Principles of Extractive Metallurgy

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Course Reference Texts

- Materials for the course were taken from multiple textbook. The main texts include:
  - *Instructor’s Lecture Notes, Prof. Nosa O. Egiebor* (2011)
Introduction - Definitions

- **Metallurgy** is the science of extracting and refining metals from ores and the compounding of metals to form alloys.
- **Extractive metallurgy** is the branch of metallurgical science & engineering which deals with the extraction and refining of metals from ores.
- An **ore** is a rock that contains commercially viable amounts of metallic/non-metallic solid minerals. Ores are complex associations of mineral grains.
- A **mineral** is a chemical compound that constitute a component of an ore, and with its own characteristic chemical composition.
Introduction – Types of Ores & Minerals

- Most metals are combined with other elements to form minerals. Few exist as pure metals. The table below provides examples of the common types of ores with minerals, their chemical formula and Common Names:

- **Native Metals (Can occur as Pure Metals)**
  - Silver-(Ag), Gold-(Au), Bismuth-(Bi), copper-(Cu), iridium-(Ir), Osmium-(Os), Paladium-(Pd), and platinum-(Pt)

- **Carbonate Minerals**
  - CaCO₃ (calcite), CaCO₃●MgCO₃ (dolomite), FeCO₃ (siderite), BaCO₃ (witherite)

- **Halide Minerals**
  - CaF₂ (fluorite), NaCl (halite)

- **Oxide Minerals**
  - Al₂O₃●2H₂O (bauxite), Cu₂O (cuprite), Fe₂O₃ (haematite), Fe₃O₄ (magnetite)

- **Sulfide Minerals (Most abundant minerals on the earth’s crust)**
  - Cu₂S (chalcocite), CuFeS₂ (chalcopyrite), NiS (millerite), Fe₉Ni₉S₁₆ (pentlandite), FeS₂ (pyrite)
Bn = bornite (Cu$_5$FeS$_4$);  Cc = chalcocite (Cu$_2$S);  Cp = chalcopyrite (CuFeS$_2$);

Q = Quartz (SiO$_2$);  Tn = Tennantite (Cu$_{12}$As$_4$S$_{13}$).
Mineral Assemblage 2  ➔ Figure 2

Bn = Bornite (Cu$_5$FeS$_4$); Cp = Chalcopyrite (CuFeS$_2$); Cv = Covellite (CuS); G = Gold (Au); Tn = Tennantite (Cu$_{12}$As$_4$S$_{13}$)
Introduction – Metal Production

- There are three main steps in obtaining a pure metal from its ore.
  - primary treatment
  - extracting the metal
  - refining the metal

- Primary treatment involve the processes that are used to concentrate the mineral (ore value), usually through physical separation methods collectively known as *Mineral Processing or Ore Dressing*. It is normally conducted at or near the mine site.

- Both *Extraction & Refining* of metals & mineral values involve the application of one or more of the following:
  - Pyrometallurgy – Application of high temperature reactions to achieve metal extraction
  - Hydrometallurgy – Extraction using aqueous solution reactions for metal separation
  - Electrometallurgy – Extraction using electrical energy via electrodes
General Approach to Extractive Metallurgy.1: Flowsheets

- Extractive metallurgical systems are often represented by Process Flowsheets.
  - A process flowsheet is a diagramatic representation of a complete or partial extraction process showing the individual Unit Processes or Unit Operations as rectangular boxes in the order in which the processes are carried out.
- Additional details of the unit processes, such as physical forms, major chemical compositions, process rates may or may not be included in a Process Flowsheet.
- **For example**: The extraction of aluminum metal (Al) from bauxite (a mixture of aluminum hydroxide & other minerals), may be represented by the Process Flowsheet shown in Figure 3.
Flowsheet of Aluminum extraction from Bauxite ores (Figure 3)

**Bauxite Ore** → Grinding

Steam + NaOH → Pressure digestion

Solid/Liquid Separation → Precipitation of Al(OH)₃

‘Red mud’ reject solid

Heating to 1000°C → Calcination of Al(OH)₃ to Al₂O₃

99.6% Al₂O₃ solid

Electrical Power → Electrolysis

99.6% Al₂O₃ solid
General Approach to Extractive Metallurgy.2: Process Aims & Objectives

- For a given raw material, such as an ore or concentrate, a range of products may be possible. The **aims and objectives** of a process depends on the compositions of the ores/concentrates.

- Viable process **alternatives to products** (Range of process options)

- Ore/Concentrate

```
A  B  C
```

```
Product #1
```
Simple class Quiz.1: A copper ore contains 1.5% Cu. After ore dressing, 4.5 kg of concentrate with 30% Cu is produced from 100 kg of ore. Calculate (a) the concentration ratio (b) the recovery, and (c) the wt. and Cu % content of the discarded gangue (tailings).

Solution:

(a) 4.5 kg of concentrate is obtained from 100 kg of ore. Hence

Concentration ratio \( = \frac{100 \text{ kg}}{4.5 \text{ kg}} = 22.2 \)

(b) The ore contains a total of \( 0.015 \times 100 = 1.5 \text{ kg} \) Cu. The concentrate contains \( 0.30 \times 4.5 = 1.35 \text{ kg} \). Therefore, the recovery \( = \frac{1.35}{1.5} \times 100 = 90\% \).

(c) The weight of the tailing (gangue) \( = 100 - 4.5 = 95.5 \text{ kg} \). The Cu content in kg \( = 1.5 - 1.35 = 0.15 \text{ kg} \). This should give a Cu percentage \( = \frac{0.15}{95.5} \times 100 = 0.157\% \).
Pyrometallurgy: General Characteristics

- Pyrometallurgy is metal extraction involving the application of heat or high temperatures. The objective is to chemically alter the mineral and ultimately to reduce it to the free metal.

- Depending on the type of minerals involved, pyrometallurgical extraction may include one or more unit processes, namely:
  - Calcination
  - Roasting
  - Smelting
  - Refining or Converting
Pyrometallurgy: Calcination

- **Calcination** is the heating of an ore to bring about its decomposition and the elimination of a volatile product. The volatile product could be, for example, CO₂ or H₂O. Carbonates are often calcined to drive off CO₂, forming the metal oxide. For example,

  - \[ \text{PbCO}_3(s) + \text{heat} \rightarrow \text{PbO}(s) + \text{CO}_2(g) \]  
  
  - \[ \text{CaCO}_3(s) + \text{heat} \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]  

- Most carbonates decompose reasonably rapidly at temperatures in the range of 400 to 500°C, although CaCO₃ requires a temperature of about 1000°C.

- Most hydrated minerals lose H₂O at temperatures on the order of 100 to 300°C.
Calcination: Schematics of a Shaft Kiln

Figure 4

Shaft Kiln

Diagram showing the flow of limestone, air, and fuel through the kiln, with exhaust and lime outlet.
Calcination: **Schematics of Rotary Kiln**

**Figure 5**

- Gas fired calcination kiln
Pyrometallurgy: Roasting

- **Roasting** is a thermal treatment process, conducted at around 400 – 700°C, that is aimed at causing chemical reactions between the ore or concentrate and the furnace atmosphere.

- Roasting may lead to oxidation or reduction and may be accompanied by calcination.

- An important roasting process is the oxidation of sulfide ores, in which the metal is converted to the oxide, as in the following examples:
  - \[ 2\text{ZnS (s)} + 3\text{O}_2 (g) \rightarrow 2\text{ZnO(s)} + 2\text{SO}_2 (g) \] \[\text{[3]}\]
  - The sulfide ore of a less active metal, such as mercury, can be roasted to the free metal:
  - \[ \text{HgS (s)} + \text{O}_2 (g) \rightarrow \text{Hg (s)} + \text{SO}_2 (g) \] \[\text{[4]}\]
Roasting: Multiple Hearth Roaster
Figure 6
Roasting: Fluidized Bed Roaster

Figure 7
Pyrometallurgy: Smelting

- **Smelting** is a melting process conducted at 1200 – 1600°C in which the materials formed in the course of chemical reactions separate into two or more layers.

- Smelting is normally conducted in high-temperature furnaces such as Reverberatory Furnace, Electric Furnace, and Outokumpu Furnace.

- The two main product layers formed during smelting are
  - molten metal
  - slag

- The molten metal may consist almost entirely of a single metal, or it may be a solution of two or more metals.
Smelting (contd.)

- **Slag** consists mainly of molten silicate minerals, with aluminates, phosphates, fluorides, and other ionic compounds as constituents.

- A slag is formed when a basic metal oxide such as CaO reacts at high temperatures with molten silica, SiO₂ to form a silicate:
  - \[ \text{CaO (l)} + \text{SiO}_2 \ (l) \rightarrow \text{CaSiO}_3 \ (l) \]

- Sometimes additional materials, known as **Flux**, are added to the solid smelter charge to facilitate the melting and metal-slag separation and stability. Flux materials may be CaO, SiO₂, and other compounds.
Smelting: Reverberatory Furnace

Figure 8
Smelting: Electric Furnace (Figure 9)
Smelting: Outokumpu Furnace (Figure 10)
Refining or Converting is the treatment of a crude and relatively impure metal product from a pyrometallurgical process to improve its purity and to define its composition better.

The process involves the addition of chemical compounds to the molten crude metal to react with the impurities in the molten metal and form a separate phase, such as gas or slag, that can be easily separated from the purified metal.

- For example, in the removal of excess carbon from molten pig-iron, oxygen is blown into the molten iron charge in a converter where the carbon reacts with the carbon to form gas phase carbon dioxide.

Sometimes the goal of the refining process is to obtain the metal itself in pure form. However, the goal may also be to produce a mixture with a well-defined composition, as in the production of steels from crude iron, which we now examine.
Refining: Pierce-Smith Converter

Figure 11

View of horizontal side-blown Pierce-Smith converter used in the copper and nickel industry.

