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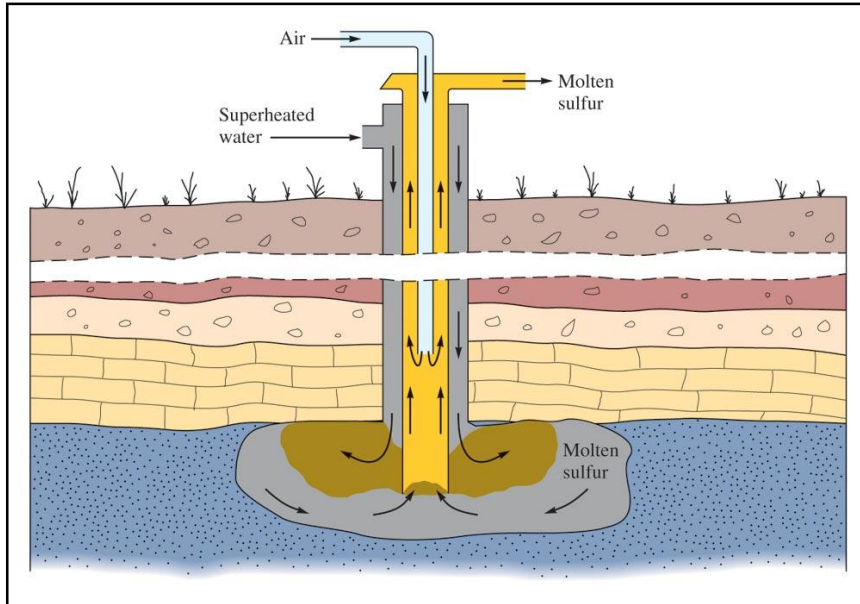
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Topic 8: Mining Methods

Part IV: In-Situ Leaching (ISL)/ Solution Mining



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 - 2) Sylvinite
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INTRODUCTION

- ❑ Depend on water or another liquid (e.g., dilute sulfuric acid, weak cyanide solution, or ammonium carbonate) to extract the mineral.
- ❑ Solution mining are **among the most economical of all mining methods** but can only be applied to limited categories of mineral deposits.
- ❑ *Solution mining (in-situ recovery)* = resources in a deep deposit are dissolved in a liquid and siphoned out.
- ❑ Salts, potash, sulfur, lithium, boron, bromine, copper, uranium.
- ❑ Used most commonly on **evaporite** (e.g. salt and potash) and **sediment-hosted uranium** deposits, and also to a far lesser extent to recover copper from low-grade oxidized ore.
- ❑ The dissolving solution is pumped into the orebody from a series of injection wells, and is then pumped out, together with salts dissolved from the orebody from a series of extraction (production) wells.
- ❑ The very best to use the solution mining technology is:
 - a great height of the deposit, and
 - a low depth
- ❑ But by using new developed technologies the winning of mineral salts in deposits with low height is possible. This new technology is named solution mining with **“tunnel caverns”**. In this case one bore hole was drilled vertically and the other was drilled at first vertically and then it follows in the deposit the direction of the salt layer with a deviation.
- ❑ This technologie is not usable if the deposit has tectonical breakdown and other disturbances or great changes in the direction.
- ❑ The drilling of the bore holes can be complicated and expensivly if the overburden contains gas or water.

INTRODUCTION

Used most commonly on **evaporite** (e.g. salt and potash) and **sediment-hosted uranium** deposits, and also to a far lesser extent to recover copper from low-grade oxidized ore.

The dissolving solution is pumped into the orebody from a series of injection wells, and is then pumped out, together with salts dissolved from the orebody from a series of extraction (production) wells.

Metals and minerals commonly mined by solution mining methods.
Dissolving agent specified in each case. (From Hartman and Mutmanský, 2002, and references therein).

Metal or Mineral	Approximate Primary production	Dissolution Agent/ Method
Gold	35%	Sodium cyanide (NaCN)
Silver	25%	Sodium cyanide (NaCN)
Copper	30%	Sulphuric acid (H_2SO_4); Ammonium carbonate (alkali) $\{(\text{NH}_4)_2\text{CO}_3\}$
Uranium	75%	Sulphuric acid (H_2SO_4); Ammonium carbonate (alkali) $\{(\text{NH}_4)_2\text{CO}_3\}$
Common Salt	50%	Water
Potash	20%	Water
Trona	20%	Water
Boron	20%	Hydrochloric acid (HCl)
Magnesium	85%	Seawater, lake brine processing
Sulfur	35%	Hot water (melting)
Lithium	100%	Lake brine processing

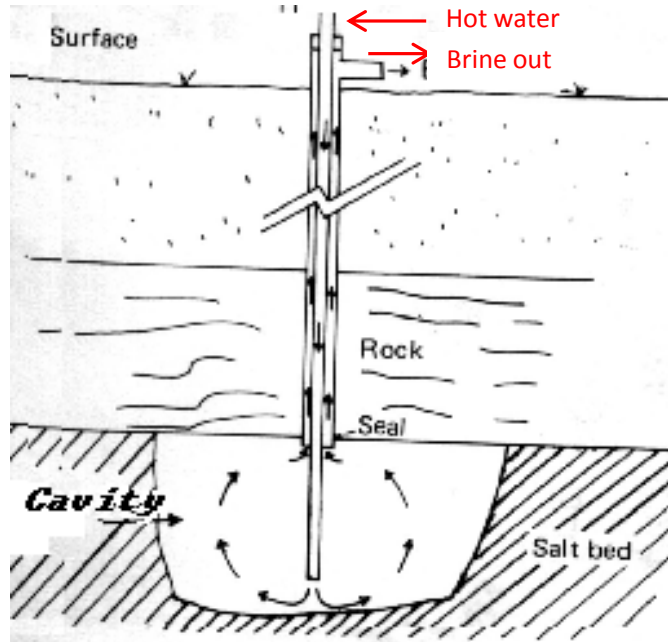
Aside: The same reagents are often used for processing mined ores in hydrometallurgical plants

BASIC CONCEPT

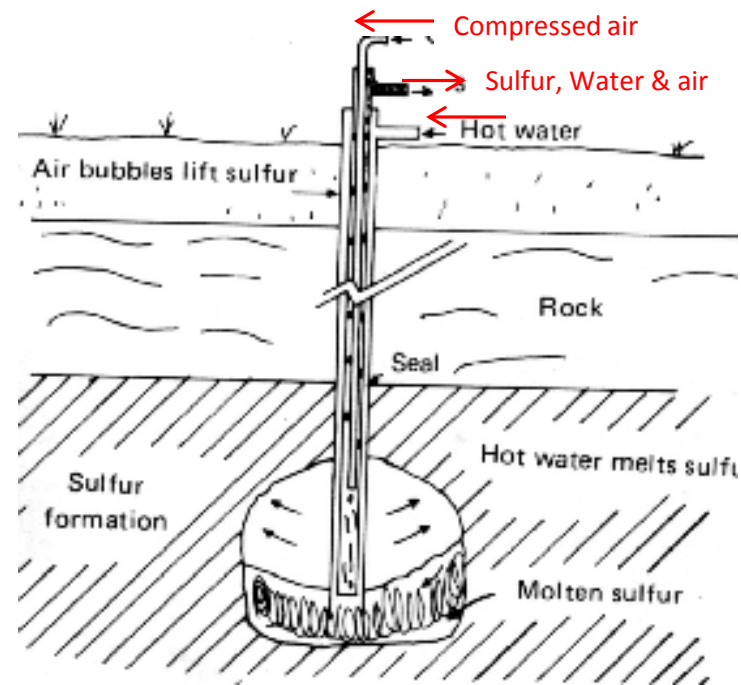
- ❑ The theory and practice of leaching are well-developed because for many years leaching has been used to separate metals from their ores and to extract sugar from sugar beets. Environmental engineers have become concerned with leaching more recently because of the multitude of dumps and landfills that contain hazardous and toxic wastes. Sometimes the natural breakdown of a toxic chemical results in another chemical that is even more toxic. Rain that passes through these materials enters ground water, lakes, streams, wells, ponds, and the like.
- ❑ Although many toxic materials have low solubility in water, the concentrations that are deemed hazardous are also very low. Furthermore, many toxic compounds are accumulated by living cells and can be more concentrated inside than outside a cell. This is why long-term exposure is a serious problem; encountering a low concentration of a toxic material a few times may not be dangerous, but having it in your drinking water day after day and year after year can be deadly.
- ❑ The main theory of leaching neglects mechanisms for holding the material on the solid. Although adsorption and ion exchange can bind materials tightly to solids, we will simplify the analysis and consider only dissolving a soluble constituent away from an insoluble solid. An example is removing salt from sand by extraction with water.
- ❑ Countercurrent stage wise processes are frequently used in industrial leaching because they can deliver the highest possible concentration in the extract and can minimize the amount of solvent needed. The solvent phase becomes concentrated as it contacts in a stage wise fashion the increasing solute-rich solid. The raffinate becomes less concentrated in soluble material as it moves toward the fresh solvent stage.

