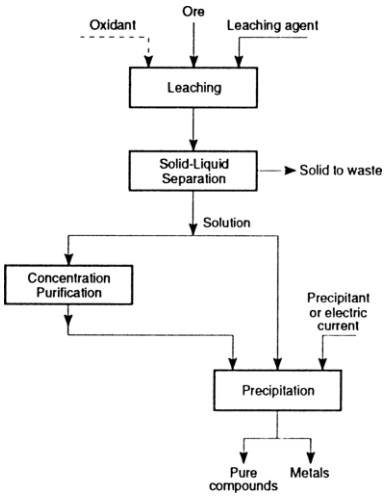
UNIT PROCESSES IN HYDROMETALLURGY: LEACHING, PURIFICATION OF LEACH LIQUOR

BY
SWETA SUMAN (2019UGMM030)
ADITYA KUMAR JHA (2019UGMM065)
MANTHAN HARISH BHAGAT (2019UGMM095)

Hydrometallurgy is a technique within the field of extractive metallurgy to obtain metals from their ores. Hydrometallurgy involve the use of aqueous solutions for the recovery of metals from ores, concentrates, and recycled of residual materials. The Unit processes of hydrometallurgy includes the leaching of particularly low grade ores for the recovery of metals, the separation of leaching solution from the ore and also the recovery of the dissolved metal from the solution.

STEPS INVOLVED IN HYDROMETALLURGICAL PROCESS:



1. Leaching:- Leaching is the process in which desired elements in the ore are selectively dissolved in an appropriate solvent known as leaching reagent. Proper leaching may involve preliminary ore preparation opertaion such as grinding, sizing, physical benefication, roasting etc.

2.Separation of leach liquor:- In this step, the solution i.e. leach liquor is separated from solid residues by one of the methods of material separation. ex: settling, thickening, filtration etc.

3.Recovery of metal from the leach liquor:-The metal in the elemental form is obtained in the recovery step. Methods employed to treat enriched liquor include evaporation, distillation, precipitation, cementation, electrolysis, ion exchange, solvent extraction etc.

4. Reagent Recovery:- The leaching reagent is generally recycled after purification and readjustment of composition.

ADVANTAGES OF HYDROMETALLURGY:

1. Ideally suited for lean and complex ores. With gradual depletion of rich ore deposits, it is becoming increasingly difficult in many situations to apply conventional pyrometallurgical methods for metal extraction.

2. Greater control over every step of processing resulting in recovery of valuable by-products. Handling of material is also easier.

3. It is preferable in the point of view of reducing environmental pollution.

4. A hydrometallurgical process avoid use of coke, an increasingly costly reducing agent.

5.Waste liquor from final recovery step can be recycled.

6. A hydrometallurgical process may start on the small scale and expand as required. However, a pyrometallurgical process usually must be designed as a large scale operation for reason of process economy.

DISADVANTAGES OF HYDROMETALLURGY:

1. Large amount of water used, so greater potential for contamination.

2. Chances of corrosion and erosion in handling equipment.

3. Time needed for high metal recovery.

4. Impurities problem in purification process.

LEACHING:

Leaching is a process widely used in extractive metallurgy where ore is treated with chemicals to convert the valuable metals within into soluble salts while impurity remain insoluble. In preparation for leaching, the ore is usually reduced to a small size by crushing and grinding to attain suitable fineness. This increases the surface area of particles and, therefore, the reaction rate. In some cases, preliminary may be necessary.
There are four types of leaching:

1.Cyanide leaching (e.g. gold ore)
2.Ammonia leaching (e.g. crushed ore)
3.Alkali leaching (e.g. bauxite ore)
4.Acid leaching (e.g. sulfide ore)

The choice of a leaching agent depends on the following factors:

- Chemical and physical character of the material to be leached.
- Cost of the reagent.
- Corroding action of the reagent and the materials of construction of construction required.
- Selectivity of the leaching agent for the desired constituent to be leached.
- Ability to be regenerated.