Steps in the converting cycle and position of the converter shell, relative to the hood, for each step.

Figure 6

Conventional Pierce-Smith Converter
Refining: Bessemer Converter (Figure 12)
Pyrometallurgy: **Thermodynamics of Oxide Reduction.**

- A large number of important industrial metals are produced from their oxide raw materials. Examples of such metals are iron (Fe), Manganese (Mn), Chromium (Cr), and tin (Sn).

- In other cases, as in **lead (PbS)** and **zinc (ZnS)**, the sulfide ores are first roasted and converted to their oxide forms (PbO & ZnO), before additional treatments for metal value extraction.

- The oxides of the more noble or less reactive metals, such as **Ag$_2$O, PtO, PdO, and HgO**, may be decomposed from oxide to pure metal by the direct application of heat, e.g:

\[
\begin{align*}
2\text{Ag}_2\text{O} & + \text{heat (>200°C)} \rightarrow 4\text{Ag} + \text{O}_2 \quad \text{[6]} \\
2\text{PtO} & + \text{heat (>500°C)} \rightarrow 2\text{Pt} + \text{O}_2 \quad \text{[7]} \\
2\text{PdO} & + \text{heat (>900°C)} \rightarrow 2\text{Pd} + \text{O}_2 \quad \text{[8]}
\end{align*}
\]
For all other metallic oxides, decomposition to the pure metal require the use of a reducing agent such as carbon (C), carbon monoxide (CO), and hydrogen (H₂).

The reduction of metal oxides with carbon (C) and carbon monoxide (CO), depicted in Equation 9 below, are of great industrial importance:

\[
\text{MeO} + \text{CO} \rightarrow \text{Me} + \text{CO}_2
\]

Like all chemical/metallurgical reactions, the reduction of metal oxides with C and CO is governed by the prevailing Chemical Equilibria, and also Reaction Kinetics.
From basic thermodynamics, the *Gibbs Free Energy Change* ($\Delta G$) and the *Equilibrium Constant* ($K$) may be estimated for all reactions:

For the simple metal oxide reduction by CO (Equation 9):

- $\text{MeO} + \text{CO} \rightarrow \text{Me} + \text{CO}_2$

The *Equilibrium constant* ($K$) is defined as:

$$K = \frac{(\alpha_{\text{Me}})(\alpha_{\text{CO}_2})}{(\alpha_{\text{MeO}})(\alpha_{\text{CO}})};$$

but activities of pure solids, Me & MeO are equal to 1; and for gases, partial pressures are substituted for activities, hence

$$K = \frac{P_{\text{CO}_2}}{P_{\text{CO}}};$$

------------------[10]
Pyrometallurgy: **Thermodynamics of Oxide Reduction.4**

- From Equation 10, it is clear that the Equilibrium Constant for the reduction of metal oxide with CO is a function of the ratio of the partial pressures of CO$_2$ to CO in the reacting mixture.

- The corresponding **Gibbs Free Energy Change** ($\Delta G$) for the oxide reduction reaction in Equation 9 can be defined as:

  \[
  \Delta G = \Delta G^\circ + R \cdot T \cdot \ln \left( \frac{P_{CO_2}}{P_{CO}} \right)
  \]

  - Where $\Delta G^\circ =$ **Standard** Gibbs Free Energy Change
  - $R =$ the Universal gas constant; $T =$ Temperature (K)

- If $\Delta G$ is negative (-ve), then the reaction will proceed from left to right (i.e favor production of metal). If it is positive, it will proceed in the reverse direction.

- At Equilibrium, $\Delta G = 0$
Pyrometallurgy: Thermodynamics of Oxide Reduction.5

- Therefore Equation 11 becomes:

\[ \Delta G^\circ = -R.T \ln \left( \frac{P_{CO_2}}{P_{CO}} \right) = -R.T \ln K \] \[ \text{[12]} \]

- Although the Equilibrium Constant (K) is independent of pressure, it changes with changing temperature.

- The variation of Equilibrium Constant (K) with temperature (T) is given by the van’t Hoff Equation as:

\[ \frac{d \ln K}{d \left( \frac{1}{T} \right)} = -\frac{\Delta H^\circ}{R} \] \[ \text{[13]} \]

- If we know the enthalpy change for the reaction, we can calculate the variation of Equilibrium constant (K) or Equilibrium gas ratio with temperature.

- Figure 13 shows the variation of Equilibrium gas ratio \((P_{CO_2}/P_{CO})\) with Temperature for reduction of various metal oxides.
Figure 13. Equilibrium gas ratio \((\text{CO}_2/\text{CO})\) as a function of inverse temp. \((1/T)\) for the reduction of metal oxides.
It is clear from the equilibrium metal oxide reduction lines of Figure 13 that the $P_{CO_2}/P_{CO}$ ratios range from about:

- $10^5$ ($\log P_{CO_2}/P_{CO} = +5$) for the reduction of $Cu_2O$ to $Cu$ and $Fe_2O_3$ to $Fe_3O_4$, to values of the order of
- $10^{-5}$ ($\log P_{CO_2}/P_{CO} = -5$) or lower for the reduction of $MnO$ and $SiO_2$ to their corresponding metals.

In Figure 13, reduction of the oxides to the metals will take place when the $CO_2/CO$ ratio in the reacting atmosphere falls below the equilibrium line in question, at any given Temperature ($T$).

**Example:** At $900^{\circ}C$, nickel oxide ($NiO$) will not be reduced to the metal when the $P_{CO_2}/P_{CO}$ ratio is about 100 (or $\log P_{CO_2}/P_{CO} = +2$).

Conversely, at a ratio of say $P_{CO_2}/P_{CO} = 10$ (or $\log P_{CO_2}/P_{CO} = +1$), then NiO will be completely reduced to the nickel (Ni) metal.
Therefore, the oxides of Cu, Pb, and nickel will be reduced at gas ratios between $10^5$ and $10^2$. This means that even very low or very small concentrations of CO in the gas mixture will reduce these oxides [i.e. $\text{PbO} + \text{CO} = \text{Pb} + \text{CO}_2$ has a large Equilibrium constant ($K$)]

That is, if pure CO is originally used, practically all of the CO will react to be converted into CO$_2$ before the reaction stops.

On the other hand, the Equilibrium plots in Figure 13 tells us that the more reactive metal oxides of e.g. manganese (MnO) and silica (SiO$_2$) will require a gas ratio which is virtually free of CO$_2$.

- For example: At 1000°C, the reduction of MnO to Mn metal requires a $P_{\text{CO}_2}/P_{\text{CO}}$ of $10^{-5}$ or less for the reaction:
  - $\text{MnO} + \text{CO} \Rightarrow \text{Mn} + \text{CO}_2$ to proceed significantly to the right. i.e. This reaction has a very low equilibrium constant ($K$).
Therefore, the reduction of the oxides SiO$_2$, Cr$_2$O$_3$, MnO, Al$_2$O$_3$ by carbon monoxide (CO) is practically impossible. Whereas, the oxides of FeO, Fe$_3$O$_4$, PbO, NiO, and Cu$_2$O can be readily reduced to their corresponding metals at elevated temperatures.

Note that the reduction of ZnO is an exceptional case, as depicted in Figure 13.

In this case, at the lower temperatures (i.e. 500°C – 900°C), ZnO is reduced to form **Liquid Zn** metal [ZnO + CO $\rightarrow$ Zn(l) + CO$_2$].

At temperatures above about 900°C, Zn vapor is formed:

- ZnO + CO $\rightarrow$ Zn (g) + CO$_2$. Here, the gas ratio is given as:
- $\frac{P_{CO_2}}{P_{CO}} = \frac{K}{P_{Zn}}$, where $K$ = **Equilibrium Constant** and
- $P_{Zn}$ = partial pressure of Zn vapor.
In Figure 13, the higher temperature plots for ZnO is made at a $P_{Zn} = 1.0 \text{ atm}$.

The higher temperature Zn vapor plot intersects the lower temperature Zn liquid plot at the boiling point of Zn = 907°C.

At this temperature point, both liquid Zn and Zn vapor are at equilibrium with each other under the same gas atmospheres.

If solid carbon is present in the reaction mixture, then the two reactions below will occur simultaneously:

- $\text{MeO} + \text{CO} \rightarrow \text{Me} + \text{CO}_2$
- $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$
Pyrometallurgy: Thermodynamics of Oxide Reduction

- MeO + CO $\rightarrow$ Me + CO₂
- C + CO₂ $\rightarrow$ 2CO

Equation 14 is known as the Boudouard reaction, and it is shown clearly in Figure 13 (at $P_{CO} + P_{CO_2} = 1.0$ atm) running across the oxide reduction equilibrium lines.

With the two reactions represented by Equations (9) and (14) above occurring together, a simultaneous equilibrium between MeO, Me, and C will occur at the temperature where the two curves intersect for the individual oxides.

For example: For the metal tin (Sn), we see that SnO₂, Sn, and C will be at equilibrium at 610°C, where the SnO₂ reduction line intersects the Boudouard reaction line.
The above means that \( \text{SnO}_2 \) may be reduced by carbon at temperatures above 610°C.

Similarly, \( \text{Fe}_3\text{O}_4 \) will be reduced to \( \text{FeO} \) by carbon above 650°C.

\( \text{FeO} \) will, in turn be reduced to \( \text{Fe} \) above 700°C.

\( \text{MnO} \) and \( \text{SiO}_2 \) may also be reduced by carbon at temperatures above about 1400°C and 1600°C.