TECHNOLOGY OF SOLUTION MINING

In-situ leaching (ISL)/ *Solution Mining*



ISL salt mine

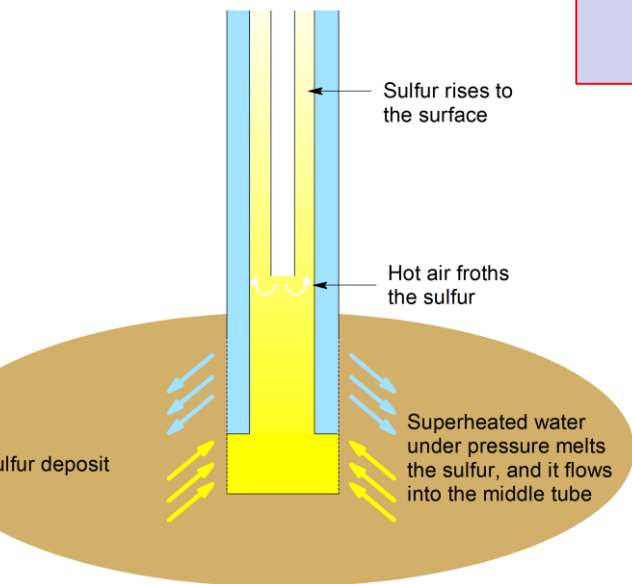


ISL sulfur mine

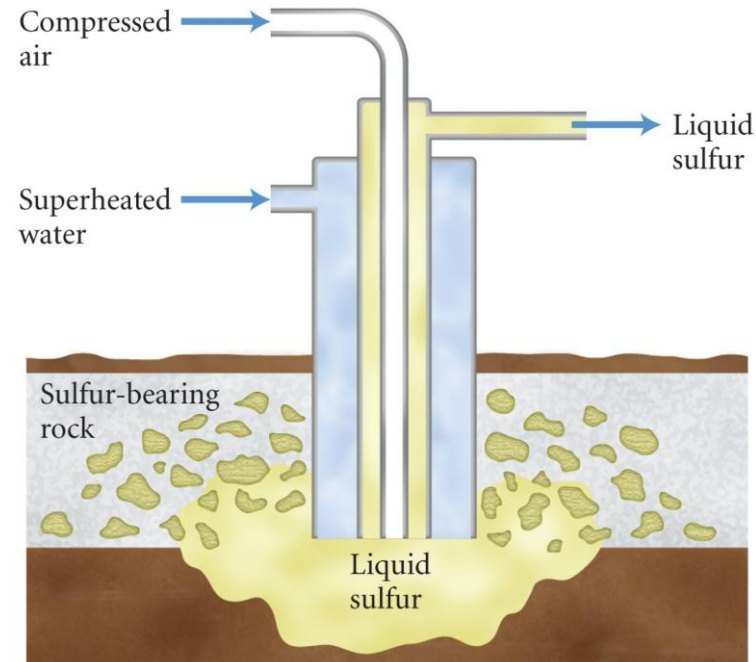
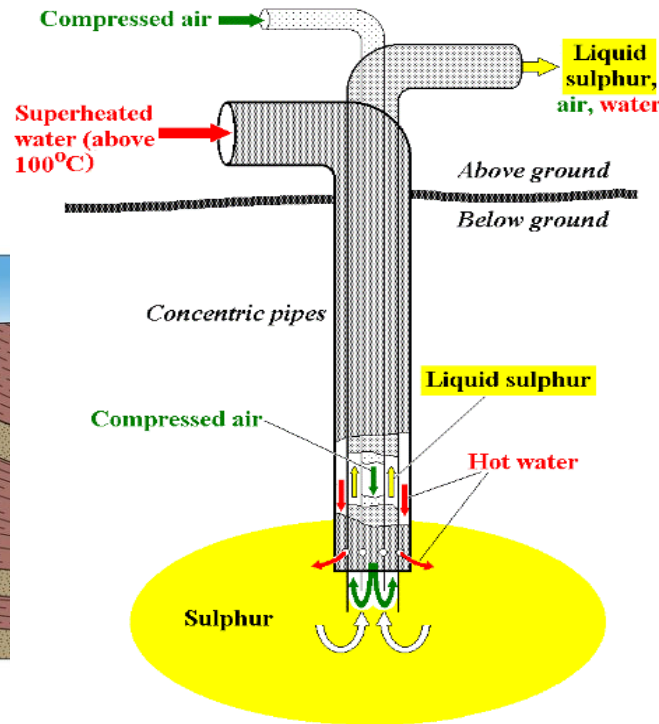
Solution mining includes both borehole mining, such as the methods used to extract sodium chloride or sulfur, and leaching, either through drillholes or in dumps or heaps on the surface.

I) FRASCH PROCESS

- Subsurface sulfur recovered by the **Frasch Process**:
 - superheated water pumped down into deposit, melting the sulfur and forcing it up the recovery pipe with the water



