heat to the ore.

- In case of smelting gangue minerals are in liquid state.

- Gases formed during smelting are SO_2, N_2, O_2, CO, CO_2.

- O_2 is produced when excess air is used. CO/CO_2 get evolved when fuel is used.



Cu_2S+FeS ← MATTE

Matte:-

- Matte is molten mixture of sulphide $Cu_2S + FeS$.
  (It may contain oxygen in form of Fe_3O_4)

- Matte is always given in terms of copper because it is used to produce copper.

- Density of matte – 5 to 5.5 g/cm^3 and melting point range from 1100-1200^{o}c.

- Matte are also used to collect impurity from a metal phase. For example, In case of antimony smelting.

- Molten mattes are insoluble in both slag and metal phases.

Copper grade of matte is important. Assuming that matte consists of Cu_2S and FeS in copper smelting then copper grade is defined as

$$\text{Cu grade} = \frac{(\text{Amount of Cu in matte})}{(\text{Amount of } Cu_2S + \text{Amount of FeS})} \times 100$$

Matte smelting :-

- When metal is separated as sulphide from smelting then it is called matte smelting.

- In matte smelting we have, ore concentrated + flux + air + fuel (if necessary) then we use matte slag and gases.

- In matte smelting use separate gangue mineral and produce matte.

- When metal is separated as liquid then it is called reduction smelting.

- In reduction smelting we separate gangue mineral and produce liquid metals.

- Low melting point of matte : [Cu_2S + FeS] = 1000°C(approx.)

- Cu_2S which is contained in matte does not required any reducing agent.

Reactions Involved:-

- Relatively few chemical reactions are carried out during matte smelting, as its main purpose is simply to allow compounds to segregate into whichever phase they are most soluble in (slag or matte). The main important reaction is the conversion of copper oxides back into copper sulfide so that they will go into the matte phase:

  $FeS + 6CuO \Longrightarrow 3Cu_2O + FeO + SO_2$

  $FeS + Cu_2O \Longrightarrow FeO + Cu_2S$

  $Cu_2S + FeS \Longrightarrow Cu_2S \bullet xFeS$ (matte)

- In order for matte smelting to work, it is very important that the feed be only partially oxidized, and that enough sulfur remains in the charge for all of the copper to form copper sulfides.

- Matte smelting is carried out in a neutral or slightly reducing atmosphere to prevent overoxidation of the charge. A typical matte consists of Cu_2S and FeS, and can have anywhere from 30% Cu to 80% Cu.

Slag :-

- Slag is a molten mixture of mainly oxides and unreduced sulphides.

- Slag usually consist of :-
  SiO_2 , Al_2O_3 , CaO , CuO , FeO , Fe_2O_3 , Fe_3O_4.

- Slag is normally low viscous.

- Density of slag – 2.8 to 3 g/cm^3.

- It has low melting point from 1200^oC to 1300^oC.

Other Properties Of slag:-

- **Solubility:-** i.e , slag should be able to dissolve the oxides which are being separated during smelting of ore concentration.

- Slags have low surface tension and higher diffusivity in order to achieve there objectives.

- The slag must have the following properties:
  - ✓ Immiscible with the matte phase.
  - ✓ Low solubility of Cu2S in the slag.
  - ✓ Good fluidity, to minimize entrainment of droplets of copper-bearing material into the slag.

- Slag viscosity increases as it becomes more oxidized, because the iron becomes particles of solid magnetite which are not molten at copper smelting temperatures. It is therefore important to avoid overoxidizing the slag, so that the iron remains as liquid FeO.

- In order to achieve these properties, the composition of the slag must be carefully controlled. It is particularly important that the viscosity be kept as low as possible as slag would entrap more droplets of the matte if viscosity is higher.
- Smelter slags typically have the following composition:

Fe (as FeO, Fe3O4)	30 - 40%
SiO2 (from fluxes, or recycled slags)	35 - 40%
Al2O3	up to 10%
CaO	up to 10%

Matte-Slag Immiscibility:-

- The structure of matte and slag and the effects of silica upon them , explain the observed matte-slag immiscibility behaviour.

- When silica is absent the oxides and sulphides combine into one covalently bonded, semiconducting Cu-Fe-O-S phase.

- However when it is present, it combines with the oxides to form strongly bonded silicate polymer anions e.g

$$2FeO + 3SiO_2 = 2Fe^{3+} + SiO_4^{4-}$$

which group together to form a slag phase.