If the reduction reactions take place at the equilibrium temperatures, the resulting gas mixture will be given by the value which corresponds to the intersection between the two curves in Figure 13.
Thus, for the reduction of SnO₂ at 610°C, the P_{CO₂}/P_{CO} ratio is about 3.0 \{i.e. \log P_{CO₂}/P_{CO} = 0.48\}.

Similarly, for the reduction of MnO at 1500°C the P_{CO₂}/P_{CO} ratio = 10^{-4} \{\log P_{CO₂}/P_{CO} = -4\}.

Note that: In Figure 13, the curve for NiO and for the oxides of the more noble (less reactive) metals, such as Cu₂O and PbO, do not intersect the carbon curve anywhere.

- In these cases, the temperature of the reduction and the composition of the gas mixture is entirely determined by the reaction kinetics.
- Generally, these oxides require a few hundred degrees Celcius, and reaction occurs on the carbon surface at above red heat and higher
Pyrometallurgy: Thermodynamics of Oxide Reduction.13

• The Enthalpy change ($\Delta H^o$) for the different reactions can be calculated from the slope of the curves by the van’t Hoff Equation (13):

$$\frac{d \ln K}{d \left(1/T\right)} = -\frac{\Delta H^o}{R}$$

[13]:

• Knowing $K$, $T$, and $R$, then the van’t Hoff Equation 13 can be used to estimate the enthalpy change ($\Delta H^o$).

• In general, the reduction of the oxides of the relatively noble (less reactive) metals with CO is Exothermic (positive slope of equilibrium curve).

• Whereas, the reduction of the less noble (more reactive) metal oxides is Endothermic.
Pyrometallurgy: **Thermodynamics of Oxide Reduction.**

- Also, the Boudouard reaction (between C and CO$_2$) is Strongly Endothermic.

- Consequently, the reduction of practically all metal oxides with carbon is Endothermic, and the reduction Enthalpy increases with increasing oxide stability (MnO higher than FeO).

- Therefore, the reduction of the stable oxides with carbon requires both high temperatures and a large amount of heat at that temperature.

- In the case of Iron Oxide (FeO & Fe$_3$O$_4$), the required temperature and heat is generally average between the very stable and reactive oxides (e.g. MnO) and the more noble metal oxides such as PbO.
Another graphical method of studying metal oxide REDOX reactions is through the 2nd Law of Thermodynamics, which says that for any reaction:

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -R.T \ln K \]

- \( \Delta G^\circ \) = Standard enthalpy change of reaction
- \( \Delta H^\circ \) = Absolute temperature (K), and
- \( \Delta S^\circ \) = Standard entropy change for the reaction

The enthalpy change (\( \Delta H \)) is a measure of the actual energy that is liberated when the reaction occurs (i.e. “heat of reaction”). *If it is negative, then the reaction gives off energy, while if it is positive the reaction requires or absorbs energy*

The entropy change (\( \Delta S \)) is a measure of the change in the orderliness or disorderliness in the products compared to the reactants. For example, if a solid (an ordered state) reacts with a liquid (a somewhat less ordered state) to form a gas (a highly disordered state), there is normally a large positive change in the entropy for the reaction.
Pyrometallurgy: **Thermodynamics of Oxide Reduction: Ellingham Diagrams**

**Equation 15** can be used to study Oxidation-Reduction (Redox) reactions of metals and their reducing agents, such as:

- \(2\text{Fe (s)} + \text{O}_2(\text{g}) = 2\text{FeO(s)}\)
- \(2\text{Mg (s)} + \text{O}_2(\text{g}) = 2\text{MgO(s)}\)
- \(4\text{Ag(s)} + \text{O}_2(\text{g}) = \text{Ag}_2\text{O(s)}\)
- \(\text{C(s)} + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})\)
- \(2\text{C(s)} + \text{O}_2(\text{g}) = 2\text{CO(g)}\)

From Equation 15, if we make a series of plots of \(\Delta G^\circ\) vs Temperature \((T)\) for various Redox reactions, then we get straight lines with:

- **a.** A Slope \(= -\Delta S^\circ\), and
- **b.** An Intercept \(= \Delta H^\circ\) (at \(T = 0\))

We get straight lines because in the absence of phase changes, the values of \(\Delta H^\circ\) and \(\Delta S^\circ\) are independent of temperature, and thus a plot of \(\Delta G^\circ\) against \(T\) will be a straight line graph.

Such plots are known as **Ellingham Diagrams** as shown below.
Pyrometallurgy: **Thermodynamics of Oxide Reduction: Ellingham Diagrams**.3 (Figure 14)
Pyrometallurgy: **Thermodynamics of Oxide Reduction: Ellingham Diagrams** (Fig. 15)
There are three main uses of Ellingham diagrams:

1. Determine the relative ease of reducing a given metallic oxide to metal;
2. Determine the partial pressure of oxygen that is in equilibrium with a metal oxide at a given temperature; and
3. Determine the ratio of either $\text{CO:CO}_2$ or $\text{H}_2:\text{H}_2\text{O}$ that will be able to reduce a given oxide to the metal at a given temperature.

In constructing Ellingham Diagrams, the oxygen partial pressure is taken as 1 atmosphere, and all of the reactions are normalized to consume one mole of $\text{O}_2$.

Note that the Free Energy of formation is negative for most metal oxides, and so the diagram is drawn with $\Delta G=0$ at the top of the diagram, and the values of $\Delta G$ shown are mostly negative numbers.
Construction of Ellingham Diagrams.

- $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -R.T\ln K$ [15]

- If we apply Equation 15 to a general metal oxidation reaction such as $M + O_2 \rightarrow MO_2$

- Then we can write Equation 15 in terms of Equilibrium Constant (K):
  - $\Delta G^\circ = -R.T \ln K$

- And the Equilibrium Constant (K) is given as
  - $K = (\alpha_{MO_2})/(\alpha_M) \cdot (\alpha_{O_2})$ [16]
    - where $\alpha_x$ = activities of various components

- Since the activities of pure elements and compounds in their standard states = 1, then we can write
  - $K = 1/P(O_2)$

- Hence Equation 15 can now be written as;
  - $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = RT \ln P(O_2)$ [17]
Construction of Ellingham Diagrams.

- Equation (17) gives the variation of the partial pressure of oxygen, \( p(O_2) \), with temperature required for equilibrium between the pure metal, the pure oxide, and the gaseous phase oxygen.
  - The variation of oxygen partial pressures with temperature and equilibrium conditions of the relevant reactions is given as a Nomograph on the RHS of Ellingham Diagrams.

- Now, consider the following two oxidation reactions, with their corresponding variation of \( \Delta G^\circ \) with Temp:
  
  - (a) for the reaction: \( 2Fe + O_2 \rightarrow 2FeO \) \[18\]
    \[ \Delta G^\circ = -529,800 + 113.0 \times T \]  (Unit in Joules)
  
  - (b) for the reaction: \( 4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \) \[19\]
    \[ \Delta G^\circ = -498,900 + 281.3 \times T \]  (unit in Joules)

- The Ellingham lines for the two reactions above are shown in the next figure.
Construction of Ellingham Diagrams.3
(Figure 14)
Let us consider another specific example of the formation of Ag₂O from its elements:

\[4\text{Ag(s)} + \text{O}_2(g) = 2\text{Ag}_2\text{O(s)}\]

From Table 1 $\Delta G^\circ$ for the formation of Ag₂O (i.e. $\Delta G^\circ = -10.8\text{ kJ mol}^{-1}$) indicates that Ag₂O is thermodynamically stable at 298.15 K with respect to silver and oxygen.

The entropy change ($\Delta S^\circ$), is expected to be negative, since there is a decrease in the number of moles of gas.

Thus the term $-T\Delta S^\circ$ will be positive and will increase with temperature, like most metal oxidation reactions as shown in Figure 16.
## Construction of Ellingham Diagrams:
### Some Thermodynamic Data (Table 1)

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<th>Substance</th>
<th>State</th>
<th>$H^\circ$ / kJ mol$^{-1}$</th>
<th>$G^\circ$ / kJ mol$^{-1}$</th>
<th>$S^\circ$ / J K$^{-1}$ mol$^{-1}$</th>
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<td>197.5</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>g</td>
<td>−393.5</td>
<td>−394.4</td>
<td>213.7</td>
</tr>
<tr>
<td>Ca</td>
<td>s</td>
<td>0</td>
<td>0</td>
<td>41.4</td>
</tr>
<tr>
<td>Ca</td>
<td>g</td>
<td>178.2</td>
<td>144.3</td>
<td>154.8</td>
</tr>
<tr>
<td>CaO</td>
<td>s</td>
<td>−635.1</td>
<td>−604.0</td>
<td>39.7</td>
</tr>
<tr>
<td>Cu</td>
<td>s</td>
<td>0</td>
<td>0</td>
<td>33.3</td>
</tr>
<tr>
<td>Cu</td>
<td>g</td>
<td>338.3</td>
<td>298.6</td>
<td>166.3</td>
</tr>
<tr>
<td>CuO</td>
<td>s</td>
<td>−155.8</td>
<td>−128.0</td>
<td>42.6</td>
</tr>
<tr>
<td>Fe</td>
<td>s</td>
<td>0</td>
<td>0</td>
<td>27.1</td>
</tr>
<tr>
<td>FeO</td>
<td>s</td>
<td>−272.0</td>
<td>−251.5</td>
<td>60.7</td>
</tr>
<tr>
<td>O$_2$</td>
<td>g</td>
<td>0</td>
<td>0</td>
<td>205</td>
</tr>
</tbody>
</table>
Construction of Ellingham Diagrams.6 (Figure 16)
Construction of Ellingham Diagrams.

- Obviously, with increasing slope, a point will be reached at which $\Delta G^o$ will be $= 0$, and subsequently become positive.

