

# Extraction of Non-Ferrous metals



(Basic principles-2)

# Steps in hydrometallurgical extraction process

1-Preparation of ore for leaching

2-Leaching

3-Separation of leach liquor

4-Recovery of metallic values from leach liquor

# Steps in hydrometallurgical extraction process (continue..)

## 1-Preparation of ore for leaching

- (a) Grinding
- (b) Removal of specific impurities by physical methods
- (c) Roasting
- (d) Special chemical treatment to render these values soluble to the subsequent leaching operation or to prevent the leaching reagent from being consumed by impurities.

# Steps in hydrometallurgical extraction process (continue..)

## 2-Leaching

In leaching, by using a suitable liquid reagent the metallic values in an ore are selectively dissolved.

The selective dissolution depends upon the nature of reagent.

Rate of leaching depends upon:-

- (a)-temperature
- (b)-pressure
- (c)-volume of leaching liquid
- (d)-ore particle size
- (e)-the composition and concentration of the reagent
- (f)-the pulp density
- (g)-duration of the leaching reaction
- (h)-degree of aeration of the leaching reagent

# Steps in hydrometallurgical extraction process(continue..)

## **3-Separation of leach liquor**

Leach liquor is separated from the residue by process such as:-

- (a)-settling
- (b)-thickening
- (c)-filtrations
- (d)-washing

# Steps in hydrometallurgical extraction process (continue..)

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# Objectives of typical hydrometallurgical process

1. To produce a pure compound which can later be processed by pyrometallurgy to yield the metal.
2. To produce the metal either the crude or the metal compound which has already been prepared by other method.
3. To produce a metal directly from an ore or concentrate.

# Advantages of hydrometallurgical process

- 1-Hydrometallurgical methods are ideally suited for lean and complex ores
- 2-Hydrometallurgical operation ensures great control than other conventional method over every step in the processing of ore. Resulting in the recovery of valuable by products.
- 3-It is ecofriendly, it does not create much pollution like pyro metallurgical operation.
- 4-Process are generally carried out at room temperature or slightly elevated temperature.
- 5-The waste liquor from the final recovery step can be recycled to the initial leaching operation.
- 6-Besides meeting the mounting demand for both the quantity and quality of metals hydrometallurgy can produce metal in a variety of physical form such as powders, nodules, and coherent surface deposit.



# Disadvantages

- 1-Handling of large amount of chemicals become difficult and also a large amount of space is required.
- 2-The cost of the reagent and equipment is high.
- 3-Corrosion and erosion of tanks and ducts used for strong and handling fluids.
- 4-In hydrometallurgy, the disposal of effluent without causing pollution poses a serious problem.

# Concentrate for leaching

Leaching is a process which selectively dissolves the feed material. In leaching metallic values containing the main metal goes into the solution leaving behind the gangue and solid residue.

But some exception is there where gangue desirable to leach in case of Thorium.

To facilitate material handling and to minimize the consumption of the leaching reagent an ore is usually concentrate prior to leaching, except when leaching is carried out In situ, as in solution mining, dump leaching, heap leaching or vat leaching

# Leaching solution preparation

➤ Leaching solution contains:-

- main solvent
  - wide variety of reagent (helps in the dissolution because of their chemical effects)
- For example-these chemicals help in obtaining an oxidized or reduced state of a metal or a metal compound.
- Example of reagent-Inorganic salts (ferric chlorides) and acidified sodium chlorides can be used.
- All the solvents are water based. In some isolated case, plain water itself can be used as a solvent.
- In most cases, acids or alkalis, in varying degree of concentration are employed.
- Acid is much stronger solvent than alkali. So acidic solution do not required fine grounding of the ore or concentrate but alkali required this.