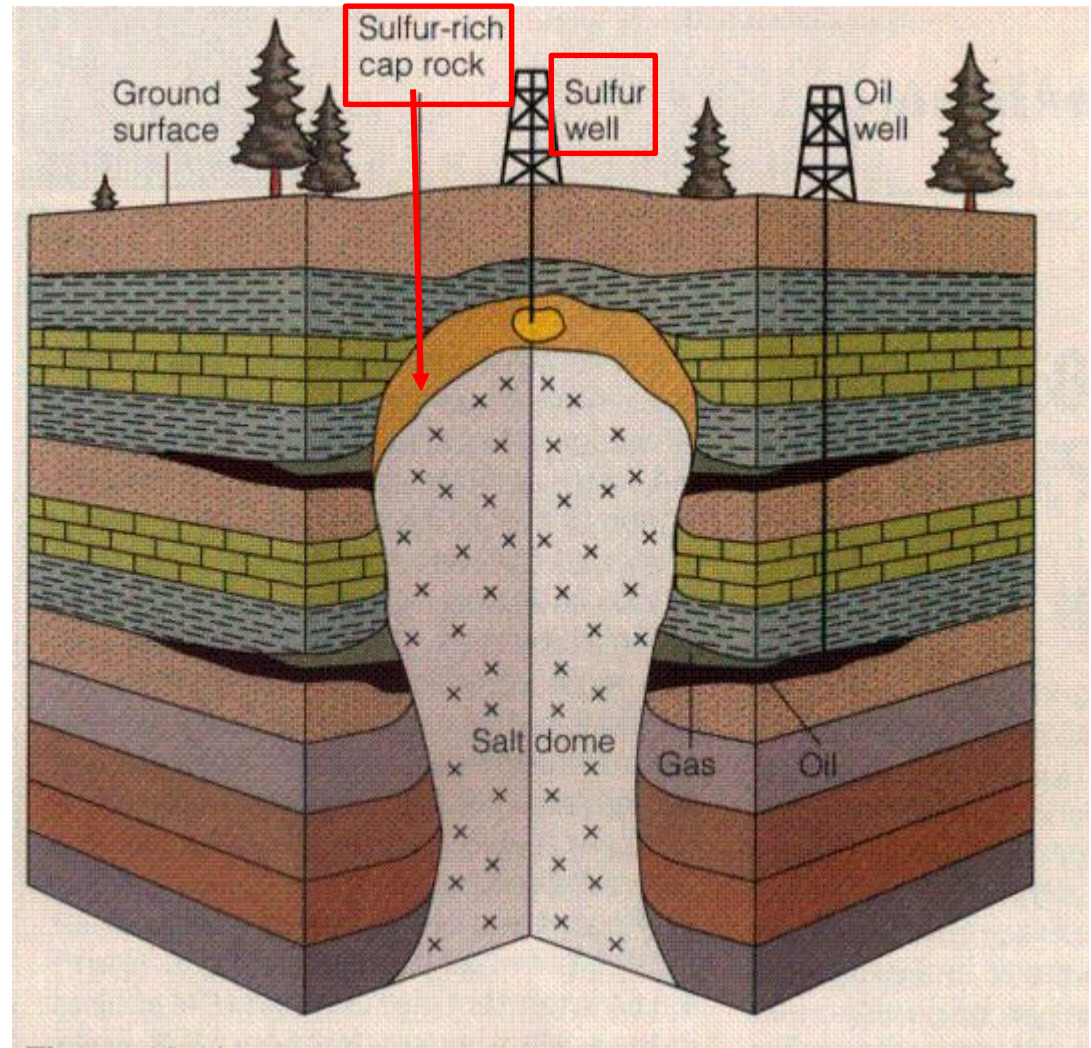
The Frasch Process



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Sulfur Production

- ❑ As a mineral, native sulfur under salt domes is produced by the action of ancient bacteria on sulfate deposits.
- ❑ It was removed from such salt-dome mines mainly by the [Frasch process](#).
- ❑ In this method, superheated water was pumped into a native sulfur deposit to melt the sulfur, and then compressed air returned the 99.5% pure melted product to the surface.
- ❑ Throughout the 20th century this procedure produced elemental sulfur that required no further purification. However, due to a limited number of such sulfur deposits and the high cost of working them, this process for mining sulfur has not been employed in a major way anywhere in the world since 2002.



II) TECHNOLOGY OF THE SALT PRODUCTION

What is Rock salt ?

- ❑ Salt, also known as sodium chloride, the most common evaporite salt is an ionic chemical compound which has a chemical formula NaCl . It is an inexpensive bulk mineral also known as halite which can be found in concave rocks of coastal areas or in lagoons where sea water gets trapped and deposits salt as it evaporates in the sun.
- ❑ The most important salt minerals, which produced by solution mining are:
 - Rock salt (or Halite) (NaCl)
 - Sylvinite ($\text{NaCl} + \text{KCl}$)
 - Carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$)
 - Trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$),
 - Nahcolite (NaHCO_3),
 - Epsomite {or Epsom salts} ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$),
 - Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ or $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$)
- ❑ Has been used for many decades to extract soluble evaporite salts from buried evaporite deposits in UK, Russia, Germany, Turkey, Thailand and USA.
- ❑ A low salinity fluid, either heated or not, is injected underground directly into the evaporite layer; the “pregnant” solutions (brines) are withdrawn from recovery boreholes and are pumped into evaporation ponds, to allow the salts to crystallize out as the water evaporates.
- ❑ Because these minerals have very different thermodynamic properties, the production technology for each salt had to developed specifically.

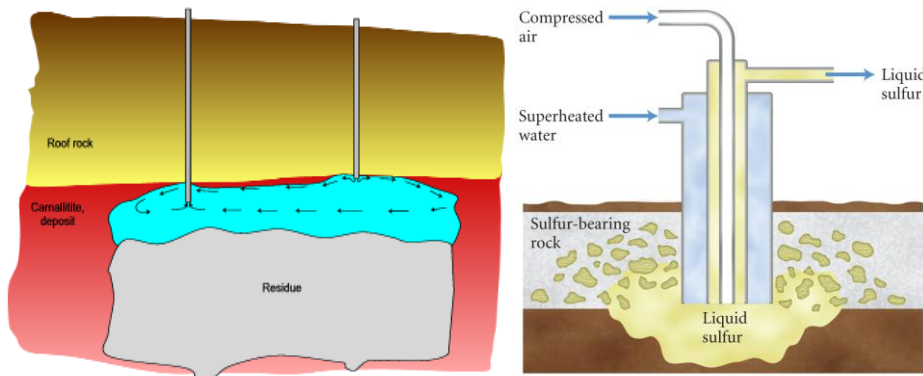
Evaporite deposits

1) Buried deposits :

- *Evaporite* deposits that formed during various warming Seasonal and climatic change periods of geologic times.
 - Like: Shallow basin with high rate of evaporation – **Gulf of Mexico, Persian Gulf, ancient Mediterranean Sea, Red Sea**
- The most significant known evaporite depositions happened during the Messinian salinity crisis in the basin of the Mediterranean

Extracted by Solution mining techniques (or Frasch Process)

- ✓ Two wells
- ✓ Selective dissolution
- ✓ Hot leaching



2) Brine deposits:

Evaporite deposits that formed from evaporation:

- **Seawater or ocean** (Ocean water is the prime source of minerals formed by evaporation) . Then, solutions derived from normal sea water by evaporation are said to be **hypersaline**
- **Lake water**
- **Salt lakes**
- **Playa lake**
- **Springs**

Extracted by Normal evaporation techniques

- ✓ Pond
- ✓ Marsh

Requirements

- ✓ • arid environment, high temp
- ✓ • low humidity
- ✓ • little replenishment from open ocean, or streams





Brines form by strong evaporation.
These ponds on the shores of *Great Salt Lake* are sources of magnesium as well as salt.



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Water well drilling on
the western portion of
Allana Potash license, Dallol
Project-Ethiopia



Sylvite
KCl



Potash salt and halite crystallization in pilot
test evaporation ponds

Major groups of evaporite minerals

More than eighty naturally occurring evaporite minerals have been identified. The intricate equilibrium relationships among these minerals have been the subject of many studies over the years. This is a chart that shows **minerals that form the marine evaporite rocks**, they are usually the most common minerals that appear in this kind of deposit.

Mineral class	Mineral name	Chemical Composition	Rock name
Halites (or Chlorides)	Halite	NaCl	Halite; rock-salt
	Sylvite	KCl	
	Carnallite	$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$	
	Kainite	$\text{KMg}(\text{SO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$	Potash Salts
Sulfates	Polyhalite	$\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$	
	Langbeinite	$\text{K}_2\text{Mg}_2(\text{SO}_4)_3$	
	Anhydrite	CaSO_4	Anhydrite
	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Gypsum
	Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	--
Carbonates	Dolomite	$\text{CaMg}(\text{CO}_3)_2$	Dolomite, Dolostone
	Calcite	CaCO_3	Limestone
	Magnesite	MgCO_3	--

- Evaporite minerals start to precipitate when their concentration in water reaches such a level that they can no longer exist as solutes.
- The minerals precipitate out of solution **in the reverse order of their solubilities**, such that the order of precipitation from sea water is
 - ✓ Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$)
 - ✓ Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4).
 - ✓ Halite (i.e. common salt, NaCl)
 - ✓ Potassium and magnesium salts
 - ✓ The abundance of rocks formed by seawater precipitation is in the same order as the precipitation given above. Thus, limestone (calcite) and dolomite are more common than gypsum, which is more common than halite, which is more common than potassium and magnesium salts.
- Evaporites can also be easily recrystallized in laboratories in order to investigate the conditions and characteristics of their formation.