- At this point, and $\text{Ag}_2\text{O}$ will become thermodynamically unstable with respect to its elements.

- Under this condition, decomposition of $\text{Ag}_2\text{O}$ to its component elements will then occur i.e. Equation 20 is reversed as
  
  \[ 2\text{Ag}_2\text{O}(s) \rightarrow 4\text{Ag}(s) + \text{O}_2(g) \]

- The temperature at which $\Delta G^o$ becomes zero is known as the thermodynamic decomposition temperature of that compound.
Construction of Ellingham Diagrams

- Now, referring back to Equation 15: \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \)
  - When \( \Delta G^\circ (T) = 0 \) at a particular temperature \( T \), then
    - \( \Delta H^\circ = T \Delta S^\circ \) \[22\]
    - \( \therefore T_{\text{decomp}} = \Delta H^\circ / \Delta S^\circ \) \[23\]

- Therefore, using the reaction in Equation 20 (\( 2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g) = 2\text{Ag}_2\text{O}(s) \)) and the thermodynamic data in Table 1, we have:
  - \( \Delta H^\circ(298 \text{ K}) = -30.5 \text{ kJ mol}^{-1} = -30500 \text{ J mol}^{-1} \)
  - \( \Delta S^\circ(298 \text{ K}) = (121.7 - 2 \times 42.7 - 0.5 \times 205.0) \text{ J K}^{-1} \text{ mol}^{-1} = -66.2 \text{ J K}^{-1} \text{ mol}^{-1} \)
  - \( \therefore T_{\text{decomp}} = (-30500 \text{ J mol}^{-1}) / (-66.2 \text{ J K}^{-1} \text{ mol}^{-1}) = 461 \text{ K} \)

  - When heated, silver oxide does indeed decompose at about this temperature (188°C).
The majority of the lines slope upwards, because both the metal and the oxide are present as condensed phases (solid or liquid).

- The reactions are reacting a gas with a condensed phase to make another condensed phase, which reduces the entropy.

A notable exception to this general trend is the oxidation of solid carbon. The line for the reaction;

- \( \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \) \[24\]

depicts a solid reacting with one mole of gas to produce a mole of gas, and so there is little change in entropy and the line is nearly horizontal.

However, for the reaction;

- \( 2\text{C} + \text{O}_2 \rightarrow 2\text{CO} \) \[25\]

we have a solid reacting with one mole of gas to produce two moles of gas, and so there is a substantial increase in entropy and the line slopes rather sharply downward. The corresponding Ellingham lines are shown in Figure 16.
Uses of Ellingham Diagrams

Recall the three main uses of Ellingham diagrams:

1. Determine the relative ease of reducing a given metallic oxide to metal;
2. Determine the partial pressure of oxygen that is in equilibrium with a metal oxide at a given temperature; and
3. Determine the ratio of either CO:CO₂ or H₂:H₂O that will be able to reduce a given oxide to the metal at a given temperature.

Since the 2C + O₂ → 2CO line is downward-sloping, it cuts across the lines for many of the other metals.

This makes carbon very useful as a reducing agent, because as soon as the carbon oxidation line goes below a metal oxidation line, the carbon can then reduce the metal oxide to the corresponding metal.

So, for example, the carbon reaction line crosses the FeO line at a temperature of approximately 700°C. Therefore, above about 700°C, carbon will readily reduce FeO (FeO + C = Fe + CO)
Uses of Ellingham Diagrams.2

- Carbon can even reduce highly reactive and stable compounds like \( \text{SiO}_2 \) and \( \text{TiO}_2 \) at temperatures above about 1620°C and 1650°C, respectively.
  - Unfortunately, these high temperatures are not economically feasible, and the required oxygen partial pressures are not industrially attainable.

- For less stable oxides, carbon monoxide is often an adequate reducing agent.

- **For the Equilibrium Partial Pressure of \( \text{O}_2 \):**
  - The scale on the right side of the diagram labeled “\( \text{PO}_2 \)” is used to determine what partial pressure of oxygen will be in equilibrium with the metal and metal oxide at a given temperature.
  - The significance of this is that, if the oxygen partial pressure is higher than the equilibrium value, the metal will be oxidized, and if it is lower than the equilibrium value then the oxide will be reduced.
Uses of Ellingham Diagrams

- To use the oxygen partial pressure scale, you need a straightedge or Ruler to extrapolate.

- First, you find the temperature you are interested in, and then find the point where the oxidation line of interest crosses that temperature.

- Then, line up the straightedge with both that point, and with the point labelled “0” that is marked with short radiating lines (upper left corner of the diagram).

- Now, with the straightedge running through these two points, read off the oxygen partial pressure (in atmospheres) where the straightedge crosses the “PO$_2$” scale, and this is the equilibrium partial pressure of oxygen.
Uses of Ellingham Diagrams

- For the Ratio of CO/CO₂ Needed for Metal-Oxide Reduction:
  - When using carbon or CO as a reducing agent, there will be a minimum ratio of CO to CO₂ that will be able to reduce a given oxide.
  - The harder the oxide is to reduce, the greater the proportion of CO needed in the gases to effect reduction.
  - To determine the CO/CO₂ ratio to reduce a metal oxide at a particular temperature, use the same procedure as you did for determining the equilibrium pressure of oxygen, except line up the straightedge with the point marked “C” (\textit{center of the left side of the diagram}), and read the ratio off of the scale marked “CO/CO₂”.

The most important pyrometallurgical operation in the metal industry is the reduction of iron oxide in a huge reactor known as The Blast Furnace.

Iron occurs in many different minerals, but the most important minerals for iron metal production are the iron oxide minerals: hematite ($\text{Fe}_2\text{O}_3$), magnetite ($\text{Fe}_3\text{O}_4$), and wustite ($\text{FeO}$).

The Blast Furnace consist mainly of a SHAFT, a BOSH, and a HEARTH as shown in Figure 14.

It is typically 20 to 30 m high and 4 to 7 m wide, made of a steel shell and lined on the inside with refractory brick.

The largest Blast Furnaces (60 m high x 14 m wide) can produce up to 10,000 tons per day.
Figure 14: Schematics of The Iron Blast Furnace
Figure 15: **Schematics of The Iron Blast Furnace**
Pyrometallurgy: **Iron Making.2**

- **Blast Furnace Input/Feed/Charge/Burden:**
  - Iron Ore: ➡ containing iron oxides and other minor components such as silica, MnO, Phosphates, etc.
  - Coke: ➡ Produced from coking coal & source of heat (fuel) and reducing agent CO.
  - Fluxes ➡ Mainly CaO and limestone (CaCO$_3$) enhances formation of silicate slags.
  - Air ➡ Heated air, injected into the furnace through jets called “Tuyeres”, results in the combustion of carbon (coke) to provide both heat and reducing agent CO$_2$. 

- **The Blast Furnace Reactions & Reaction Temperature Zones**

  - **At 250° - 500 °C**
    - {Top = Zone of Reduction}
    - \[3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2\] \[\text{[26]}\]
    - \[Fe_2O_3 + CO \rightarrow 2FeO + CO_2\] \[\text{[27]}\]

  - **At 850 °C**
    - \[Fe_3O_4 + CO \rightarrow 3FeO + CO_2\] \[\text{[28]}\]

  - **At 1000 °C**
    - {Middle = Zone of Fusion}
    - \[FeO + CO \rightarrow Fe + CO_2\] \[\text{[29]}\]

  - **At 1300 °C**
    - \[CO_2 + C \rightarrow 2CO\] \[\text{[25]}\]
    - \[C + H_2O \rightarrow H_2 + CO\] \[\text{[30]}\]

  - **At 1900 °C [Tuyere Zone]**
    - {Bottom = Zone of Combustion}
    - \[C + O_2 \rightarrow CO_2\] \[\text{[24]}\]
    - \[FeO + C \rightarrow Fe + CO\] \[\text{[31]}\]

  - **1400° – 1600°C**
    - {Hearth – Molten metal & Slag}
Other important Blast Furnace reactions include:

- \( \text{SiO}_2 + \text{C} \rightarrow \text{Si} + 2\text{CO} \) [some Si dissolution] \[32\]

- \( \text{MnO} + \text{C} \rightarrow \text{Mn} + \text{CO} \) [some Mn dissolution] \[33\]

- Dissolution of phosphorus (P) from phosphates in ore.

- Dissolution of Nitrogen (\( \text{N}_2 \)) from air in molten metal

- Decomposition of limestone \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \). \[34\]

- Silicate slag formation [ \( \text{SiO}_2 + \text{CaO} \rightarrow \text{CaSiO}_3 \)] \[35\]
General Blast Furnace Process Information:

1. In normal operation, the furnace contains three casts at different height levels; (a) the cast at the bottom is being tapped regularly, (b) the middle cast is descending and is undergoing reduction, and (c) the charge for a new cast is being added.

2. The charged materials comprising a cast will normally pass through the furnace in approximately 8 hours.

3. The Product of an iron Blast Furnace is raw molten iron known as Pig or Cast iron and a molten silicate slag containing impurity minerals:
   - Molten pig iron collects at the bottom of the hearth to be tapped
   - Molten slag collects at the top of the molten iron in the hearth & tapped

4. 1.0 ton of hot pig iron produced in a Blast Furnace requires about 1.7 tons of iron-bearing materials, 0.5 to 0.65 tons of coke and other fuel, 0.25 tons of fluxes, and 1.8 to 2.0 tons of air.
For each ton of hot metal produced, the process also creates:
1. 0.2 to 0.4 tons of slag,
2. 0.05 tons or less of flue dust, and
3. 2.5 to 3.5 tons of blast furnace gasses.
4. Dust is produced as solid materials are charged, totaling about 0.66% of the total input by weight.
5. The final product, hot PIG IRON metal, is about 93% iron, with other trace ingredients including Sulfur, Silicon, Phosphorus and Manganese.