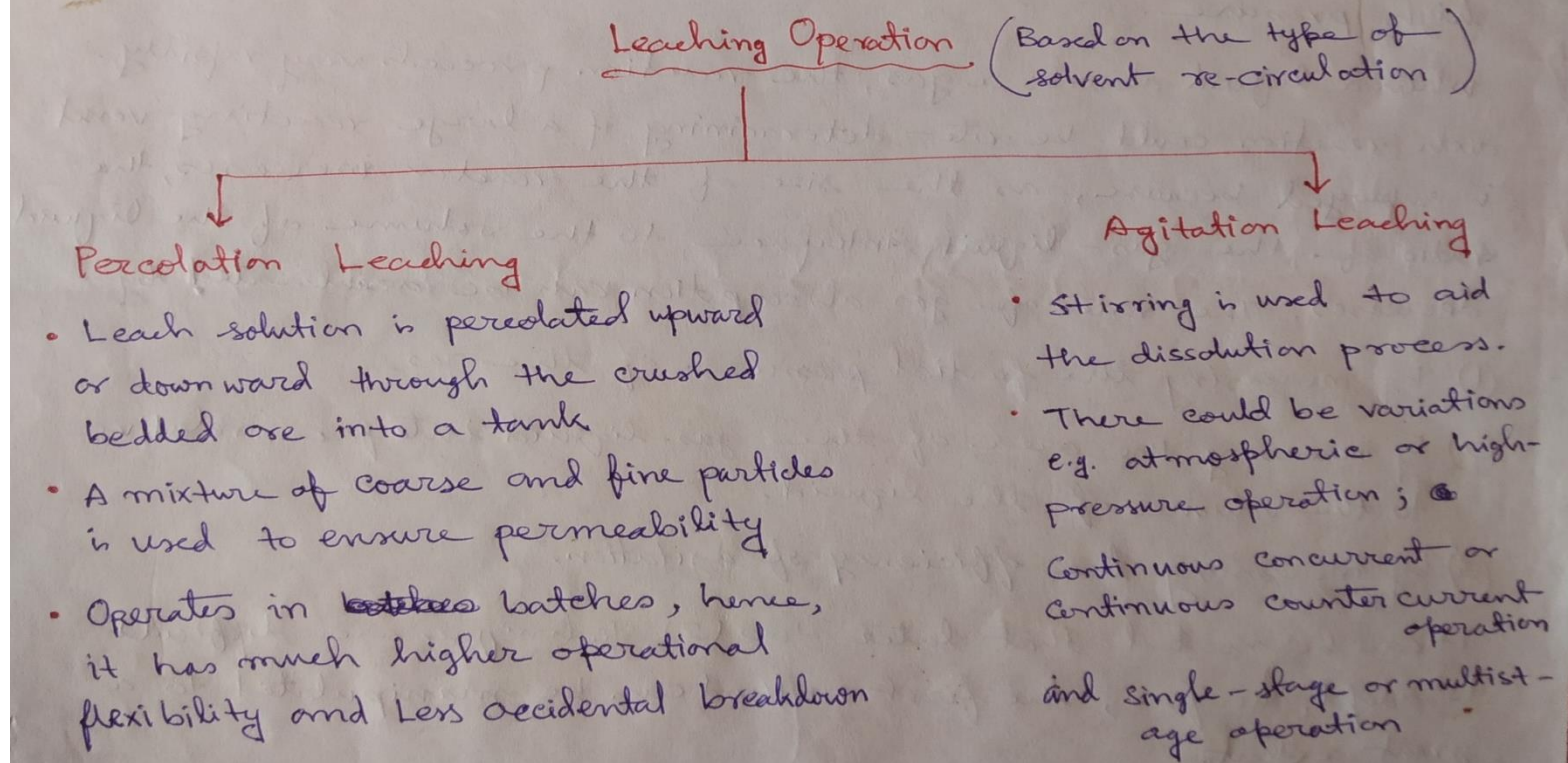
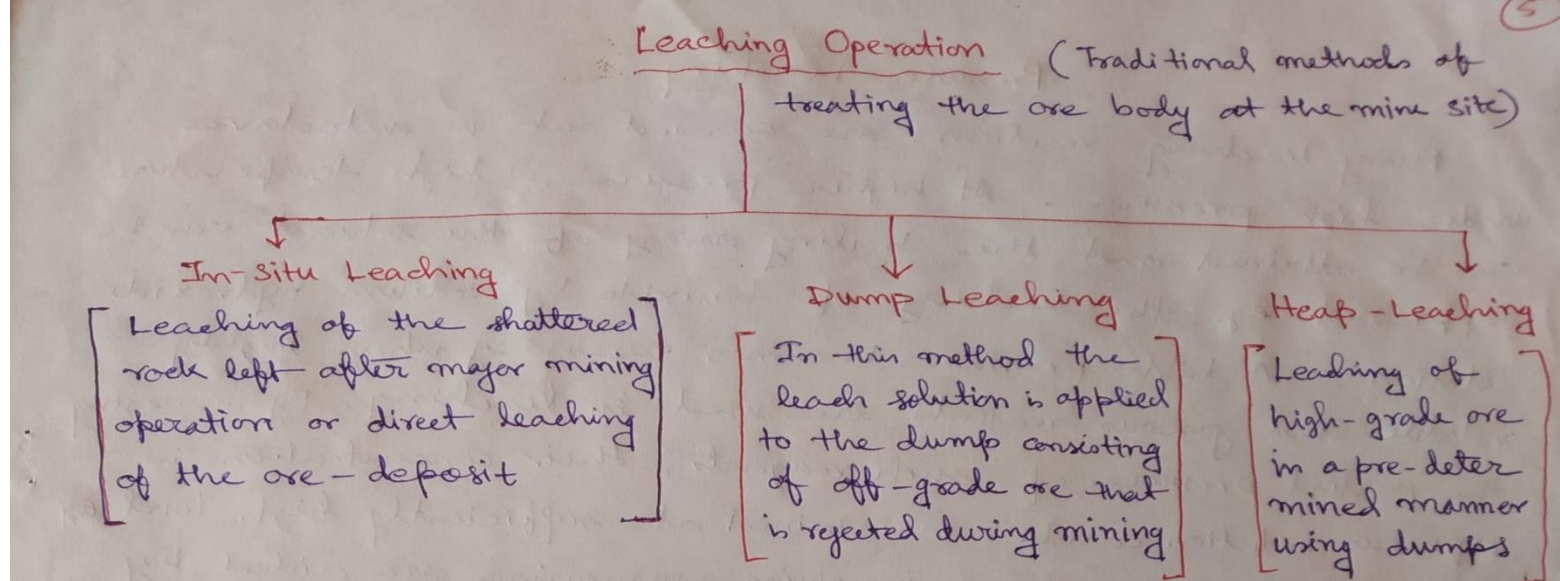
## **Examples of reagent are:**

- ✓ Acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ )
- ✓ alkalies ( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{OH}$ )
- ✓ oxidising agent ( $\text{NaClO}_3$ ,  $\text{MnO}_2$ ,  $\text{KMnO}_4$ ,  $\text{FeCl}$ )
- ✓ reducing agent( $\text{SO}_2$ ,  $\text{H}_2$ )

# Criteria of selecting a leaching reagent

- 1-Leaching by a reagent must be as selective and as rapid as possible (depends on nature of ore and reagent)
- 2-It should be possible to dissolve the reagent in order to prepare a sufficient strong leaching solution which can ensure fast rate of leaching.
- 3-The reagent should not corrode the equipment.
- 4-The reagent should be economical and should preferably allow regeneration.

# Classification of Leaching operation



# Leaching operation

## ***1- In Situ leaching (In Situ Recovery or solution mining)***

- It is a operation in which either the leaching of the shattered rock residues left behind in a mine after the major mining operation have been carried out or the direct leaching of the ore deposited .
- It works by artificially dissolving minerals occurring naturally in a solid state.
- It involves pumping of a lixiviant into the ore body via a bore hole, which circulates through the porous rock dissolving the ore and is extracted via a second bore hole.
- The lixiviant varies according to the ore deposit: For salt deposit the leachate can be fresh water in which salt can readily dissolved. For copper, acids are generally needed to enhance solubility of the ore minerals within the solution. For uranium ore, the lixiviant maybe acid or sodium bicarbonate.