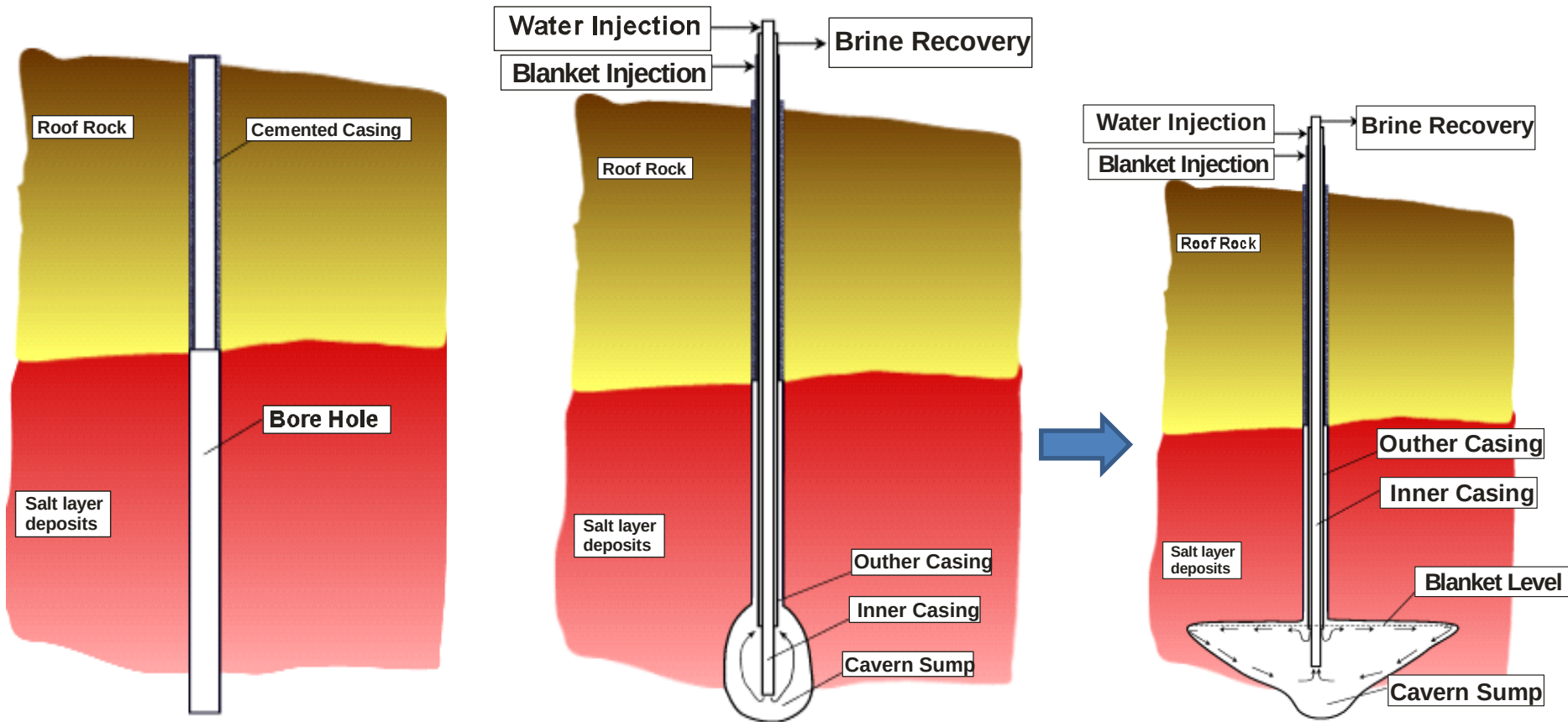


Hanksite, $\text{Na}_{22}\text{K}(\text{SO}_4)_9(\text{CO}_3)_2\text{Cl}$, one of the few minerals that is both a carbonate and a sulfate

Economic importance of evaporites

- ❑ Halite- rock salt for roads, refined into table salt
- ❑ Thick halite deposits are expected to become an important location for the disposal of nuclear waste because of their geologic stability, predictable engineering and physical behaviour, and imperviousness to groundwater.
- ❑ Gypsum- Alabaster: ornamental stone; Plaster of Paris: heated form of gypsum used for casts, plasterboard, ... etc.; makes plaster wallboard.
- ❑ Potash- for fertilizer (potassium chloride, potassium sulfates)
- ❑ Evaporite minerals, especially *nitrate minerals*, are used in the production on fertilizer and explosives.
- ❑ Salt formations are famous for their ability to form diapirs, which produce ideal locations for trapping petroleum deposits.

Technology of Solution Mining



1) A bore hole was drilled from the surface of the earth to the bottom of the salt layer:

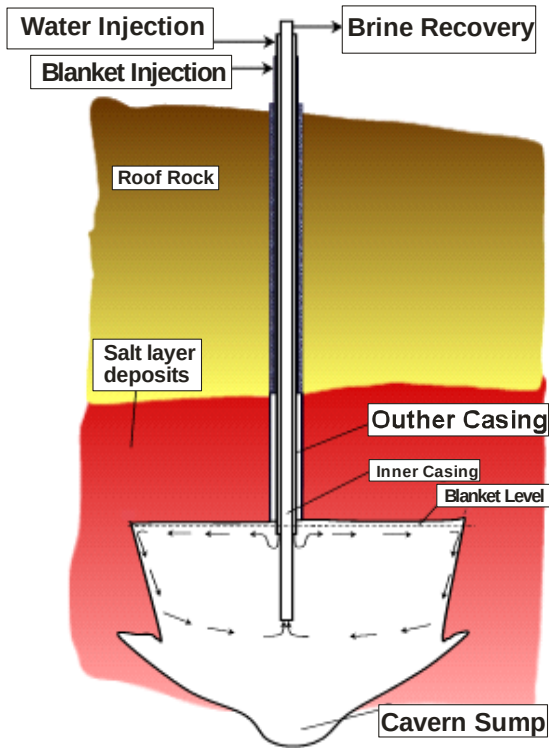
- A casing was worked in the bore well and was cemented from the surface to the top side of the deposit. The cement must shut tight against the pressure of the blanket.
- The surface of the bore hole in the area of the deposit is free. The salt can be dissolved.

2) The dissolution of the salt begins with the solution of a cavern sump. The sump shall be accommodate the insolubles of the deposit: near the casings in the well.

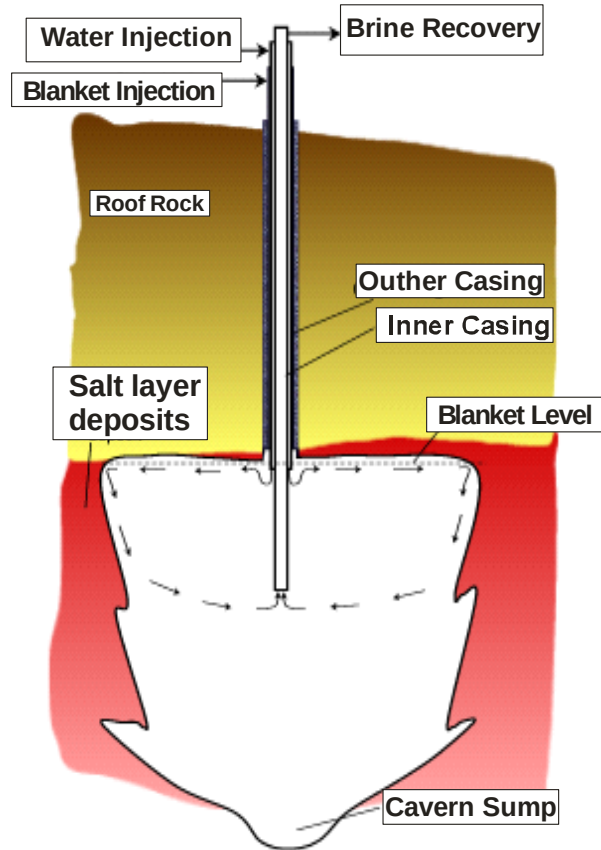
- During the solution of the sump only water is used .
- The water current is directly, that means that the current of brine in the cavern has the same direction as in the production casing.
- The solution of the sump can be ended if the diameter of the cavern is 5 – 10 m.