- The sulphides show no tendency to form these anion complexes and hence they remain as distinct covalent matte phase, quite dissimilar to the silicate slag.

- Lime and Alumina associate almost completely with the slag phase and they tend to stabilise matte-slag immiscibility . Thus, they are beneficial in small amount.

Factors Affecting Efficiency Of Isolating Copper In Matte:-

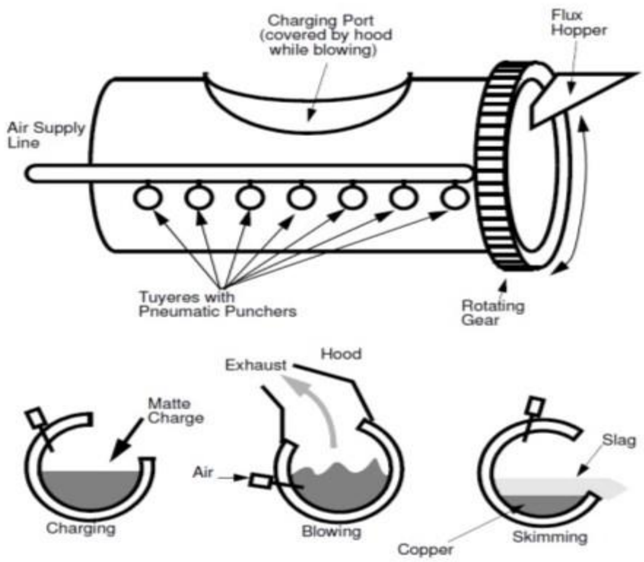
The efficiency with which the copper of the charge is isolated in the matte depends on many factors. There are however, some general conditions which promote a clear-cut matte-slag separation and a minimum loss of copper in the slag phase:

- ❖ Silica in Slag
- ❖ Lime and Alumina
- ❖ Matte grade (%Cu in matte)
- ❖ Slag Weight
- ❖ Temperature and Oxygen Potential

Converting :-

- Converting is a term used to describe a number of metallurgical smelting processing. The most commercially important use of the term is in the treatment of molten metal sulfides to produce crude metal and slag, as in the case of copper and nickel converting. Another, now uncommon, use of the term referred to batch treatment of pig iron to produce steel by the Bessemer process. The vessel used was called the Bessemer converter.

- This is a batch process, carried out in a horizontal cylindrical reactor called the Pierce-Smith Converter, which is shown in Figure. Converting is carried out in two stages: an iron-removal stage and a copper-making stage.



Iron Removal :-

- A process of removing iron from copper-based alloy scraps using oxidation slagging method is researched, in which the iron is oxidized to FeO and then reacted with SiO_2 forming Fe_2SiO_4 and enter into the slag phase. The addition of SiO_2 could restrict the Fe_2SiO_4 generation through the transformation of FeO to $2FeO \cdot SiO_2$ in a certain O_2 pressure, which is favorable to decreasing the melt viscosity and increasing the separation efficiency of Cu and Fe. Under optimized conditions of O_2 flow rate of 40 ml/min, temperature of 1 673 K, oxygenation time of 8 min, and SiO_2 amount of 2.17 mass%, Fe content in the metal phase is decreased to 0.0030 mass% with Cu loss rate being of 1.14%.

- For iron removal, silica is added as a flux to keep the slag molten, and air is blown into the converter to oxidize the iron sulfide, as shown in the following reaction:

2Cu2S•FeS + 3O2 + SiO2 ==> 2FeO•SiO2 + 2SO2 + Cu2S

Copper Making :-

- A mixture of copper and iron sulfides referred to as matte is treated in converters to oxidize iron in the first stage, and oxidize copper in the second stage. In the first stage oxygen enriched air is blown through the tuyeres to partially convert metal sulfides to oxides:

$$FeS + O_2 = FeO + SO_2 \quad CuS + O_2 = CuO + SO_2$$

- Since iron has greater affinity to oxygen, the produced copper oxide reacts with the remaining iron sulfide:

$$CuO + FeS = CuS + FeO$$

- The bulk of the copper oxide is turned back into the form of sulfide. In order to separate the obtained iron oxide, flux (mainly silica) is added into the converter. Silica reacts with iron sulfide to produce a light slag phase, which is poured off through the hood when the converter is tilted around the rotation axis:

$$2FeO + SiO_2 = Fe_2SiO_4 \text{ (sometimes denoted as } 2FeO \bullet SiO_2\text{)}$$