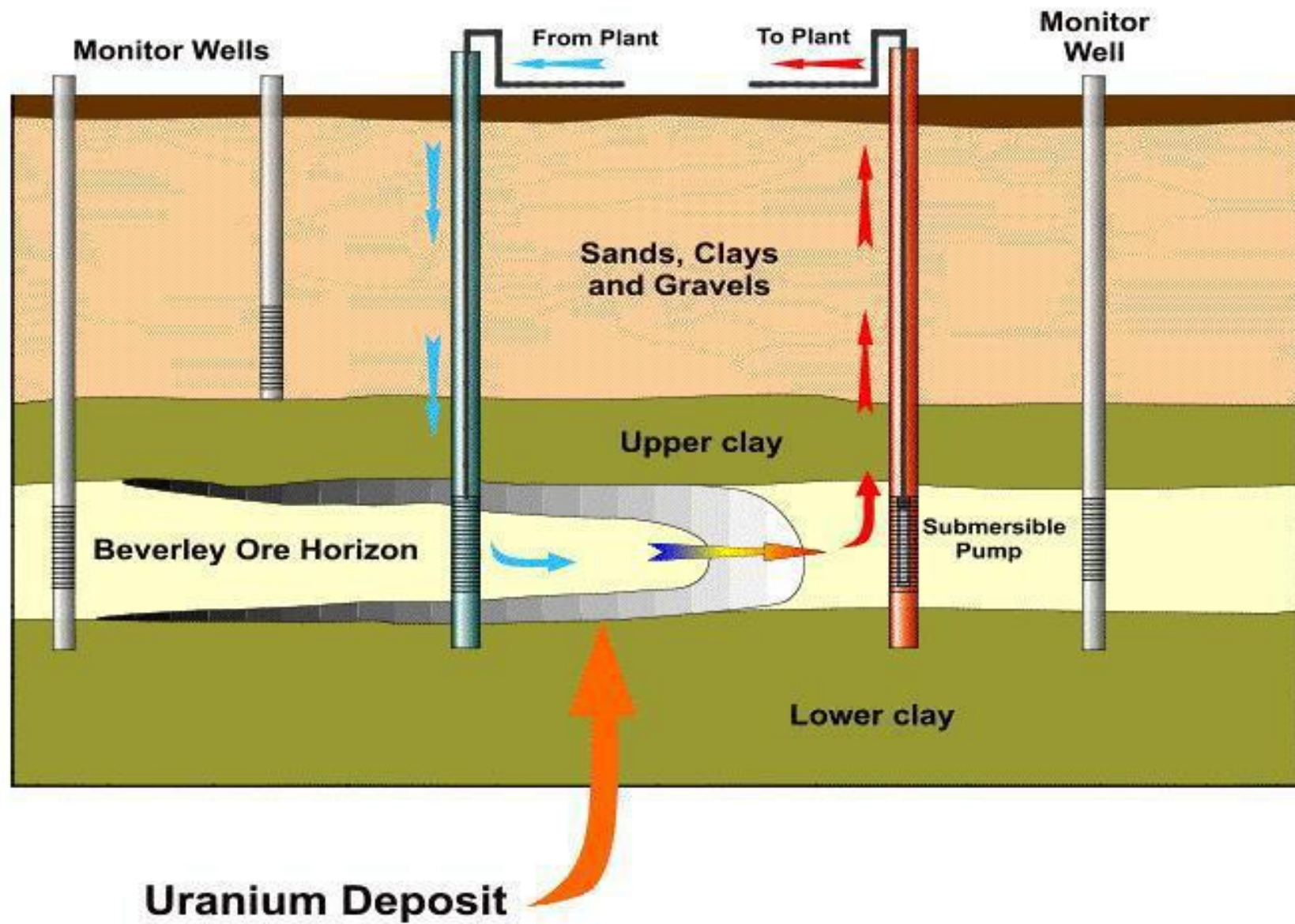
### **Advantages:-**

- Shorter mine development time
- No excavating cost
- Reduces visual and impact of mining operation
- Lower mining and infrastructure cost.

### **Disadvantages:-**

- If ore body is impermeable, it must be cracked by explosions
- Risk of contamination of ground water (compare acid rock generation) because of poor solution controlled.
- Precipitation of secondary minerals might cause permeability problems.