3) The next step is the undercut phase. The injected water is going trough the outer casing and the brine leave the cavern trough the inner casing. This current direction is named indirectly. Important for the forming of the cavern is the precise controlling of the blanket level.

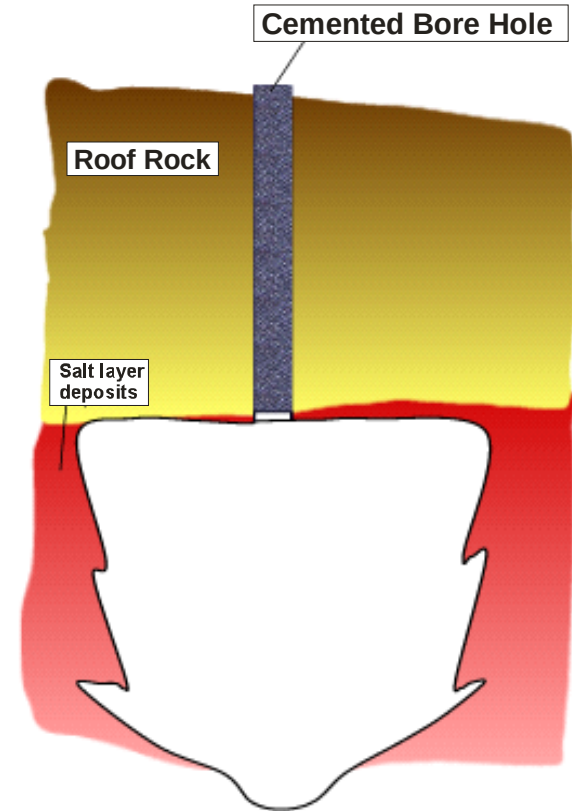
Technology of Solution Mining



4) For winning of the salt in the deposit the level of the casings and the blanket was arranged higher. Because in the cavern the density of the brine increases from the top to the bottom, the brine current goes from the end of the outer casing under the blanket level to the side and then it flows to the inner casing and to the surface.

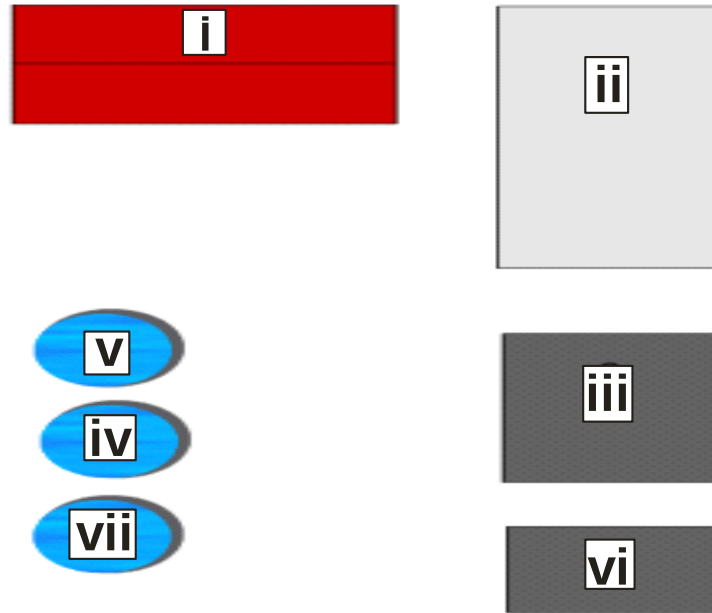


5) The last step is reached, if the cavern arrives the top of the deposit.



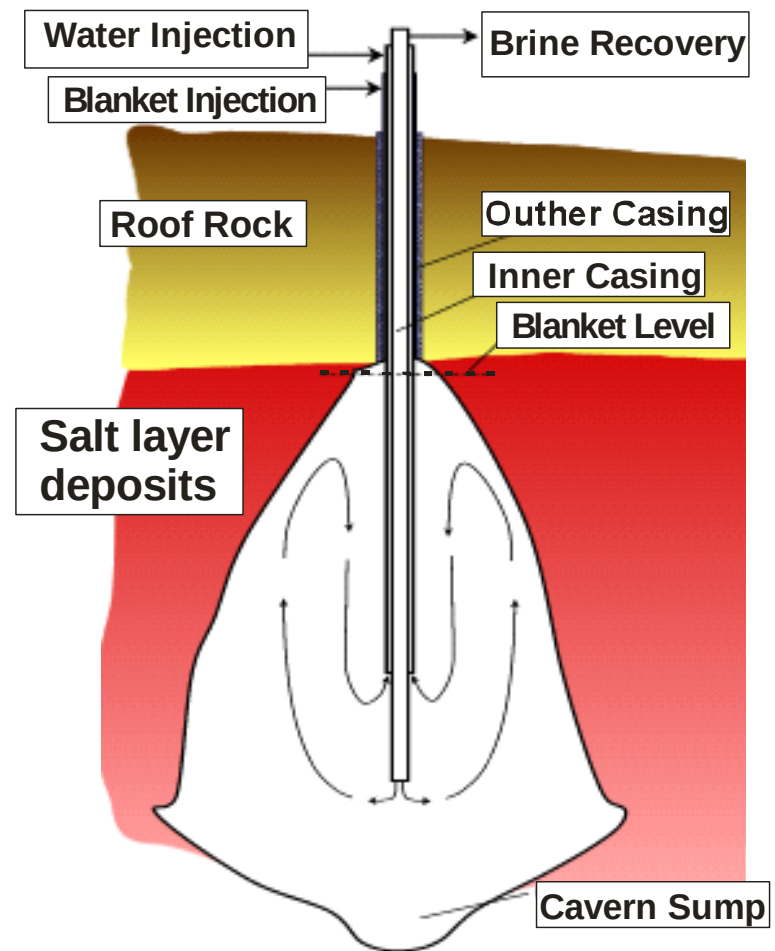
6) Last of all the tubes were removed and the bore hole will be cemented.

Technology of Solution Mining



7) The equipment of the brine place is very simply. For the production of brine is needed:

- i) a building for a control room and an office,
- ii) a workshop and a storage,
- iii) a building for pumps,
- iv) a blanket station,
- v-vii) tanks for water and brine



8) Another technology is used for the erection of underground storages. In this case the salt was dissolved after the undercut in only one step. The entry of the solvent into the cavern is through the inner tube. From there the solvent rises up, dissolves the salt and goes to the outer casing.

The sides of this cavern are more straightly as the caverns which is leached with the step-by-step technology.

A disadvantage of this procedure is that the brine is in the most cases not saturated.

9) Methods to control the size of the caverns

- i) Measurement of radial distance between the well and the cavern surface with ultrasonic sondes (sonar).
- ii) Measurement of the area by addition of blanket into the cavern and determination of height difference of the blanket level.
- iii) Mass- and volume balance of solvent injection and brine recovery

This three methods used together allows an precise assessment of the cavern area and size.

- Technology of the Salt Production:
 - 1) Rock salt (NaCl)
 - 2) Sylvinite
 - 3) Carnallite

1) Technology of the Salt (NaCl) Production

Today, there are three methods used to produce dry salt based on the method of recovery (Abu- Khader, 2006).