Typical Composition of Pig Iron or Cast Iron is as follows:

- Fe = 91 - 95%
- C = 3.5 - 4.5%
- Si = 0.25 - 3.5%
- S = 0.018 - 0.1%
- P = 0.03 - 0.1%
- Mn = 0.5 - 2.5%
Steel is essentially an alloy of iron.

In the production of steel the impurity elements in pig iron are removed by simple oxidation in a vessel called a converter, such as a Pierce-Smith Converter or Rotary Converter.

In modern steel making, the oxidizing agent is either pure $O_2$ or $O_2$ diluted with argon. Air cannot be used directly as the source of $O_2$ because $N_2$ reacts with the molten iron to form iron nitride, which causes the steel to become brittle.

A cross-sectional view of a Bessemer Converter design appears in Figure 15 below.
Pyrometallurgy: Steel Making

Figure 16: Bessemer Converter for Steel Making:
In the Bessemer converter, \( \text{O}_2 \) diluted with argon, is blown directly into the molten metal.

The oxygen reacts exothermically with carbon, silicon, and many metal impurities to form the corresponding oxides, reducing the concentrations of these elements in the iron.

Carbon and sulfur are expelled as CO and SO\(_2\) gases, respectively.

Silicon is oxidized to SiO\(_2\) and reacts with the added lime (CaO) flux to form calcium silicates that are removed from the molten metal to join the slag layer.

Other metal oxides also react with the SiO\(_2\) to form silicates that dissolve in the slag layer.
The presence of a basic slag is also important for removal of phosphorus:

$$\text{P}_2\text{O}_5 (l) + 3\text{CaO} (l) \rightarrow \text{Ca}_3(\text{PO}_4)_2 (l)$$

1. Practically all of the O₂ blown into the converter is consumed in the oxidation reactions.

2. By monitoring the O₂ concentration in the gas coming out of the converter, it is possible to tell when the oxidation is essentially complete.

3. Oxidation of the impurities present in the iron normally requires about 20 min.

4. When the desired composition is attained, the contents of the converter are dumped into a large ladle.
Pyrometallurgy: Steel Making.5

- To produce various specialty steels, with different properties, alloying elements (e.g. Cr) are added as the ladle is being filled.

- The still-molten mixture is then poured into molds, where it solidifies.

- Typical compositions of Carbon Steel & Ferro-Chromium (Fe-Cr) Stainless Steel, compared to Pig Iron are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Steel</td>
<td>99</td>
<td>-</td>
<td>1.1</td>
<td>0.3</td>
<td>0.04</td>
<td>0.3</td>
<td>0.005</td>
</tr>
<tr>
<td>Fe-Cr Stainless</td>
<td>94.5</td>
<td>5.2</td>
<td>0.05</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.003</td>
</tr>
<tr>
<td>Pig Iron</td>
<td>93</td>
<td>0.0</td>
<td>3.5</td>
<td>1.5</td>
<td>0.05</td>
<td>2.0</td>
<td>0.08</td>
</tr>
</tbody>
</table>
Pyrometallurgy: Team Assignments, Technical Reports & Presentations

- Conduct a study of the pyrometallurgical processes listed below and prepare (1) a 20 minute PowerPoint presentation to be presented by the group in class, and (2) A technical report on your topic. Your literature study, presentation, technical report and review should include:
  - Fundamentals of the technique, including the theory, equipment, reactions, etc.
  - Applications of the technique to one or more ores
  - Advantages and disadvantages of the technique including environmental implications

- (Set A) Pyrometallurgy of Nickel Sulfide:
  - Roasting & Smelting of nickel sulfide ores to produce Matte
  - Nickel Matte Refining
  - Pure Nickel Metal Production
  - Uses of nickel metal

- (Set B) Pyrometallurgy of Copper Sulfide:
  - Roasting & Smelting of copper sulfide ores to produce Matte
  - Copper Matte Refining
  - Pure Copper Metal Production
  - Uses of copper metal

- (Set C) Pyrometallurgical Metal Refining Methods:
  - Liquation
  - Fire Refining
  - Vacuum Refining
  - Zone Refining

- A 5 – 10 minute question period will follow.
Hydrometallurgy ➔ Introduction

- **Hydrometallurgy** (or “Hydromet” for short) is the branch of Extractive Metallurgy which involves the application of aqueous chemicals (sometimes organic reagents) and generally low temperatures for the extraction or separation of the metal of interest from its ores and concentrates.

- The use of low temperatures (less than 100°C), as compared to pyrometallurgy, confers the advantages of **lower energy** requirements, and generally **lower costs** to hydrometallurgical processing.

- Hydrometallurgical processes range from **Leaching** of ores and concentrates (to bring the minerals of interest into solution) to **Solution Purification** and **Recovery** of the metals or compounds by **chemical** and/or **electrochemical precipitation**.
Hydrometallurgy ➔ LEACHING.1

• Leaching is the dissolution of the mineral and/or metal of interest from its ore or concentrate into an appropriate aqueous solution from which it can be recovered economically.

• In order for the leaching process to be cost effective, the following Essential Features must be present:

  1. The valuable metal must be soluble in an economically usable solvent.
  2. The metal must be economically recoverable from solution, and
  3. Any impurity elements which are co-extracted during leaching must be capable of further separation from the resultant Pregnant leach solution.
In addition to Essential Features, there are also Desirable Features of leaching which include:

1. The gangue (unwanted) minerals should not consume excessive amounts of solvent.

2. The solvent should be recoverable (or capable of regeneration) for recycling.

3. The feed material should be free of excessive clay minerals

4. The feed material should be porous enough for ease of solvent reaction and high surface area for reaction.

5. The solvent should preferably be non-corrosive
In order to optimize leaching operations, it is sometimes necessary to conduct Pretreatment operations. Such pretreatments, which may be physical and/or chemical, fall into 3 major categories, viz:

i. Comminution
ii. Concentration
iii. Chemical changes in the minerals
iv. Structure modification

Comminution (grinding) is the fracture of ore particles for size reduction, and it is mainly conducted during the Mineral Processing phase of extractive metallurgy.

1. Reduction in particle size leads to liberation of minerals of value, and significant increase in surface area for leaching reactions.
2. For example, decreasing the mean diameter from 10.0mm to 0.1mm increases particle surface area by a factor of $10^2$. 


Pretreatment of Ores Prior to Leaching:

- **Concentration** of the mineral or minerals of interest leads to major reductions in volume of leaching reagents used, as well as reducing the consumption of solvent by gangue minerals.
  - This leads to higher metal concentration in the leach liquor.

- Pretreatment **Chemical Changes** in the minerals, which often involve pyrometallurgical processes, are aimed at obtaining the metal or metal compound of interest in a form that is more easily dissolved in the leach liquor. The following examples are illustrative:
  - \( \text{AuTe}_2(s) \xrightarrow{\text{heat}} \text{Au}(s) + 2\text{Te}(g) \)  
  - \( \text{ZnS}(s) + 1.5\text{O}_2(g) \xrightarrow{\text{heat}} \text{ZnO}(s) + \text{SO}_2(g) \)

- In the above two reactions, both gold telluride (\( \text{AuTe}_2 \)) and zinc sulfide (\( \text{ZnS} \)) are insoluble in common leaching reagents. Whereas, elemental gold (\( \text{Au} \)) is readily soluble in cyanide solutions, and zinc oxide (\( \text{ZnO} \)) is easily dissolved in dilute acid solutions.
In some pretreatments to cause chemical changes, the treatments are intended to cause chemical changes in the associated gangue minerals, in such a way as to make the gangue minerals less soluble in the leaching solution.

E.g. pyrrhotite (FeS) occurs readily in gold bearing ores. This FeS in gold ores can lead to excessive cyanide leach liquor consumption according to the following reaction:

\[
\text{FeS(s)} + 2\text{H}^+(aq) + 6\text{CN}^-(aq) \rightarrow \text{Fe(CN)}_6^{4-}(aq) + \text{H}_2\text{S(g)} \quad \text{[39]}
\]

However, by heating the ore in an atmosphere of oxygen, the pyrrhotite is converted to hematite (Fe$_2$O$_3$), which is insoluble in cyanide leach solution, according to the reaction:

\[
2\text{FeS(s)} + 3.5\text{O}_2(g) \quad \text{heat} \rightarrow \text{Fe}_2\text{O}_3(s) + 2\text{SO}_2(g) \quad \text{[40]}
\]
**Hydrometallurgy ➔ LEACHING Techniques**

**In Situ Leaching (ISL).#1**

- In situ leaching (ISL), sometimes referred to as solution mining or in situ recovery (ISR), is a process of dissolving minerals such as copper or uranium directly from their ore deposits.

- Using a series of boreholes (Injection & Extraction wells), a flow of leach solution is established to allow leaching of the ore and to recover the pregnant LEACH-LIQUOR for processing.

- In situ leaching was originally developed in the early 1960s for uranium. It contributes about 15% of the world uranium production.

- The major advantage of in situ leaching is that metals or valuable minerals can be recovered without the need for conventional mining techniques, involving surface mining or large and expensive underground facilities.
Consequently, there is only little surface disturbance and no tailings or waste-rock generated.

For ISL, the ore-body must be permeable with respect to the leaching fluid.

Typically, ores contained in permeable sedimentary formations such as sandstones or highly fractured rocks can be suitable candidates for ISL.

Furthermore, the ores should be sandwiched between relatively impermeable layers (The so-called Aquitards), in order to channel the leaching agent or leach solution through the ore and to avoid leakage.