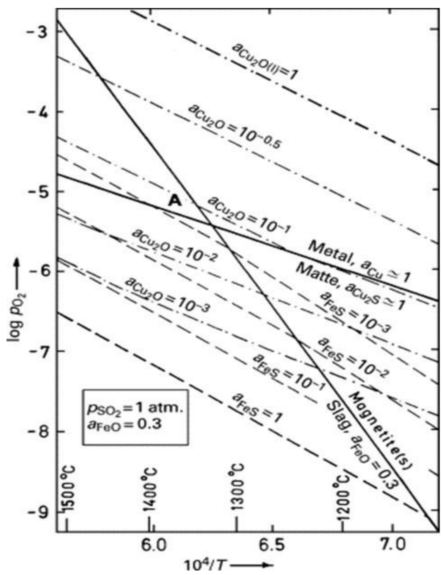
- The second stage of converting is aimed at oxidizing the copper sulfide phase (purified in the first stage), and produce *blister copper*. The following reaction takes place in the converter:

$$CuS + O_2 = Cu + SO_2$$

Blowing is continued until the copper sulfide has been completely oxidized to metallic copper and sulfur dioxide. Copper content in the obtained **blister** copper is typically more than **95%**. **Blister copper** is the final product of converting. The name is due to the fact that, if it is allowed to solidify, this copper will contain **"blisters"** due to evolution of SO_2.

Thermodynamics Of Matte Smelting (copper) :-

- Matte smelting and converting of an iron-copper sulphide concentrate is an oxidation process where iron and sulphur are gradually oxidized and removed in a slag and gas phase respectively. Under certain conditions solid magnetite may also be formed. The equilibria between the various liquid, solid, and gaseous phases will, in addition to temperature and oxygen potential, depend on the presence of other slag-forming oxides i.e., on the activity of FeO in the slag and on prevailing SO_2 pressure. For a silica-saturated iron-silicate slag where the FeO activity is about 0.3 and for 1 atm of SO_2 the various phase can be calculated from existing thermodynamic data as function of temperature and oxygen potential as shown in figure.



- At low oxygen potential an iron-copper matte with a_{FeS} between 1 and 0.1 will coexist with the slag. As the oxygen potential is raised the activity of FeS will decrease due to oxidation and slagging.

$$FeS(matte) + 1/2O_2 = FeO(slag)+SO_2$$

- Below a certain temperature, which increases with increasing oxygen potential, solid magnetite will be formed.

$$3FeS(matte) + 5O_2 = Fe_3O_4(s) + 3SO_2$$

- Coexistence between molten slag and magnetite is governed by the equilibrium.

$$3Fe_3O_4(s) + FeS(matte) = 10FeO(slag) + SO_2$$

- As the oxygen potential is increased further the activity of FeS will decrease to values of less than 10^{-3}, and the matte will be almost pure Cu_2S (white metal). On further oxidation this will convert to metallic copper(blister copper) by the roast-reaction

$$Cu_2S(l) + O_2 = 2Cu(l) + SO_2$$

Advantages Of Matte Smelting:-

- One advantage of matte smelting is its low melting point which makes it possible to smelt sulphide ores at lower temperatures than required for metals. Thus a matte with equal amounts of copper and iron sulphide melts below 1000 , whereas an alloy of Fe and Cu would melt at around 1400 . This leads to lower thermal energy requirements and gangue minerals can be separated easily as slag. Thus matte smelting comprises of the following inputs and outputs.

  Roast copper ore + Flux + Air fuel(if needed) + Heat = Matte + Slag + Gas

- One of the greatest industrial importance is iron-copper matte, which is an intermediate product in the extraction of copper from sulphide ores. Next comes the copper-nickel matte.

- One advantage of matte smelting is that some mattes may be processed to give the desired metal directly. This is for example, the case for iron-copper mattes which on oxidation and slagging of the iron component, may be converted to metallic copper by the so-called roast-reduction i.e to roast the sulphide ore and reduce the resulting oxide with carbon.

Disadvantages Of Matte Smelting:-

- The drawbacks of matte smelting is the production of large quantities of SO_2 that must be disposed of.

- One way to avoid this is to roast copper concentrate in the presence of lime or limestone, which captures sulphur as CaS or $CaSO_4$. The aim is to produce metallic copper as one of the products, while capturing substantially all sulphur. The copper can then be leached in ammonia for subsequent recovery.

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