- (a) **Underground** deposits through drilling and blasting whereby solid rock salt is removed. Mining is carried out at depths between 100 m to more than 1500 m below the surface.
- (b) **Solar evaporation method:** This method involves extraction of salt from oceans and saline water bodies by evaporation of water in solar ponds leaving salt crystals which are then harvested using mechanical means. Solar and wind energy is used in the evaporation process. The method is used in regions where the evaporation rate exceeds the precipitation rate.
- (c) **Solution mining:** Evaporated or refined salt is produced through solution mining of underground deposits. The saline brine is pumped to the surface where water is evaporated using mechanical means such as steam-powered **and mining:** Also known as rock salt mining, this process involves conventional mining of the multiple effect or electric powered vapour compression evaporators. In the process, a thick slurry of brine and salt crystals is formed.

More than one third of the salt production worldwide is produced by solar evaporation of sea water or inland brines (Sedivy, 2009). In the salt crystallization plants, saturated brine or rock salt and solar salt can be used as a raw material for the process. A summary of the possible process routes for the production of crystallized salt based on rock salt deposits is shown in Fig.2. Processes that are used in the production of vacuum salt from sea water or lake brine as a raw material are shown in Fig.3.

- 💣 Old underground mines, consisting typically of room-and-pillar workings, are often further mined using solutions to recover what remains of the deposit, i.e., the pillars (*with associated surface subsidence risk*).

1) Technology of the Salt (NaCl) Production

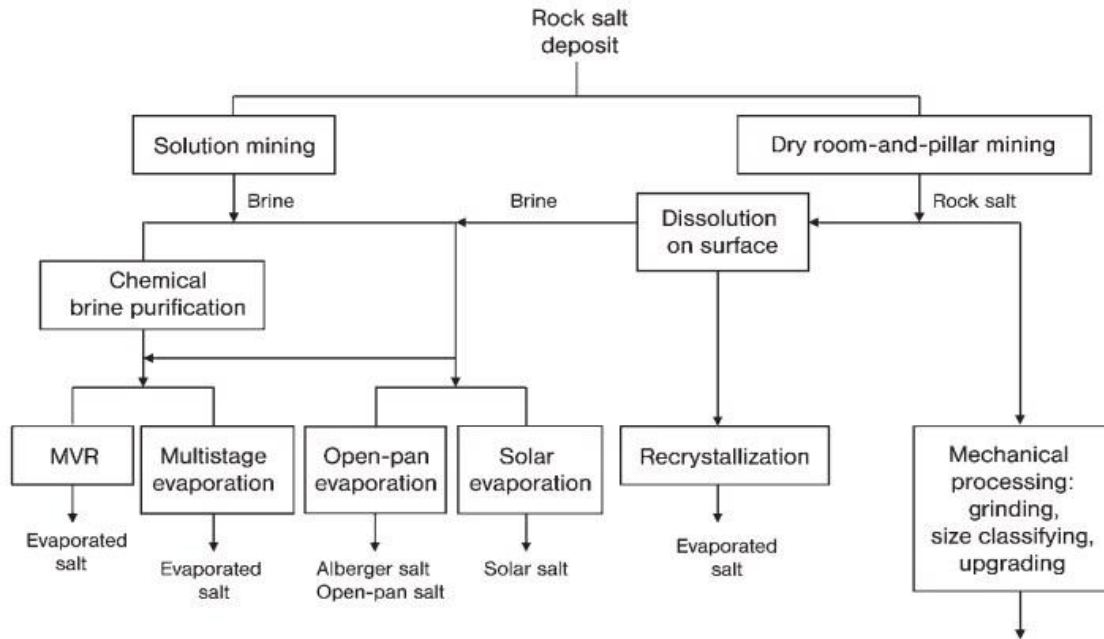
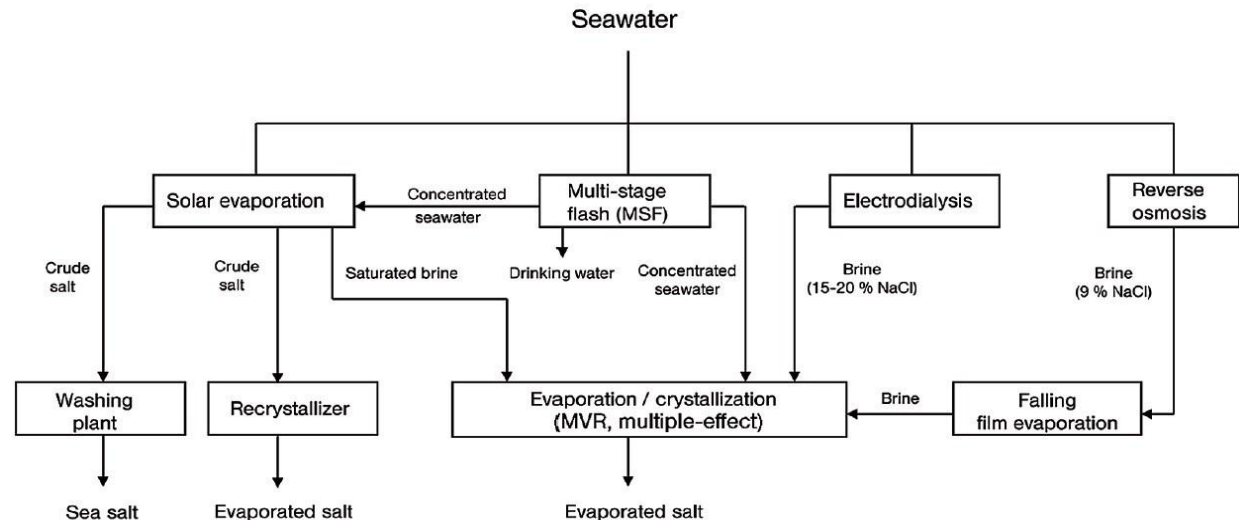


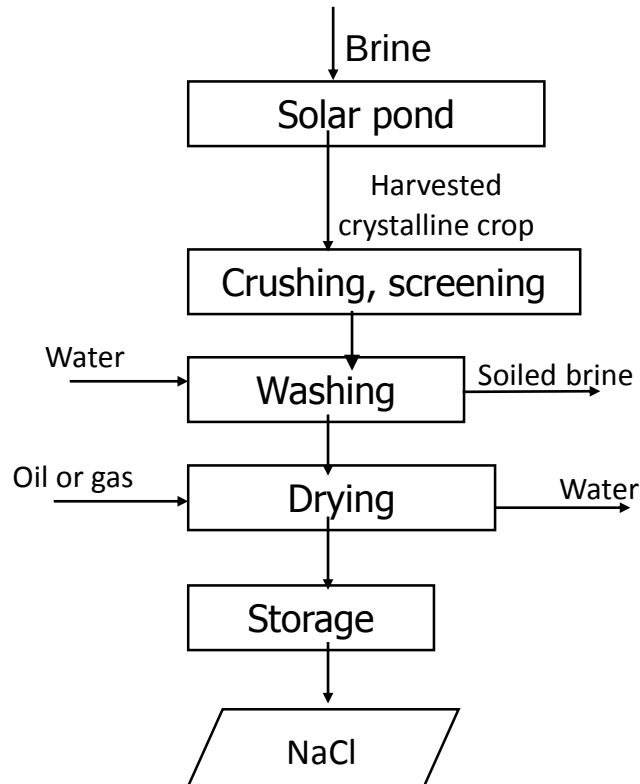
Fig.2. Processes for production of crystallized salt based on rock salt deposits (Westphal et al., 2010)

Fig.3. Processes for salt production from brine (Westphal et al., 2010)