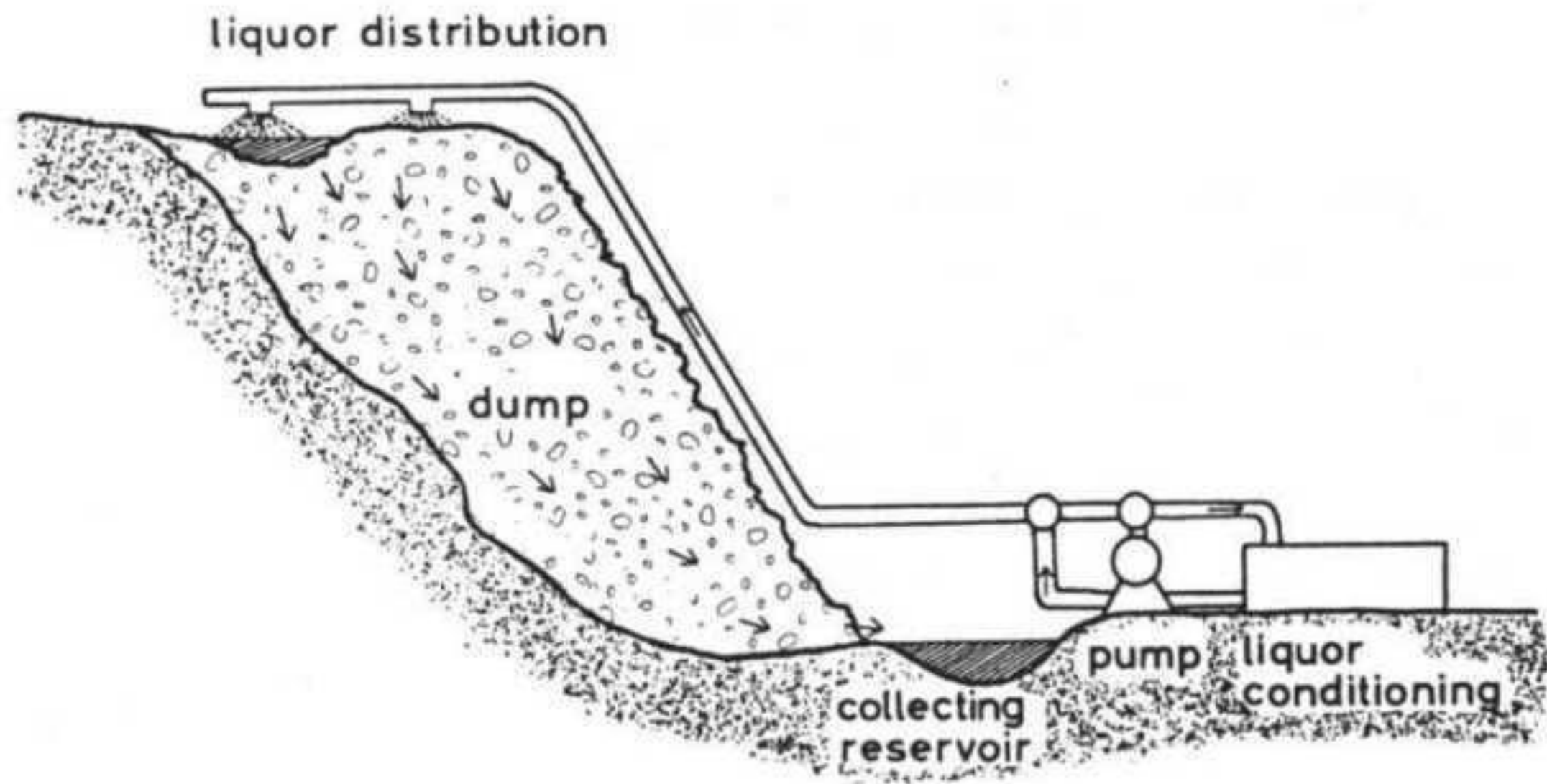


# Leaching operation (continue..)

## ***2-Dump Leaching:***

- It is the application of the leach solutions to dumps consisting of off-grade ore rejected during the normal mining operation.
- It is similar to heap leaching, however in the case of dump leaching ore is taken directly from the mine and stacked on the leach pad without crushing, where in the case of gold and silver, the dump is irrigated with a dilute cyanide solution that percolates through the ore to dissolve gold and silver.
- The solution containing gold and silver exists the base of the dump, is collected and precious metal extracted.
- The resultant barren solution is recharged with additional cyanide and returned to the dump.
- This method of leaching is usually suitable for low grade ores because it is very low cost. However, it operates with slow kinetics and make take up about 1 to 2 years to extract 50% of the desired.