LEACHING REAGENTS

The common categories of leaching reagents are:

1 WATER – Some compounds, e.g. $CuSO_4$, $ZnSO_4$, most compounds of alkali metals dissolve in water readily. Some poor grade copper sulphide ores transform slowly into water soluble sulphate.
2 ACIDS – Mineral acids, chiefly sulphuric acids, are the most common leaching agents.
3 BASES – Several bases like, NaOH solution or NH_4OH are routinely employed in many leaching operations. Bauxite is leached by hot concentrated NaOH solution under pressure, ammonia solution is used in the leaching of native copper, copper ores, NiS and Cu_2S.
4 AQUEOUS SALT SOLUTIONS – The most important example of a salt solution as a leachant is seen in the dissolution of gold during its extraction from veins in silica rock. Gold is dissolved by a solution of NaCN. The reaction is,
$4Au(s) + 8NaCN(aq.) + O_2(g) + 2H_2O(aq.) \leftrightharpoons 4NaAu(CN)_2(aq.) + NaOH(aq.)$

LEACHING TECHNIQUES

IN-SITU LEACHING

- It is also known as solution mining.
- It is a mining process used to recover minerals such as copper and uranium through boreholes drilled into a deposit.
- The process initially involves the drilling of holes into the ore deposit. Leaching solution is pumped into the deposit where it makes contact with the ore. The solution bearing the dissolved ore content is then pumped to the surface and processed.
- Solvent is injected through a set of pipes drilled down in the ore. Resulting liquor is removed through different set of pipe shape drills.
- Through these pipe shaped drills, solvent flow down and is penetrated in to ore body for leaching. Solvent moves through the pipe shaped drills and ore body and solute is leached.

HEAP LEACHING

- It is an industrial mining process to extract precious metals, copper, uranium and other compounds from ore via a series of chemical reactions that absorb specific minerals and then re-separates them after their division from other earth materials.
- Heap leaching mining places ore on a liner, then adds the chemicals via drip systems to the ore.
- In heap leaching, ore is digged and prepared in the form of very large size heap.
- A pond is prepared at the top of the heap for placing solvent in it.
- Solvent is pumped over the ore through these pipe shaped drills and is flown down and is penetrated in the ore body for leaching.
- Solvent moves through the pipe shaped drills and ore body and solute is leached.
- Whole solution is collected as it drains from the heap.

VAT LEACHING

- The ore meant to be leached is loaded into vats that are typically made up of concrete. When leaching has been completed, the residual solid are dug out of the vat and replaced by fresh batch of ore.
- Suitable for porous and sandy materials.
- Commonly used for gold and silver ore.

AGITATION LEACHING

- A process where soil is slurried with the extraction of fluid for a period of time. When equilibrium between the metals on the soil surface and metal contained by the solution is approached, the solubilization of metal in the soil is slowed and extraction is considered to be complete.

AUTOCLAVE LEACHING

- Autoclave reactors are used for reactions at higher temperatures, which can enhance the rate of reaction. Autoclave enable the use of gaseous reagents in the system.

SEPARATION OF LEACH LIQUOR:

Practically all hydrometallurgical processes involve leaching of solids to dissolve valuable constituents. This usually is followed by a solid-liquid separation before producing the final product. In this step, the solution of leach liquor is separated from solid residues by one or more of various methods of material separation. Leach liquor is separated from the residue by process such as:

(a)Washing: This method is based on the difference in densities of the metallic ore and impurities. ore is treated with a stream of running water when the lighter impurities are washed away and heavier ore particles are left behind.

(b)Filtration: Filtration is the separation of a suspension into a solid filter cake and a liquid filtrate by passing it through a permeable filtering material. Important factors in this process are the properties of the suspension (e.g., size distribution, concentration), the properties of the filtering materials (e.g., the width and shape of pores), and the forces applied to the suspension.

(c)Thickening: Thickening is a process where a slurry or solid-liquid mixture is separated to a dense slurry containing most of the solids and an overflow of liquor in leaching processes. The solids in a suspension settle under the influence of gravity in a tank and form a thick pulp. This pulp, and the clear liquid at the top of the tank, can be removed continuously or intermittently.