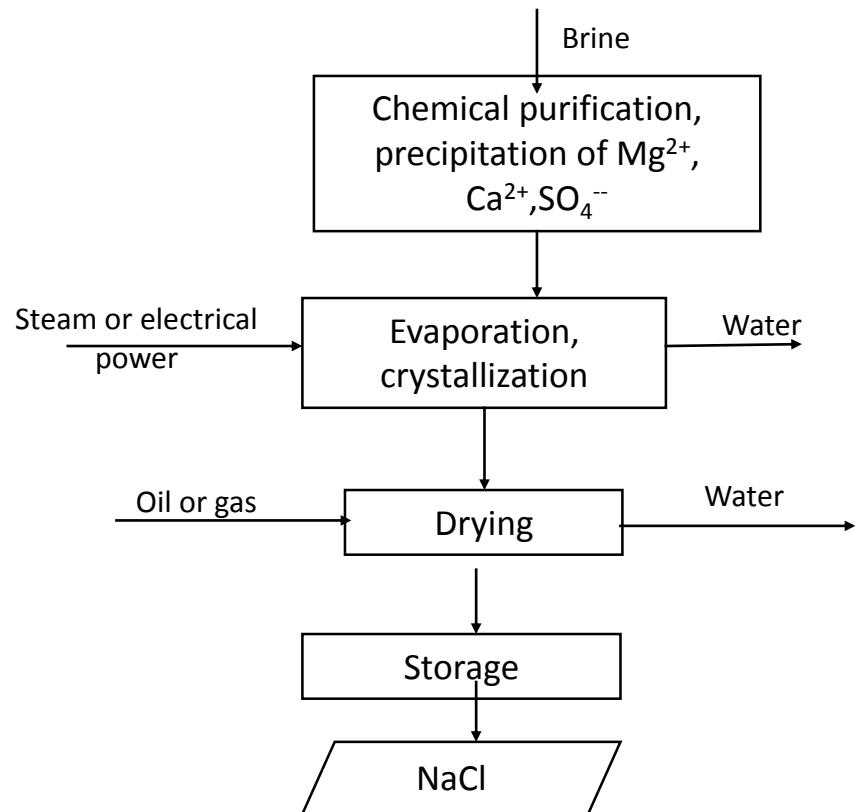


1) Technology of the Salt (NaCl) Production

Flowsheet of NaCl production in a solar pond process



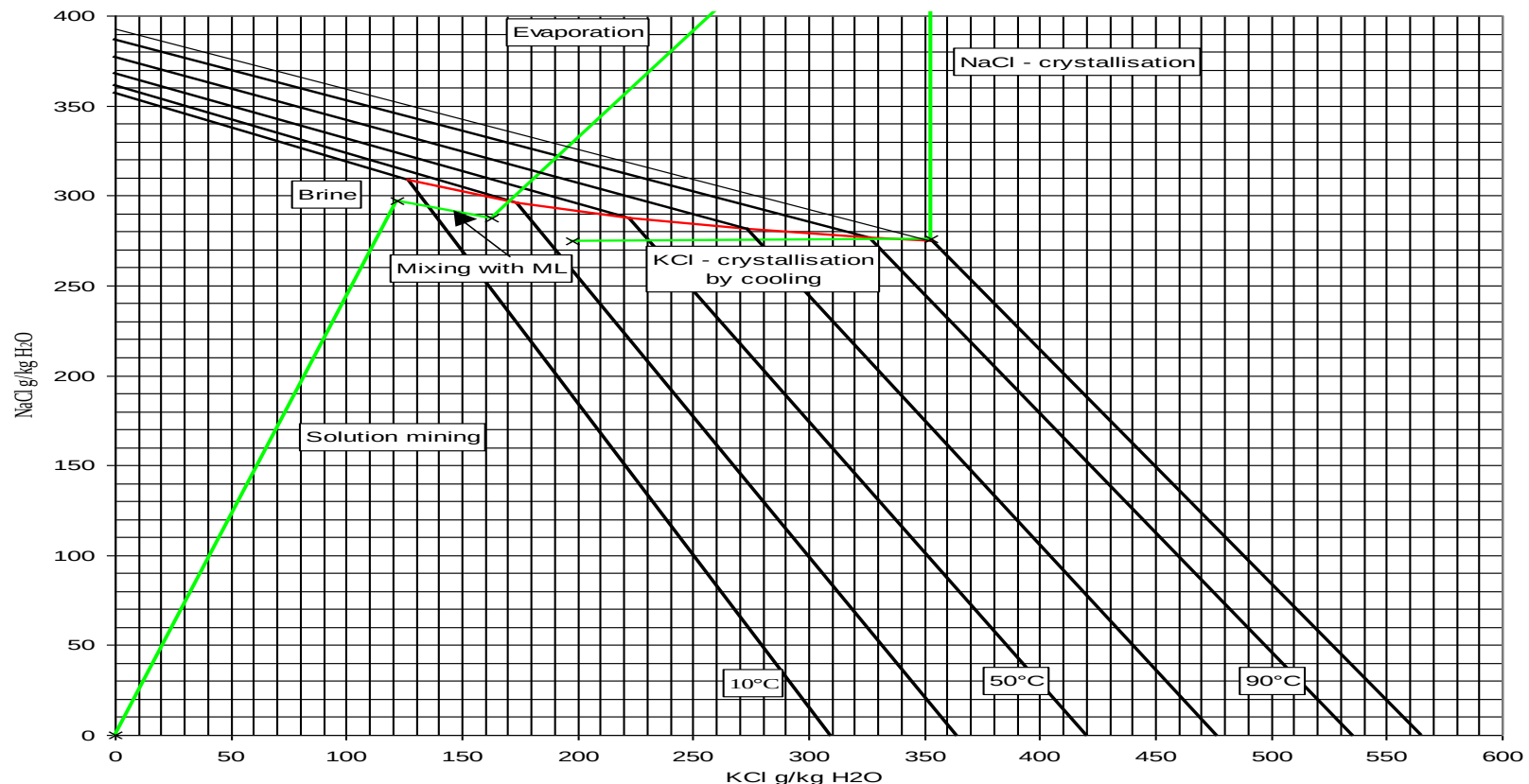
Flowsheet of NaCl production in a technical process



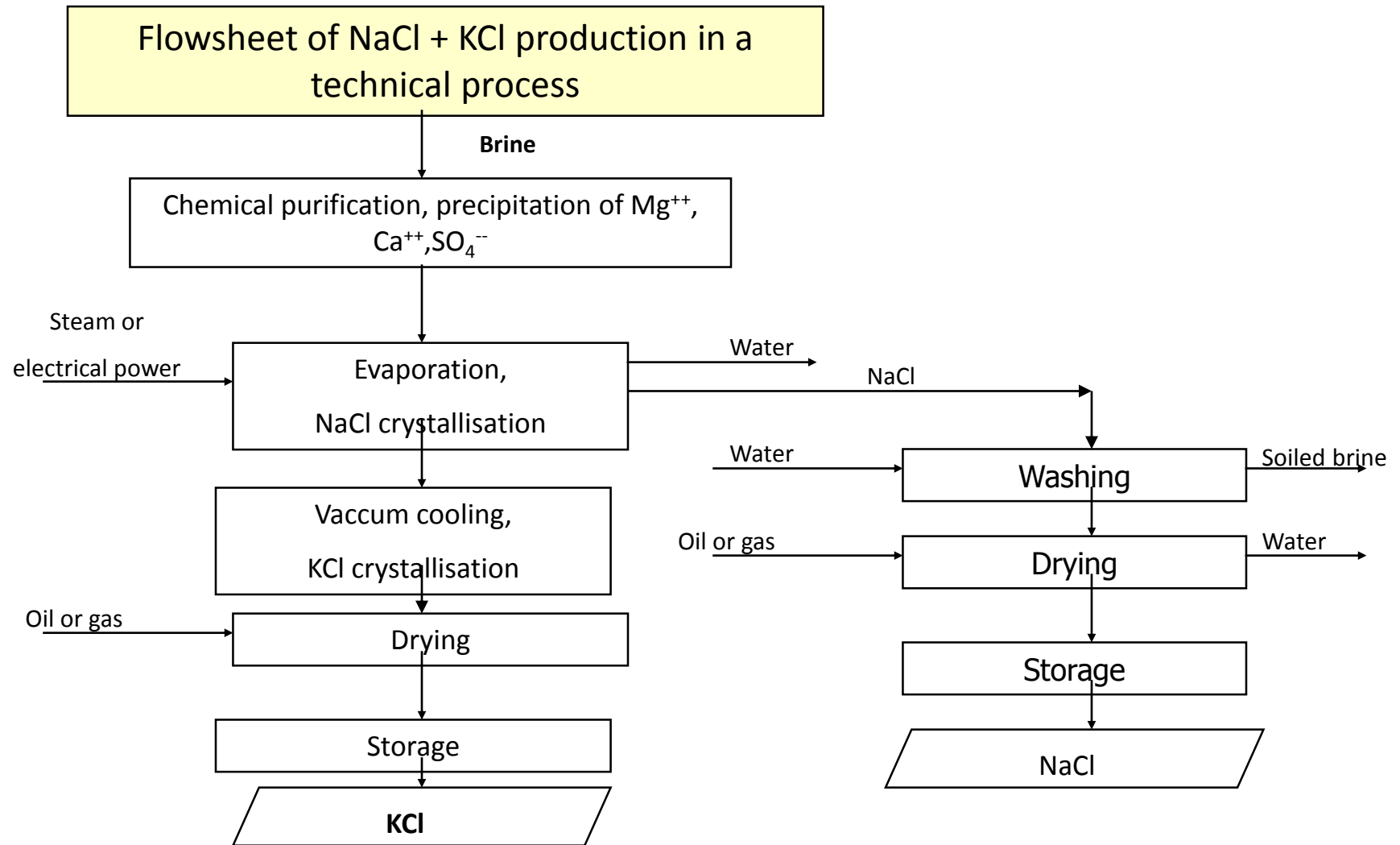
2) Technology of the Sylvinite Production