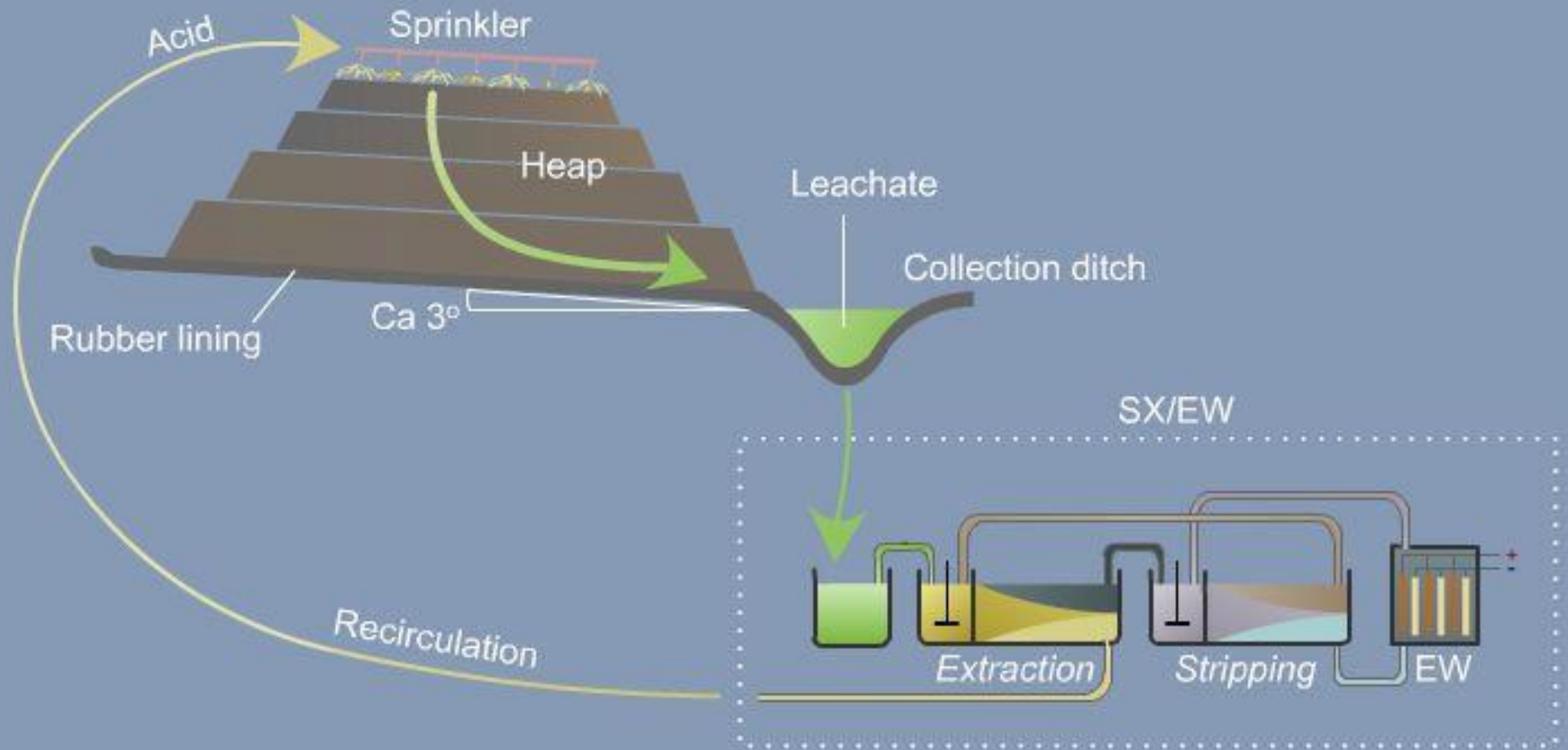


dump ore leaching on a slope

# Leaching operation(continue..)

## *3-Heap Leaching*

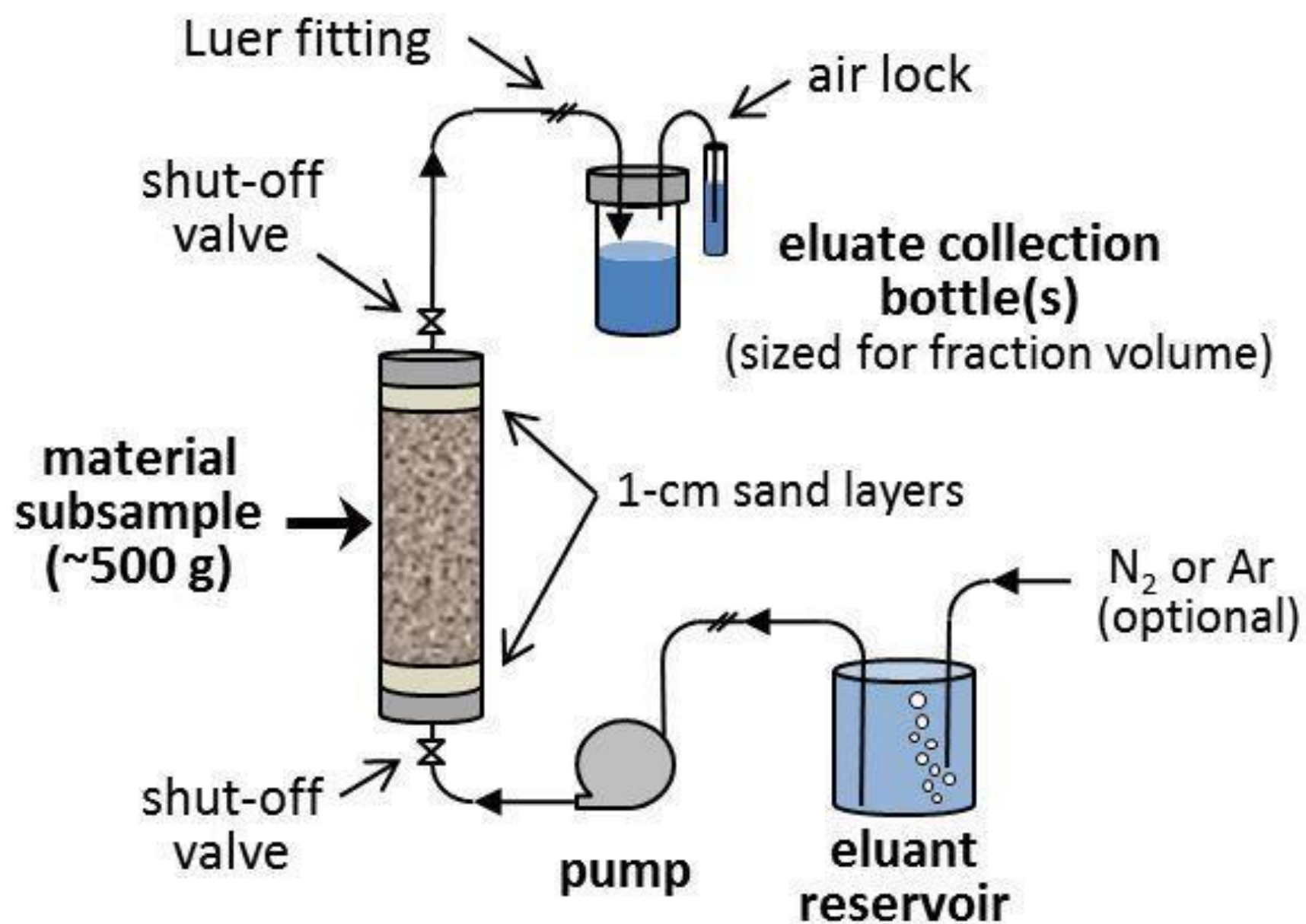
- It is a technique where run-of-mine crushed(generally >5mm) and agglomerated ores are stacked over an engineered impermeable pad, wetted with lixiviant (solvent) chemicals under atmospheric condition and leachate(metal loaded solution) are collected for metal recovery processes. The mined ore is generally crushed into small chunks and heaped on an impermeable plastic and/or clay lined leach pad where it can be irrigated with leach solution to dissolve the valuable metal.
- While sprinklers are occasionally used for irrigation, more often operation use drips [irrigation to minimize irrigation, provide more uniform distribution of leach solution and avoiding damaging the exposed mineral.
- The solution then percolates through the heap and leaches both the target and other minerals. This process, called the LEACH CYCLE, generally takes from one or two months for simple oxide ore (e.g. most gold ores) to two years.
- The leach solution containing the dissolved mineral is then collected, treated in a process called to recover the target minerals and then recycle to the heap after reagent levels are adjusted.
- Ultimate recovery of the target minerals can range from 30% of contained to over 90% for the easiest to leach ores.