(d)Settling: In this method of solid-liquid separation, the leachate obtained after leaching is neutralized and this neutralized slurry is separated and removed by adding flocculants(A flocculant is a chemical that can be added to the water to help colloids and any other suspended solids bind together and form heavier particles)

METAL RECOVERY:

Metal recovery is the final step in a hydrometallurgical process. Metals suitable for sale as raw materials are often directly produced in the metal recovery step. Sometimes, however, further

refining is required if ultra-high purity metals are to be produced. The primary types of metal recovery processes are:

(a) Precipitation: Precipitation is the selective removal of a compound of the targeted metal or removal of a major impurity by precipitation of one of its compounds. The principle technology to recover or remove metals from a solution is by chemical precipitation. Chemical precipitation is one of the most widely adopted methodologies that have been employed for heavy metal removal from inorganic effluents in industries. It principally involves the transformation of a soluble compound into an insoluble form (insoluble precipitates of heavy metals as hydroxide, sulfide, carbonate, and phosphate) via the addition of chemicals (precipitants). Once the heavy metals precipitate to form solids, they can be removed easily.

(b) Cementation: Cementation is a type of precipitation, a heterogeneous process in which ions are reduced to zero valence at a solid metallic interface. It is the process of extracting the metals from a solution based on the electrochemical reaction between the cementing metal and the ion of the precipitated metal. The precipitation of the metal is accompanied obviously by a change of its concentration of the solution, and consequently, of its potential. When the equilibrium values are reached, the process stops.

(c) Electrowinning: Electrowinning is the electrodeposition of metals from their ores that have been put in a solution. It is also called as electro extraction. It is most commonly used to recover metals like gold, silver, copper, zinc etc. because of their high electropotential values. In electrowinning process, current is passed from an inert anode through a liquid leach solution containing the metal so that the metal is extracted as it gets deposited on the cathode. Electrowinning cells provide a low-cost option for producers and higher efficiency. In addition, electrowinning produces a very clean products.

(d)Ion exchange: Ion exchange has traditionally been employed for the purification of water and the removal of metal contaminants from dilute waste streams. More recently, its use in removing trace metallic impurities from hydrometallurgical process streams (with typical background metal concentrations of 50–100 g/L) has increased substantially. It is also used as a primary recovery and concentration unit operation for certain commodities, where both technical and cost advantages become apparent for complex flow sheets. This overview discusses selected modern applications of ion exchange in hydrometallurgical processes for uranium, precious metals, copper, cobalt, nickel and zinc, and identifies some opportunities for the future.

EXAMPLE:-

GOLD EXTRACTION:-

Gold extraction refers to the processes required to extract gold from its ores. Ores in which gold occurs in chemical composition with other elements are comparatively rare. They include calaverite, sylvanite, nagyagite, petzite, krennerite.

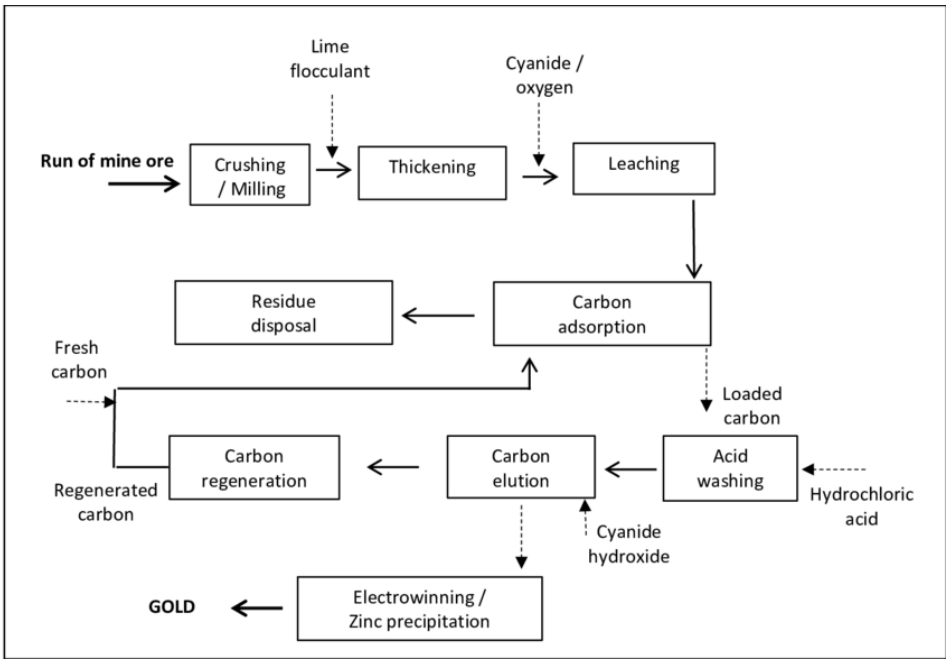


Fig: **extraction of gold**

Gold cyanidation:

It is the most commonly used leaching process for gold extraction. More gold is recovered by cyanidation than by any other process. In cyanidation, metallic gold is oxidized and dissolved in an alkaline cyanide solution. The oxidant employed is atmospheric oxygen, which, in the presence of an aqueous solution of sodium cyanide, causes the dissolution of gold and the formation of sodium cyanoaurite and sodium hydroxide.