Leakage leads to environmental contamination and reduces the efficiency of the method as the pregnant solution is lost.
Hydrometallurgy ➔ LEACHING Techniques

**In Situ Leaching (ISL).#3**

- Figure 17: Schematic Illustration of In Situ Leaching (ISL)
In Situ Leaching of Uranium Ore Deposit at Beverley Mine in Australia
Hydrometallurgy ➔ LEACHING Techniques

**Heap Leaching #1**

- **Heap leaching** is the hydrometallurgical extraction of values from ores that have been mined, crushed, and transported on impervious pads for leaching by sprinkling and percolation of the solution through the ore.

- The ore is stacked on a lined containment area behind a retention dam.

- A leach solution (or **Lixiviant** fluid) is applied to the top of the ore and allowed to percolate through the heap.

- As the solution migrates through the ore, it dissolves (leaches) the mineral of interest (e.g. Cyanide leaching of gold and silver).

- The value-bearing solution ("pregnant solution") is collected in a **Pond** at the base of the leach pad.
**Heap Leaching #2**

Important factors for a successful heap leaching operation are:

- Maintain a good **permeability**. Precipitates like gypsum, ferric hydroxides and clay minerals might cause **clogging** and **flooding**.

- A good water balance. Sprinklers or drippers buried in the heap are used to deliver the leaching solution over the heap.

- **pH** control

- A steady supply of leaching reagents

- Fine particles are agglomerated to increase permeability.
Fig. 19: Schematic Illustration of Heap Leaching Operation

Sulfuric Acid Heap Leaching of Uranium with uranium recovery from solution by Solvent Extraction (SX) & Electrowinning (EW)
Agitation leaching is the most popular leaching technique in hydrometallurgy. It involves the leaching of finely ground (≈200 µm), and relatively high grade concentrates in Continuously Stirred Tank Reactors (CSTR) in order to:

1. Improve the rate of leaching and dissolution reactions.
2. Improve mass transfer rates in the reaction slurry
3. Maintain uniform reagent concentrations
4. Maintain uniform temperature profile
Hydrometallurgy ➔ Selection of Leaching Conditions

Eₜ-pH Diagrams.1 (Pourbaix Diagrams or Predominance Area Diagrams)

- In hydrometallurgy, the solubility of the different minerals is conveniently illustrated with help of so-called Eₜ-pH diagrams (or Pourbaix diagrams or Predominance Area diagrams).

- These diagrams display the expected predominant species or precipitate solids as a function of two important variables, pH and Eₜ (redox potential).

- Eh-pH or Pourbaix Diagrams are plots of Eh versus pH showing regions or fields where dissolved species and precipitates are stable. They can be used to quickly determine the equilibrium stability fields for aqueous species.

- The effective overall boundaries of the diagram are determined by the stability field for water.
For example, consider the various oxides and sulfide species of Copper (Cu) that can be stable in solution, depending on the prevailing pH and $E_h$:

1. Copper Sulfate ($CuSO_4$) – dissolved sulfate species
2. Chalcopyrite ($CuFeS_2$) – solid sulfide species
3. Bornite ($Cu_5FeS_4$) – solid sulfide species
4. Chalcocite ($Cu_2S$) – solid sulfide species
5. Covellite ($CuS$) – solid sulfide species
6. Cuprite ($Cu2O$) – solid oxide species
7. Malachite ($Cu_2CO_3(OH)_2$) – solid oxide species
8. Chrysocolla ($CuSiO_3$) – solid silicate species
9. Tenorite ($CuO$) – solid oxide species
1. We can see that in reducing conditions, mineral chalcopyrite is the expected predominant iron species, together (although less dominant) with bornite, chalcocite, metallic Cu and covellite.

2. In oxidizing and intermediate and high pH conditions, cuprite, malachite and possibly Antlerite (Cu3(SO4)(OH)4) or Brochantite (Cu4(SO4)(OH)6) seem to be able to form, at least from a thermodynamic view point (absence of kinetics).

3. In oxidizing conditions and low pH dissolved copper sulfate is predominantly stable in solution.
The effective overall boundaries of the Eh-pH diagram are determined by the stability boundary/field for water.

- One boundary is determined by the stability of water with respect to reduction to $H_2$ at 1 atm:
  
  $$2 e^- + 2 H_2O (l) \rightarrow H_2 (g) + 2 OH^- (aq)$$

- Writing the usual expression for the Gibb’s free energy change:
  
  $$\Delta G = \Delta G^o + RT \ln \left[ \frac{a_{H_2} \ a^2_{OH^-} \ a^2_{H_2O}}{a^2_{H_2O}} \right]$$

- We also know that:  
  
  $$\Delta G = -n \ F \ E$$

where ‘F’, Faraday’s constant, is the charge on a mole of electrons and is equal to 96,570 Coulombs, and ‘n’ is the number of moles of electrons transferred in the oxidation or reduction, and ‘E’ is the reaction Potential in Volts associated with the reaction.
Using the fact that the activities of molecular hydrogen at 1 bar (1 atm) and liquid water can be set equal to 1 gives:

- \( n \ F \ E = \Delta G^\circ + 2.303 \ \text{RT} \ \log a^2_{\text{OH}^-} \) \[44\]

or:

\( E = -\Delta G^\circ / (n \ F) - (2.303 \ \text{RT} / (n \ F)) \ \log a^2_{\text{OH}^-} \) \[45\]

(\textit{Note that this is the Nernst Equation which relates reaction potential (}E_h\text{) to concentration of participating species, e.g. }H^+\text{ or }OH^-\text{ ions or pH})

At 25 °C:

- \( 2.303 \ \text{RT} / F = 2.303 \ (8.314 \ \text{J/mol K}) \ (298.15 \ \text{K}) / (96,486.8 \ \text{C}) \)

\[ = 0.05917 \text{ V} \]
Therefore:

\[
E = - \frac{\Delta G^o}{nF} - \left( \frac{0.05917V}{n} \right) \log a^{2OH^-} (aq)
\]

\[
= - \frac{\Delta G^o}{2F} - 2 \left( \frac{0.05917V}{2} \right) \log a^{OH^-} (aq)
\]

\[
= - \frac{\Delta G^o}{2F} - \left( 0.05917V \right) \log a^{OH^-} (aq)
\]

\[
= - \frac{\Delta G^o}{2F} + \left( 0.05917V \right) pOH
\]

\[
= - \frac{\Delta G^o}{2F} + \left( 0.05917V \right) \left( 14.0 - pH \right)
\]

We now have an expression relating the reaction potential \(E_h\) to pH and \(\Delta G^o\).

But \(\Delta G^o\), the **Standard Gibbs Free Energy of formation** - can be estimated from thermodynamic data.
From Thermodynamics we can find $\Delta G^\circ$ at 298.15 K:

$$\Delta G^\circ = 2 \Delta G^\circ_{m, f, \text{OH}^- (aq)} - 2 \Delta G^\circ_{m, f, \text{H}_2\text{O} (l)}$$

$$= 2 (-157.300 \text{ kJ}) - 2 (-237.2 \text{ kJ})$$

$$= +159.8 \text{ kJ}$$

$$E = -\frac{\Delta G^\circ}{2F} + (0.05912 \text{ V}) (14.0 - \text{pH})$$

$$= -(+159.8 \times 10^3 \text{ J}) / (2 \times 96,570 \text{ C}) + 0.8283 \text{ V}$$

$$= (0.05911 \text{ V}) \text{ pH}$$

$$E = \sim 0 \text{ V} - (0.05911 \text{ V}) \text{ pH} \quad \text{[47]}$$

This equation can now be plotted as an $E_h$–$\text{pH}$ line as in Fig. 21 below.
The Eh-pH plot line for Equation 47 represents the lower (reduction) stability line for water as in Figure 21 below.

**Figure 21**: Below this line, water is unstable with respect to the reductive decomposition to $H_2 (g)$ at 1 bar of pressure.
With the above procedure, the stability boundary for the oxidative decomposition of water to \( \text{O}_2 \) (g) at 1 atm. is easily estimated:

- \( \text{H}_2\text{O} \) (l) \( \rightarrow \) \( \frac{1}{2} \) \( \text{O}_2 \) (g) + 2 \( \text{H}^+ \) (aq) + 2 e\(^-\)

Note for consistency in constructing the diagram that this decomposition must be written as a reduction:

- \( \frac{1}{2} \) \( \text{O}_2 \) (g) + 2 \( \text{H}^+ \) (aq) + 2 e\(^-\) \( \rightarrow \) \( \text{H}_2\text{O} \) (l) \( \text{---------}[48] \)

As before we can estimate the Potential (\( E_h \)) as follows:

- \( E = - \Delta G^\circ / (n \text{ F}) - (0.05911 \text{ V} / n) \log \left( \frac{a_{\text{H}_2\text{O}}^{2 \text{ (l)}}}{a_{\text{O}_2}^{2 \text{ (g)}} a_{\text{H}^+}^{2 \text{ (aq)}}} \right) \)
  
  \[ = - \Delta G^\circ / (2 \text{ F}) - \left(0.05911 \text{ V} / 2\right) \log a_{\text{H}^+}^{-2 \text{ (aq)}} \]

\[ E = - \Delta G^\circ / (2 \text{ F}) - \left(0.05911 \text{ V}\right) \text{pH} \]
Calculating $\Delta G^0$ in this case gives:

$$\Delta G^0 = +1 \Delta G^0_{m,f,H_2O(l)} = +1 \left( -237.2 \text{ kJ} \right)$$

$$= -237.2 \text{ kJ}$$

gives:

$$E = \frac{-\Delta G^0}{2F} - (0.05917 \text{ V}) \text{ pH}$$

$$= \frac{-(-237.2 \times 10^3 \text{ J})}{2((96,486.8 \text{ C}))} - (0.05911 \text{ V}) \text{ pH}$$

$$E = +1.23 \text{ V} - (0.05911 \text{ V}) \text{ pH} \[49\]$$

This equation can be plotted on an Eh-pH diagram to give the upper stability boundary for water as below:
Figure 22: Above the upper stability line indicated, water is unstable with respect to oxidative decomposition to $O_2$ (g) at 1 bar of pressure.
Now that we have the stability region or boundary for water, we can start estimating the stability areas for other metallic species in aqueous solution.