# Leaching operation(continue..)

## ***4-Percolation Leaching***

- It is a selective removal of the metal values from a mineral by causing a suitable solvent or leaching agent to seep into and through a mass or pile of material containing the desired material.
- In this process, the leach solution is percolated upward or downward through an ore which has already been crushed and bedded into tanks.
- Usually, a mixture of coarse and fine ores is used so as to ensure permeability.
- By subjecting the ore to 10 or more leach cycle, 80 to 90% of the metal values are recovered.
- Percolation leaching has certain advantage because it is operated in batches. For example, since each batch is separated or distinct, operational flexibility is greater and accidental break down are not that serious.
- A percolation leaching circuit is more versatile and can be employed in the case of ore where the leaching rate is very slow.

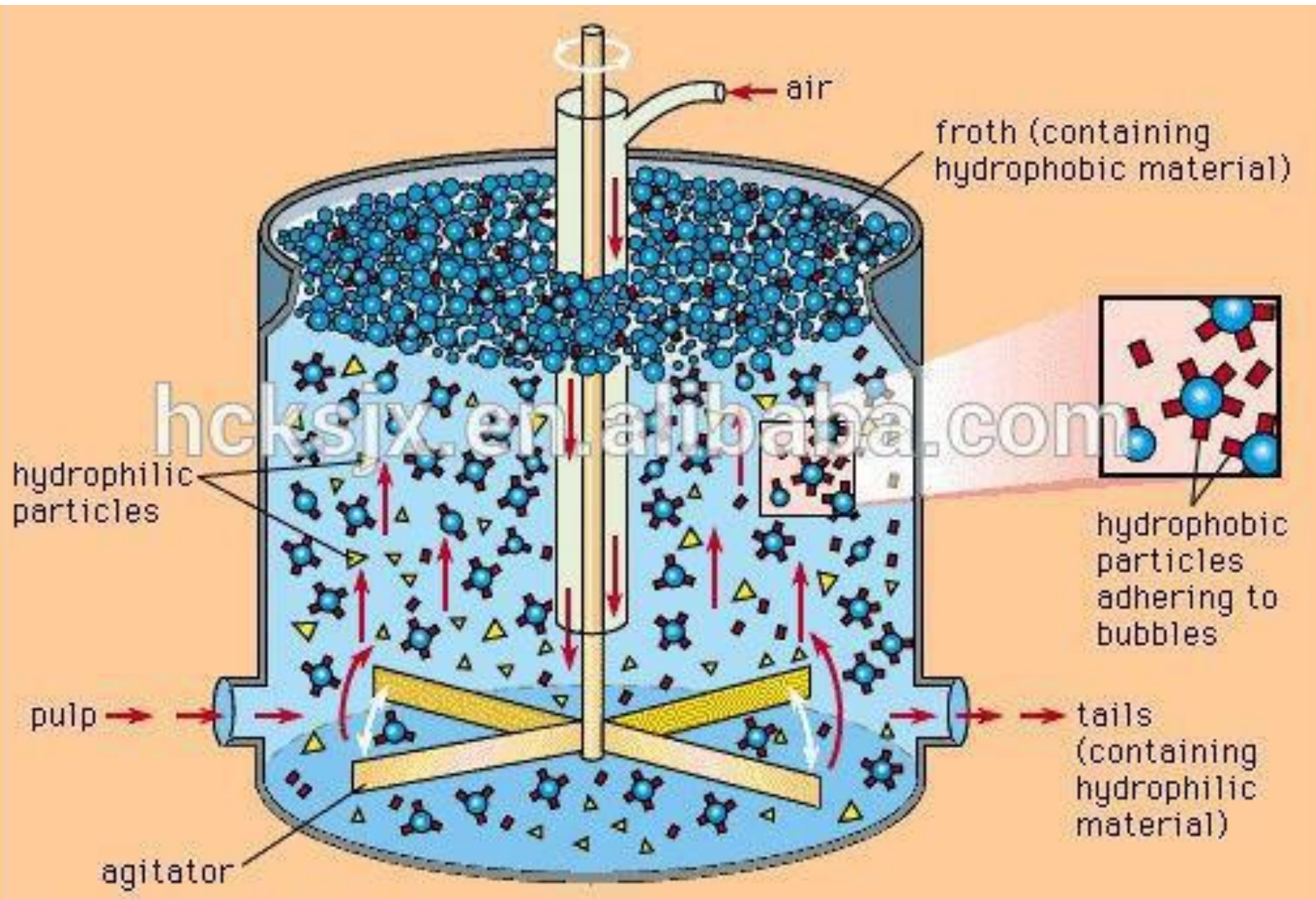


# Leaching operation(continue..)

## *5-Agitation Leaching*

- It is a process where the soil slurred with the extraction fluid for a period of time.
- When equilibrium between the metal on the soil surface and the metal contained by the solution is approached, the solubility of the metal in the soil is slowed, and the extraction is said to be complete.
- At equilibrium, additional metal will not be extracted from the soil's surface unless the soil is subjected to fresh extraction solution.
- Once the process is said to be at equilibrium, the soil is separated from the extraction fluid using sedimentation, thickening or clarification.
- The extraction process may be continued in a separate extraction vat with clean extraction solution to enhance extraction.
- An agitation vat coupled with a solid-liquid separation vessel (sedimentation or clarification) is considered to be a single stage.