The chemical reaction for the dissolution of gold

$$4\,Au(s) + 8\,NaCN(aq) + O2(g) + 2H2O(l) \rightarrow 4\,Na[Au(CN)2](aq) + 4\,NaOH(aq)$$

When gold dissolution is complete, the gold-bearing solution is separated from the solids.

- With ores of higher gold content (greater than 20grams of gold per ton of ore), cyanidation is accomplished by vat leaching, which involves holding a slurry of ore and solvent for several hours in large tanks equipped with agitators.

- For extracting gold from low-grade ores heapleaching is practiced. The huge heaps described above are sprayed with a dilute solution of sodium cyanide, and this percolate down through the piled ore, dissolving gold.

Recovery of gold from cyanide solution:-

The common processes for recovery of the solubilized gold from solution are **:**

1. Carbon in pulp: Carbon in a pulp is an extraction technique of recovery of gold which has been liberated in a cyanide solution as a part of gold cyanidation process. Carbon in Pulp is regarded as a simple and cheap process. As such it is used in most industrial applications where the presence of competing silver or copper does not prohibit its use. Leached pulp and carbon are transferred in a counter current flow arrangement between a series of tanks, usually numbering 4 to 6. In the final tank, fresh or *barren carbon* is put in contact with low grade or tailing solution. At this tank the fresh carbon has a high activity and can remove trace amounts of gold. As it moves up the train, the carbon loads to higher and higher concentrations of gold, as it comes in contact with higher grade solutions. Typically concentrations as high as 4000 to 8000gramsof gold per tonne of carbon (g/t Au) can be achieved on the final loaded carbon, as it comes in contact with freshly leached ore and leach liquor solution. This can be measured by comparing the amount of gold extracted from the carbon to the amount of carbon used.

   The final loaded carbon then is removed and washed before undergoing desorption of gold cyanide at high temperature and pH. Ethanol can also be used to desorb gold from activated carbon.

2. Merrill crowe process: The Merrill crowe process is a separation technique for removing gold from solution obtained by leaching of gold ore. The solution is separated from the ore by methods such as filtration(e.g. vertical leaf type clarifier filters) and counter current decanation. Afterwards a very clear solution is achieved by using pre-coated filters applying diatomaceous earth. Oxygen is then removed by passing the solution through a vacuum de-aeration column. Zinc dust is added to the clarified, de-aerated solution which precipitates the gold. Zinc having the high affinity to cyanide than gold. The gold precipitate (mixed with zinc dust) is then filtered out of the solution, and the zinc dust and gold are mixed with sulphuric acid to dissolve the zinc. The solution is filtered, and the remaining solids are smelted to a gold bar. These bars are

sent to a refinery to remove the copper and silver, the specific process used depending upon the impurities in the gold.

3. Electrowinning: Electrowinning is a process used to recover metals(e.g. silver and gold) from concentrated solution by applying a voltage across electrodes immersed in a concentrated solution. The positive terminal from the rectifier is connected to the anode where the oxidation reaction occur and electrons are generated. These generated electrons are consumed at cathode which is connected to the negative terminal of the rectifier. The reduction reaction results in the deposition of metal on the cathode .The following reduction reactions takes place during electrolysis of the alkaline gold cyanide solution:

   Cathode: $Au\,(CN)^{-}{}^{2} + e^{-} \rightarrow Au + 2CN^{-}$

   Anode: $2H_2O \rightarrow 4H+ + O2 + 4\bar{e}^{-}$

   In cyanide solution, gold is present as stable auro-cyanide complex ion with a relatively high cathodic potential. The cathodic shift demand higher cell voltage and consequently other cathodic reaction like formation of H2 and reduction of O2 can also occur.