Let us consider a common metallic element, iron (Fe), in solution.

The stability areas where Fe$^{3+}$ and Fe$^{2+}$ are stable in solution can be estimated using the equation involving the reduction of Fe$^{3+}$ to Fe$^{2+}$ as follows:

\[ \text{Fe}^{3+} (\text{aq}) \rightarrow \text{Fe}^{2+} (\text{aq}) + \text{e}^- \]

For this reaction:

\[ \Delta G^o = \Delta G^o_{m, f, \text{Fe}^{2+}} - \Delta G^o_{m, f, \text{Fe}^{3+}} = -78.87 \text{ kJ} - (-4.6 \text{ kJ}) = -74.27 \text{ kJ} \]
The equivalent potential equation is given as:

\[ E = - \Delta G^0 / (n F) - (0.05911 \, V / n) \log \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right) \]

\[ = - \left( \frac{-74.27 \times 10^3 \, J}{(1 \, \text{C})} \right) \]

\[ - (0.05911 \, V / 1) \log \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right) \]

\[ = + 0.769 \, V - (0.05911 \, V) \log \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right) \]

To further develop this equation requires making a choice about the activities of Fe\(^{3+}\) and Fe\(^{2+}\). The usual choice is to take the activities of dissolved species as 10\(^{-6}\):

\[ E = + 0.769 \, V - (0.05911 \, V) \log \left( \frac{10^{-6}}{10^{-6}} \right) \]

\[ E = + 0.769 \, V \quad \text{-----------------------------------}[51] \]
Notice that the Potential (Eh) in Equation 51 above is independent of pH. **Does Anyone know why?**

Therefore the Eh-pH plot will be a straight line parallel to the pH axis, as shown in Figure 23 below.

Also Note that the more oxidized species, in this case Fe$^{3+}$, is stable at the higher Eh levels, while the reduced species, Fe$^{2+}$ is stable at the lower Eh levels.
Figure 23: Eh-pH line for Ferric Fe$^{3+}$ reduction to Ferrous Fe$^{2+}$
Now, let us consider the relative stability of $\text{Fe}^{3+} \text{(aq)}$ and the mineral goethite $\text{FeO(OH)} \text{(s)}$, in the equation:

$$\text{FeO(OH)} \text{(s)} + 3 \text{H}^+ \text{(aq)} \rightarrow \text{Fe}^{3+} \text{(aq)} + 2 \text{H}_2\text{O} \text{(l)}$$

Note that in this equilibrium no species is being oxidized or reduced.

$$\Delta G^0 = \Delta G_{\text{m,f,Fe}^{3+}} + 2 \Delta G_{\text{m,f,H}_2\text{O} \text{(l)}} - \Delta G_{\text{m,f,FeO(OH)} \text{(s)}}$$

$$= (-4.6 \text{ kJ}) + 2(-237.2 \text{ kJ}) - (-488.57 \text{ kJ})$$

$$= +9.6 \text{ kJ}$$

When no electron transfer is involved, $n = 0$ and potential $E = 0$. Therefore,

$$\text{(n = 0) } E = -\frac{\Delta G^0}{F} - (0.05911 \text{ V}) \log \left[ \frac{a_{\text{Fe}^{3+}}}{a_{\text{FeO(OH)} \text{(s)}}} \right]$$

$$- (0.05911 \text{ V}) 3 \text{ pH}$$
Hydrometallurgy ➔ Selection of Leaching Conditions

**Eh-pH Diagram Construction**

1. The equation for the Eh-pH relationship is:
   
   \[ 0 = - \left( + 9.6 \times 10^3 \text{ J} \right) / (96,570 \text{ C}) - (0.05911 \text{ V}) \log \left[ 10^{-6} / 1 \right] \]
   
   \[ - (0.05911 \text{ V}) \times 3 \text{ pH} \]

   
   \[ = (- 9.94 \times 10^{-2} \text{ V}) - 6 (-0.05911 \text{ V}) - (0.1773 \text{ V}) \text{ pH} \]

   
   \[ = +0.26 \text{ V} - (0.1773 \text{ V}) \text{ pH} \]

   
   \[ \text{pH} = 1.44 \]

2. We can see that when the equilibrium did not involve and oxidation or reduction, pH is independent of potential E and will plot as a straight line parallel to the Eh axis on the Eh-pH diagram.

3. This is clearly shown in the Eh-pH diagram in Figure 24 below.
Hydrometallurgy ➔ Selection of Leaching Conditions

Eh-pH Diagrams Construction.15

Figure 24: Eh-pH Diagram Construction for Iron Species in Solution
Now consider the relative stability of Fe\(^{2+}\) (aq) and FeO(OH) (s):

\[
\text{FeO(OH)} (s) + 3 \text{H}^+ (aq) + \text{e}^- \rightarrow \text{Fe}^{2+} (aq) + 2 \text{H}_2\text{O} (l)
\]

\[
\Delta G^o = \Delta G^o_{m, f, \text{Fe}^{2+}} + 2 \Delta G^o_{m, f, \text{H}_2\text{O}(l)} - \Delta G^o_{m, f, \text{FeO(OH)}(s)}
\]

\[
= (-78.87 \text{kJ}) + 2(-237.2 \text{kJ}) - (-488.57 \text{kJ})
\]

\[
= -64.7 \text{kJ}
\]

\[
E = -\Delta G^o / (nF) - \left( 0.05911 \text{ V} / n \right) \log [a_{\text{Fe}^{2+}}] - \left( 0.05911 \text{ V} \right) 3 \text{pH}
\]

\[
= -(-64.7 \times 10^3 \text{ J}) / (1) \left( 96,570 \text{ C} \right) - \left( 0.05911 \text{ V} / 1 \right) \log [10^{-6}]
\]

\[
- \left( 0.05911 \text{ V} \right) 3 \text{pH}
\]

\[
E = +0.670 \text{ V} + 0.355 \text{ V} - (0.1773 \text{ V}) \text{ pH}
\]

\[
E = +1.025 \text{ V} - (0.1773 \text{ V}) \text{ pH}
\]
We can see from Fig. 25 that any oxidation or reduction equilibrium that involves $H^+ \text{(aq)}$ or $OH^- \text{(aq)}$ will plot as a sloped line on these Eh-pH diagrams.
Next, let us consider the relative stability of goethite \([\text{FeO(OH)} \text{ (s)}]\) and magnetite \([\text{Fe}_3\text{O}_4 \text{ (s)}]\) using the reaction:

\[
3 \text{FeO(OH)} \text{ (s)} + \text{H}^+ \text{ (aq)} + e^- \rightarrow \text{Fe}_3\text{O}_4 \text{ (s)} + 2 \text{H}_2\text{O} \text{ (l)}
\]

We calculate our Gibbs Free Energy (\(\Delta G^o\)) Change & Potential (\(E_h\)):

\[
\Delta G^o = \Delta G^o_{m,f,\text{Fe}_3\text{O}_4 \text{ (s)}} + 2 \Delta G^o_{m,f,\text{H}_2\text{O} \text{ (l)}} - 3 \Delta G^o_{m,f,\text{FeO(OH)} \text{ (s)}}
\]

\[
= (-1015 \text{ kJ}) + 2 (-237.2 \text{ kJ}) - 3 (-488.57 \text{ kJ})
\]

\[
= -24.13 \text{ kJ}
\]

\[
E = -\Delta G^o / (n \text{ F}) - (0.05911 \text{ V}) \times 1\text{ pH}
\]

\[
= -(-24.13 \times 10^{-3} \text{ J} / (1 ((96,570 \text{ C}))) - (0.05911 \text{ V}) \times 1\text{ pH}
\]

\[
E = +0.250V - (0.05911 \text{ V}) \times \text{pH}
\]
Hydrometallurgy ➔ Selection of Leaching Conditions $E_h$-$pH$ Diagrams Construction.17

The corresponding $Eh$-$pH$ line for Equation 54 is shown below Figure 26:
Now, let us consider the stability regions for Fe$^{2+}$ (aq) and Fe$_3$O$_4$ (s), magnetite:

\[
\text{Fe}_3\text{O}_4 (s) + 8 \text{H}^+ (aq) + 2 \text{e}^- \rightarrow 3 \text{Fe}^{2+} (aq) + 4 \text{H}_2\text{O} (l)
\]

\[
\Delta G^\circ = 3 \Delta G^\circ_{m,f, \text{Fe}^{2+}} + 4 \Delta G^\circ_{m,f, \text{H}_2\text{O} (l)} - \Delta G^\circ_{m,f, \text{Fe}_3\text{O}_4 (s)}
\]

\[
= 3 (-78.87 \text{ kJ}) + 4 (-237.2 \text{ kJ}) - (-1015 \text{ kJ}) = -170 \text{ kJ}
\]

\[
E = -\frac{\Delta G^\circ}{nF} - (0.05911 \text{ V} / n) \log [a^3 \text{Fe}^{2+}] - ((0.05911 \text{ V}) 8 / 2) \text{pH}
\]

\[
= -((-170 10^{+3} \text{ J} / (2(96,570 \text{ C}))) - 3 (0.05911 \text{ V} / 2) \log [10^{-6}]
\]

\[
- ((0.05911 \text{ V}) 8 / 2) \text{pH}
\]

\[
= +0.880 \text{ V} + 0.532 \text{ V} - (0.1773 \text{ V}) \text{pH}
\]

\[
E = +1.025 \text{ V} - (0.2364 \text{ V}) \text{pH}
\]

The corresponding Eh-pH line is shown in Figure 27 below.
Hydrometallurgy ➔ Selection of Leaching Conditions $E_h$-pH Diagrams Construction.19

Figure 27

$\text{Fe}_3\text{O}_4 (s) + 8 \text{H}^+ (aq) + 2 e^- \rightarrow 3 \text{Fe}^{2+} (aq) + 4 \text{H}_2\text{O} (l)$
Finally, a good question to ask is Where does elemental iron occur in this Eh-pH diagram?