## Pressure Leaching

### Pressure Leaching

Many leaching reactions are carried out in autoclave under high pressure. At higher pressure, a high temperature can be attained and the boiling away of the solvent can be suppressed e.g. the leaching of bauxite by sodium hydroxide solution. A high pressure becomes necessary when highly volatile and gaseous reagents are used in leaching. By increasing the partial pressure of such reagents, their concentration in aqueous solution can be maintained at sufficiently high level e.g. all leaching operations involving ammonia are aided by high pressure.

When a liquid absorbs a gas, the reaction proceeds very rapidly. Such reaction could be rate-determining if a large reacting vessel is employed because, as the size of the reactor increases, the ratio of the gas-liquid interface to the volume of the liquid decreases. The rate of gas absorption can be accelerated by -

- (1) by increasing the partial pressure of the gas.
- (2) by increasing the area of the gas-liquid interface relative to the volume of the liquid.
- (3) by increasing the efficiency of agitation.

It can be noted that latter two (2) techniques are difficult to adopt, therefore, the first method can be manipulated to a great extent.



## Pressure Leaching Applications

### Applications:-

- (1) Leaching of oxides of metals such as Al, V, Ti and U.
- (2) Sulphide minerals such as  $ZnS$ ,  $PbS$ ,  $MoS_2$ ,  $FeS_2$ ,  $FeS$ ,  $CuFeS_2$ ,  $FeS \cdot NiS$ , ~~and~~,  $CuS$  and the mixed concentrates of these minerals are rapidly oxidized under high pressure at an elevated temp. in aqueous solutions of  $H_2SO_4$ , Ammonia or Sodium Hydroxide.

(3) Complex low-grade sulphides concentrates of Zn and Pb produced by flotation is pressure leached in autoclaves using sulphuric acid solution. This yields  $ZnSO_4$  solution and a residue containing  $PbSO_4$ , elemental sulphur and pyrite.

To separate the pyrite, sulphur and  $PbSO_4$ , the leach slurry is heated above the melting point of elemental sulphur. As a result, pellets of pyrite and elemental sulphur are formed, which can be separated from  $PbSO_4$  by screening.

The advantage of such process are —

- (i) Zinc is not lost as zinc-ferrite (which is formed during <sup>roasting</sup>)
- (ii) Sulphuric acid production from <sup>gases</sup> is not required unlike the roasting process.
- (iii) Sulphur is recovered in elemental form.

## Pressure Leaching Applications

(4) Blast furnace smelting of lead yields speiss (solution of iron and arsenic, ~~raises~~ <sup>oxygen partial pressure</sup>  $\text{Fe}(\text{As})_4$ ). About 98% arsenide can be recovered by high pressure (20 atm) leaching with  $\text{NaOH}$  sol<sup>n</sup> (225 g/lit) for 4h.

(5) During the matte smelting of Ni-ores, a matte containing 60-75% Ni along with Cu and Fe produced; As and Sb may also be present. Ni, Cu and As can be extracted by leaching finely grounded matte ( $\approx 325$  mesh) at  $120-125^\circ\text{C}$  under 1.5-7 atm oxygen partial pressure in slightly acidic medium (PH 4.5-5).

(6) Complex ore of zinc is leached 4h in concentrated  $\text{H}_2\text{SO}_4$  at  $110^\circ\text{C}$  at 6 atm partial pressure of  $\text{O}_2$ . About 98% Zn can be recovered by this technique.



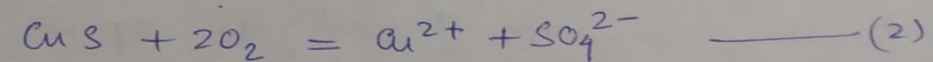
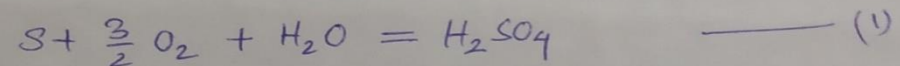
## Bacterial or Microbial Leaching

### Bacterial or Microbial Leaching:—

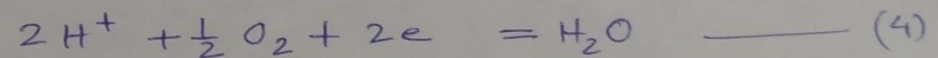
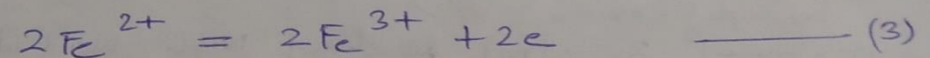
Many sulphide minerals form water-soluble sulphates. However, the natural dissolution process is very slow. It has been found that certain types of bacteria could considerably speed up the natural conversion processes. Bacteria leaching not only leads to an enhanced dissolution rate but also effectively improves metal recovery.

Three most important types of bacteria from leaching viewpoint are *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans*. They are capable of growing in purely inorganic media and obtain their energy by oxidizing the inorganic substances such as sulphur, thio sulphate and ferrous ion. The enzyme synthesized by the bacteria accelerates the rate of oxidation reaction.

Oxidation of sulphide minerals occurs as

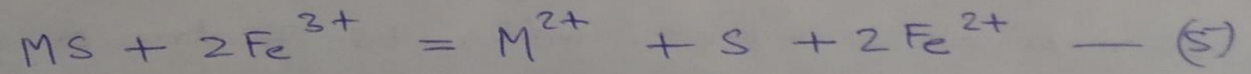


Iron oxidation occurs as



## Bacterial or Microbial Leaching

Iron sulphide is the common impurity in most sulphide minerals. During leaching, ferric ion acts as oxidant and attacks the metal sulphide



The bacteria reoxidize the ferrous ion to the ferric ion. Therefore, the leaching mechanism given by reaction (2) is direct mechanism and reaction (5) is indirect mechanism.