Refining of gold:

Gold extracted by cyanidation contains a variety of impurities, including zinc, copper, silver, and iron. Two methods are commonly employed for purification: The Miller process, Wohlwil process,

1. The Miller process is based on the fact that virtually all the impurities present in gold combine with gaseous chlorine more readily than gold does at temperatures equal to or greater than the melting point of gold. The impure gold is therefore melted and gaseous chlorine is blown into the resulting liquid. The impurities form chloride compounds that separate into a layer on the surface of the molten gold.

2. Wohlwil process, in this process, a casting of impure gold is lowered into an electrolyte solution of hydrochloric acid and gold chloride. Under the influence of an electric current the casting functions as a positively charged electrode, or anode. The anode dissolves, and the impurities either pass into solution or report to the bottom of the electro refining tank as an insoluble slime. The gold migrates under the influence of the electric field to a negatively charged electrode called the cathode, where it is restored to a highly pure metallic state.

Other Methods of refining of gold:

- **USING ACID:** This is the most common method to purify gold. In this method, strong acids are used as a means of dissolving impurities. Hydrochloric acid and nitric acid are the acids used in this process. When gold is added to the solution containing the acids, impurities separate from the gold. After removing the other substances, the precipitate that remains is 99.999% gold**.**

- **USING FIRE:** Another process that is used to refine gold involves the application of heat. This is the oldest method of obtaining pure gold. Gold scraps are placed in a crucible (a container that can withstand very high temperatures). This crucible is then placed in a furnace which is heated up to almost 2,000 degrees Fahrenheit. The gold melts at such a high temperature. It is then transferred to another container, leaving the impurities and other substances floating at the surface.

- **CUPELLATION:** Cupellation is a process that purifies ores by separating gold and silver from base metals and other impurities. The process makes use of a cupel – a high temperature resistant flat bowl. The ore is placed in this cupel which is put in a special furnace. Hot air is then passed through it to remove the impurities. The impurities and other metals either vaporise or are oxidised or absorbed by the cupel.

- The gold that refining companies receive for purification is called ‘doŕe form of gold’. A doŕe bar is basically an alloy of gold and some other metals. This is re-liquified in a

furnace. The gold is separated from impurities and other metals when borax and soda ash is added to the mix. And this is how pure gold is obtained.

- It is also possible to refine gold without any large-scale equipment. In this process, nitric acid is first added to the gold that needs purification. Then, Hydrochloric acid or Muriatic acid is added to the mixture. Once the mixture settles, impurities are removed by filtering the solution. Since a lot of acids were added, the remains are treated to neutralise those acids. Once all this is done, the resultant muddy precipitate is gold! This muddy substance is then rinsed thoroughly in water and treated with aqueous ammonia. White vapours form because of the treatment. After rinsing once again and allowing it to dry, refined gold is obtained.

APPLICATION OF GOLD:

- Gold is considered as the best filling for cavities and crowns, bridges and other orthodontic appliances because the metal is ductile and can easily take shapes. It is also chemically passive and doesn't react easily when missed with other metals. It is also easy to insert and is non-allergic. Dentists have used gold as the best substitute for misplaced/ dislocated teeth for ages.

- Gold is of the top metals when it comes to being good conductors of electricity. It is able to carry electrical charges easily and because of this property, this metal is found in small portions in many electrical devices like mobile phones. Television sets, GPS devices. It is also sometimes found in computers and laptops for transferring data quickly.

- Gold is considered as a highly auspicious and precious metal it is used in the making of winning medals for popular world games, championships and awards. Its beauty holds significance and a permanent place in the human eye. Because of its exceptional magnificence, it is also used in the making of religious statues and Idols.

- As per statistics, about 80% of gold is converted into jewellery. It is the most standard use if gold and is common amongst all cultures.

REFERENCE:

1. Brent Hiskey "Metallurgy, Survey" in Kirk-Othmer Encyclopedia of Chemical Technology, 2000, Wiley-VCH, Weinheim .doi:10.1002/0471238961.1921182208091911.a01

2. Recent Trends in Extractive Metallurgy" Journal of Mining and Metallurgy, Section B: Metallurgy 2009, Volume 45, pp. 1- 13.

3. Adams, Mike D. (2005-12-02). *Advances in Gold Ore Processing*.

4. "Dictionary of Mining, Mineral, and Related Terms". Hacettepe University. Archived from the original on 9 June 2011. Retrieved 10 September 2010 .

5. Alexander Watt, *Electro-Deposition a Practical Treatise*, Read Books (2008), p. 395. ISBN 1-4437-6683-6