Then, let us consider the reduction of Fe$^{2+}$ (aq) to Fe (s):

- Fe$^{2+}$ (aq) + 2 e$^{-}$ -----> Fe (s)

Then $\Delta G^\circ = \Delta G^\circ_{m, f, Fe(s)} - \Delta G^\circ_{m, f, Fe^{2+}} = (0 \text{ kJ}) - (-78.87 \text{ kJ})$

$= +78.87$ kJ

$E = \Delta G^\circ / (n F) - (0.05911 \text{ V} / n) \log [1 / a_{Fe^{2+}}]$

$E = - ( +78.87 \times 10^3 \text{ J} / (2 (( 96,570 \text{ C} ))) - (0.05911 \text{ V} / 2) \log [1 / a_{Fe^{2+}}]$

$= - 0.4084 \text{ V} - (0.05911 \text{ V} / 2) \log [1 / 10^{-6}]$

$= - 0.4084 \text{ V} - 0.1773 \text{ V}$

$E = -0.5857 \text{ V}$
Also let us consider a related reaction, i.e. the reduction of magnetite to elemental iron:

Fe$_3$O$_4$ (s) + 8 H$^+$ (aq) + 8 e$^-$ -----> 3 Fe (s) + 4 H$_2$O (l)

$\Delta G^\circ = 4 \Delta G^\circ_{m,f, H_2O (l)} - \Delta G^\circ_{m,f, Fe_3O_4 (s)}$

$= 4 (-237.2 \text{ kJ}) - (-1015 \text{ kJ})$

$= +66.2 \text{ kJ}$

$E_h = - \Delta G^\circ / (n F - ((0.05911 \text{ V}) 8 / 8) \text{ pH}$

$= - (+66.2 \times 10^3 \text{ J} / (8 (96,570 \text{ C})))$

$= -(0.05911 \text{ V}) \text{ pH}$

$E_h = -0.086 \text{ V} - (0.05911 \text{ V}) \text{ pH}$

[57]
The Eh-pH plots of Eq. 56 & 57 are shown in red in Figure below Figure 28.

Question: Would you expect to find elemental iron in a wet oxygen rich environment?
Mineral Production in West Africa

Hydrometallurgical Extraction of Gold.1

- For many African countries, mineral exploitation constitute significant contributors to their economies, and remain key to future economic growth.

- The mineral industry is an important source of export earnings for many African nations.

- In West Africa, the mining & mineral industry is fast gaining recognition in the resources world.

- In West Africa, Gold is a major mineral resource and it is widely deposited throughout the region in the **Birimian Greenstone**.
Gold bearing Birimian Greenstone deposits are found widely in West Africa. Major deposits are found in Ivory Coast, Burkina Faso, Ghana, Mali, Guinea, Senegal, Liberia, Niger, & Nigeria.

**Figure 29**: Gold Bearing - Birimian Greenstone Deposits in West Africa (Green)
Gold Production in West Africa

Hydrometallurgical Extraction of Gold.2

- The mining and mineral industry in West Africa is relatively mature in Ghana, Senegal, Guinea, Niger, Mali, Burkina Faso, & Ivory Coast.

- Natural Resources Canada (NRC) estimate mining investments in Africa to have increased from $7 billion in 2006 to $14 billion in 2010.

- Much of the new mining investments were expected to be in West Africa.

- Within West Africa, the top mining investment destinations are expected to be Ghana, Mali, Guinea, and Burkina Faso.
Gold Production in West Africa

The Hydrometallurgy of Gold.

- The major mineral resources in Burkina Faso include: Gold, Phosphate, Zinc, Dolomite, & Marble.
- Gold mining and processing has received major investments and rapid developments over the past few years in Burkina Faso.
- Some of the major gold mining companies in Burkina Faso include:
  - High River Gold (HRG)
    - Taparko-Bouroum mine (200 km NE of Ouaga) ➔ Commercial gold production started October 2007.
    - Bissa Gold Property (80 km North of Oauga) ➔ Continuing exploration of significant gold find as of 2008.
  - Etruscan Ltd. Gold Operations
    - Banfora Property (continuing exploration as of 2009)
**Fig. 30: Gold Deposits & Production in West Africa**

The West African Birimian Greenstone Gold Deposits and Existing Project Locations
The Hydrometallurgy of Gold.

- In nature, gold and silver (precious metals) are known to occur mainly in their native state as metallic gold or metallic silver.

- The most important primary deposits of gold and silver are:
  - Oxide ores (quartzite ores) in which gold (and silver) is present as free gold particles dispersed in quartz mineral grains in concentrations often under 3 g/ton.
  - Refractory sulfide deposits (arsenopyrite, pyrite, among others) in which gold (and silver) is locked into the matrix of the sulfide mineral grains.
  - Refractory carbonaceous ores containing fine carbon mixed with sulfide and sometimes quartz mineral grains.
Fig. 31: General Block Flow Diagram for Gold Processing Showing Alternative Routes for Gold Recovery

Alternative routes for gold extraction from its ores. Gold concentrate in this figure refers to unrefined gold such as Galamsey gold product or Dore Gold.
The Hydrometallurgy of Gold.5

- **Hydrometallurgical Extraction Process:**
  - Gold and silver are among the most noble (non-reactive) metals and therefore difficult to leach unless complexation agents are used for their solubilization.

- Cyanide leaching of finely ground gold ores and concentrates, *in highly alkaline solution*, is still the most widely used process for the hydrometallurgical extraction of gold.

- The general equation for the cyanide dissolution of gold during alkaline solution leaching is represented as:

  \[ Au + 2 \text{NaCN} + \frac{1}{2} \text{O}_2 + \text{H}_2 \text{O} \rightarrow \text{Au(CN)}_2^- + 2 \text{NaOH} \]
The Hydrometallurgy of Gold

- The concentration of NaCN in the leaching solution is generally in the 0.10-0.25 percent by weight range.

- The NaCN consumption depends on the ore composition, but is usually in the range of 0.1 – 1.0 kg per ton of ore.

- Since sodium cyanide is relatively expensive, it is vital to achieve optimal conditions for a low cyanide consumption during leaching.

- Leaching is carried out at a high pH value (pH ≥11) to avoid losses of cyanide from solution in the form of gaseous HCN. In addition, HCN is a highly toxic gas.
In line with Equation 58, leaching is done in a series of aerated and agitated tanks, thus resulting in the formation of a stable aurocyanide \([\text{Au(CN)}_2^-]\) complex in solution.

After cyanide leaching or cyanidation, the gold in the pregnant Leach-Liquor is recovered by one of three main industrial processes, namely:

1. The Merrill-Crowe Process
2. Carbon-in-Pulp (CIP) Process
3. Carbon-in-Leach (CIL) Process

The differences between the three processes are found in the ways in which the dissolved gold cyanide is recovered from solution.
The Hydrometallurgy of Gold

The Merrill-Crowe Process:

- This is the oldest of the three gold recovery processes, and is no longer as common as the CIP or CIL processes.

- In this process, the leach slurry is first separated in a filtration step into (1) a pregnant leach liquor fraction containing the dissolved gold & (2) a wet solids fraction that are disposed of in a tailings pond.

- The dissolved gold in the pregnant leach liquor is precipitated by zinc cementation through the addition of zinc dust according to the reaction:

  \[ 2\text{Au(CN)}_2^- + \text{Zn}^{2+} \rightarrow 2\text{Au} + \text{Zn(CN)}_4^{2-} \]  

- The valuable sludge obtained is filtered, dried and sent for further heat treatment to form Dore Gold.
The Hydrometallurgy of Gold.

- **Carbon-in-Pulp (CIP) Process.**
  - In this process, leaching is first completed in an agitated and aerated tank reactor.
  
  - At the completion of the leaching reaction, coarse or granular Activated Carbon particles are then mixed with the cyanide leaching pulp/slurry in order to cause the adsorption of the dissolved gold cyanide complexes onto the activated carbon particles.
  
  - The activated carbon gradually adsorb the dissolved gold in a Counter-Current adsorption process (see Figure 31).
  
  - The loaded activated carbon granules are subsequently separated from the slurry by screening, and the gold is Stripped or Eluted from the activated carbon with dilute cyanide solution (see Figure 31).
  
  - The gold in the final solution is recovered by Electrowinning (see Fig 31).
Figure 31: Typical Carbon-in-Pulp (CIP) Cyanide Gold Extraction Plant Flow Sheet
The Hydrometallurgy of Gold

- The **Electrowinning** of the gold from the stripper solution is done with a **stainless steel anode** and a **cathode made out of steel mesh** onto which the precious metals are deposited.

- The cathode is subsequently calcined and melted. The slag is removed and the molten gold are casted into **doré bars** which can contain up to 90% gold. The doré bar is then further treated.

- **Carbon-in-Leach (CIL) Process:**
  - The Carbon-in-Leach (CIL) process is a simple modification of the CIP process in which the granular activated carbon is added to the agitated tank leaching reactors during the leaching process, so as to cause the simultaneous dissolution of gold and adsorption onto activated carbon.