In practice both direct and indirect mechanism operates simultaneously and their relative importance largely dependent on both (1) the type of mineral being leached and (2) the type of bacteria being employed. Thus, *Thiobacillus ferrooxidans* oxidize ferrous ion, *Thiobacillus thiooxidans* do not. Both can oxidize sulphur and thio sulphate.



## Effect of various factors on Bacteria leaching :-

(1) Effect of temperature :- Temperature has marked effect on bacterial conversion of  $Fe^{+2}$  to  $Fe^{+3}$ . Maximum bacterial activity occurs between  $30 - 35^{\circ}C$ . As temperature increases above  $50^{\circ}C$  their activity almost stops and beyond  $70^{\circ}C$  microorganisms become sterile and are destroyed. Below  $30^{\circ}C$  their activity also decreases and below  $18^{\circ}C$  it is negligible from commercial point of view.

(2) Effect of Nutrients :- Addition of nutrients such as  $FeSO_4$ ,  $FeS_2$ ,  $(NH_4)_2SO_4$  and  $Fe_2(SO_4)_3$  to the leaching solution increases the ferrous ion concentration. Consequently, the bacteria become more active and both the rate and the extent of extraction increases.

(3) Effect of particle size and Bed depth :- The bacterial oxidation rate depends on the available surface area of solid feed material because the bacteria concentrate at the solid surface and build up colonies there. Finely ground particles, therefore, leads to increase in leaching rate. However, very fine particles reduces bed permeability and air supply, thereby inhibits leaching. Leaching rate enhances for shallow bed height.

Continue...



(4) Effect of Radiation!— when exposed to direct sunlight, a bacteria culture becomes inactive but not destroyed. This culture is extremely sensitive to UV light, even a short exposure completely sterilizes it.

(5) Effect of Acidity and Aeration!— Bacterial oxidation is highly pronounced in a medium having pH 2.0-3.5. Above and below this pH values oxidation rate decreases. At pH value  $\sim 6$  the oxidation almost completely inhibited. These bacteria are destroyed in alkaline medium.

The oxygen supply to living micro-organism is vital. Generally, oxygen is supplied by aerating a portion of the bacterial solution and subsequently transferring the aerated solution to the site of bacterial activity.

## Cementation or Contact Reduction of Metal in Aqueous Solutions :-

Leaching of an ore results in two distinct products

- (i) a leach liquor containing the metallic values
- and (ii) a solid residue containing the gangue.

The reduction of the metallic ions from solution to the elemental form is generally accomplished by three (3) methods:- Cementation or contact reduction, gaseous reduction and electrolysis.

In cementation precipitation of metallic value occurs on the surface of the added metal. The basic mechanism is electrochemical in nature. The metal with more positive oxidation potential <sup>in</sup> of the electromotive series will pass into the solution and displace a metal with a less positive potential.

Continue...



However, the overall phenomena would comprise of several steps including nonelectrochemical phenomena such as diffusion processes and sequential chemical reactions.

The reduction of metals from a solution is a complex process when the overall stoichiometry is concerned, because the reducible ion may present as hydrated cations e.g.  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  or as complex ions e.g.  $\text{Ni}(\text{NH}_3)_n^{2+}$ ,  $\text{Au}(\text{CN})_2^-$ . These ions are involved in electrolysis of copper, hydrogen reduction of nickel ammines and zinc precipitation of gold from cyanide solution respectively.



Purification OF Leach Liquor

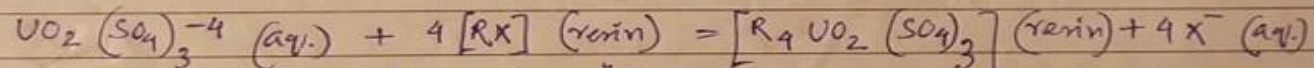
The common methods of purification of leach liquors are

(a) Precipitation:-

The impurities in the leach liquor i.e. the undesirable solutes can be eliminated through precipitation under controlled conditions of pH, concentration as well as with the help of special additives. Traditional principles of analytical chemistry is employed for such reactions.

(b) Ion-exchange:-

During ion-exchange, the leach liquor is brought into contact with an organic resin containing an active compound (RX). This active compound exchanges an ~~anion~~ a radical with the anion in solution. E.g. leaching of uranium ores with  $H_2SO_4$  produces a complex anion in aqueous solution viz.  $UO_2(SO_4)_3^{4-}$ . The impurity metals are mostly present as cations.

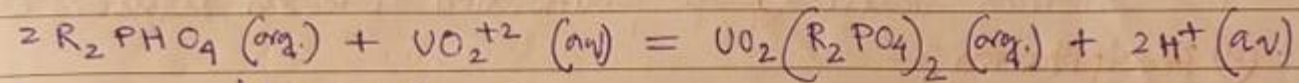


The resin is now said to be "loaded" with uranium. This is now separated and brought into contact with a strong solution of X-ions and reverse reaction takes place. The resin is regenerated and a strong, pure solution of uranium is obtained.

(c) Solvent Extraction:-

It is also known as liquid-liquid extraction. In this process the leach liquor is brought into contact with an organic liquid. One typical solvent is kerosene containing EHPA (di-2-ethylhexyl phosphoric acid) or simply phosphoric acid with two of

hydrogen replaced by 2-ethylhexyl group).



Here  $R \rightarrow$  2 ethylhexyl.

The reaction involves cation exchange. The loaded organic is separated and uranium is recovered by allowing the organic phase to react with sodium carbonate solution which regenerates the organic reagent and extracts uranium back into the aqueous phase but in a much more concentrated and pure form. Solvent extraction involves two liquids which can be agitated together to accelerate transfer of metallic values from one phase to another. It is faster and therefore more commonly used than the ion-exchange. The contacting is effectively carried out by agitating <sup>the</sup> two phases together in a vessel to produce a fine dispersion of one phase in another. Subsequently, two-phases are allowed to separate, the lighter organic phase floats on top of the aqueous phase.