Sylvinite is a mixture of NaCl and KCl.

- In the case of contact with water by solution mining will be dissolved both components.
- At first in relation of their concentration in the raw salt and later the dissolution is approaching to the invariant point M (red line), as shown in the following picture.

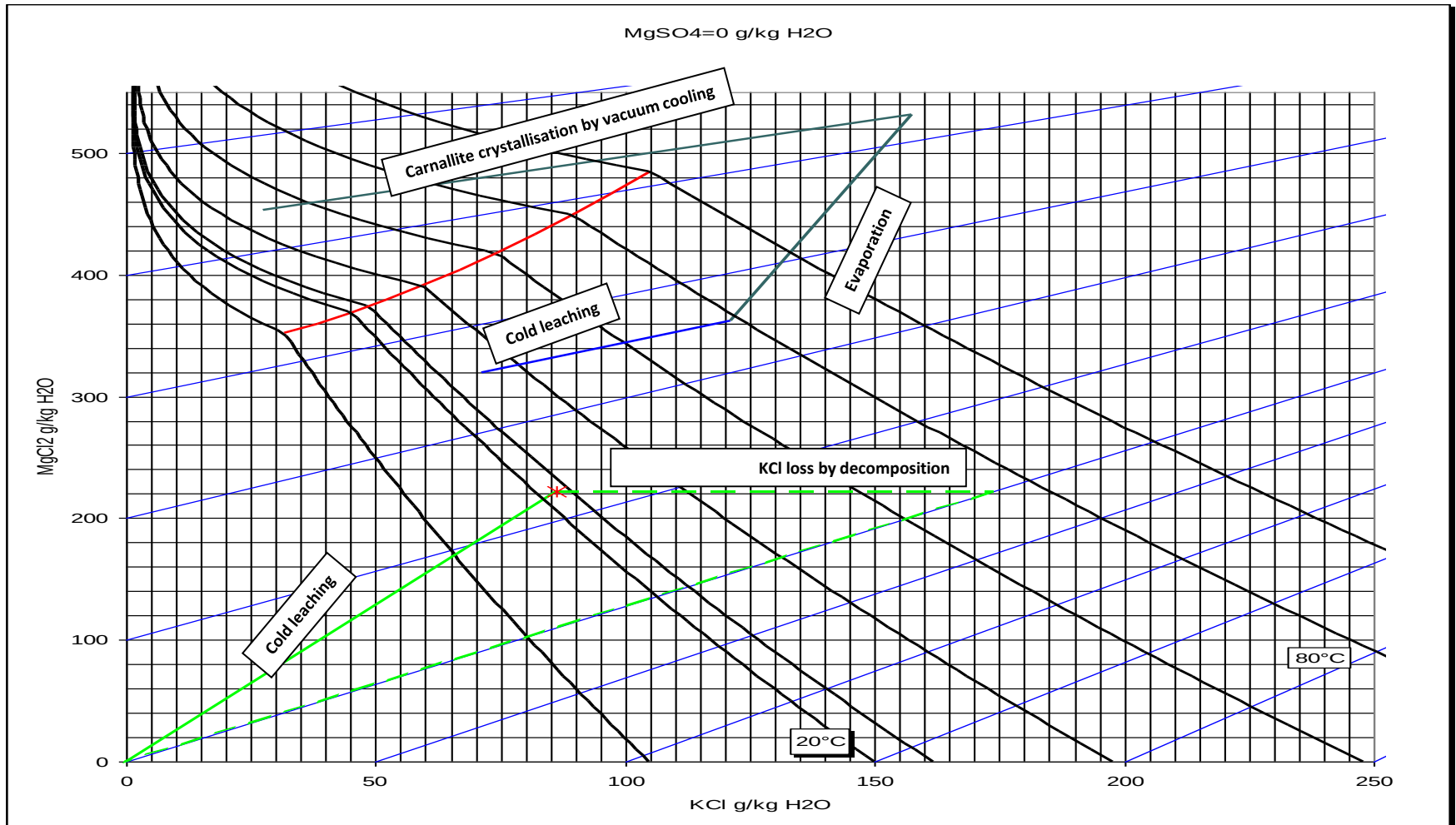


2) Technology of the Sylvinite Production



3) Technology of the Carnallite production

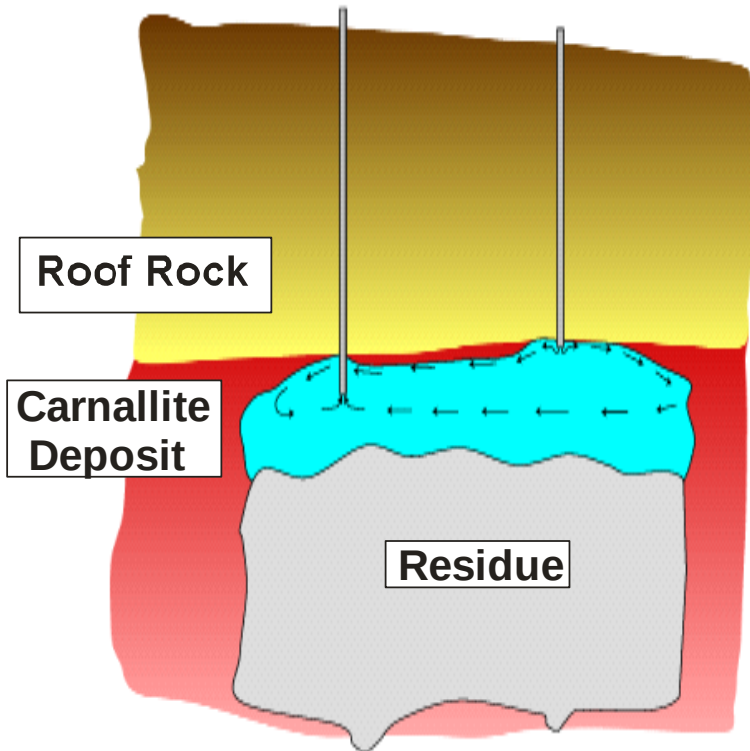
- Carnallite is a double salt of MgCl_2 , KCl and six crystall water ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6 \text{H}_2\text{O}$).
- The solubility of the system $\text{Mg} - \text{K} - \text{Cl} - \text{H}_2\text{O}$ is shown in the following diagram.



3) Technology of the Carnallite Production

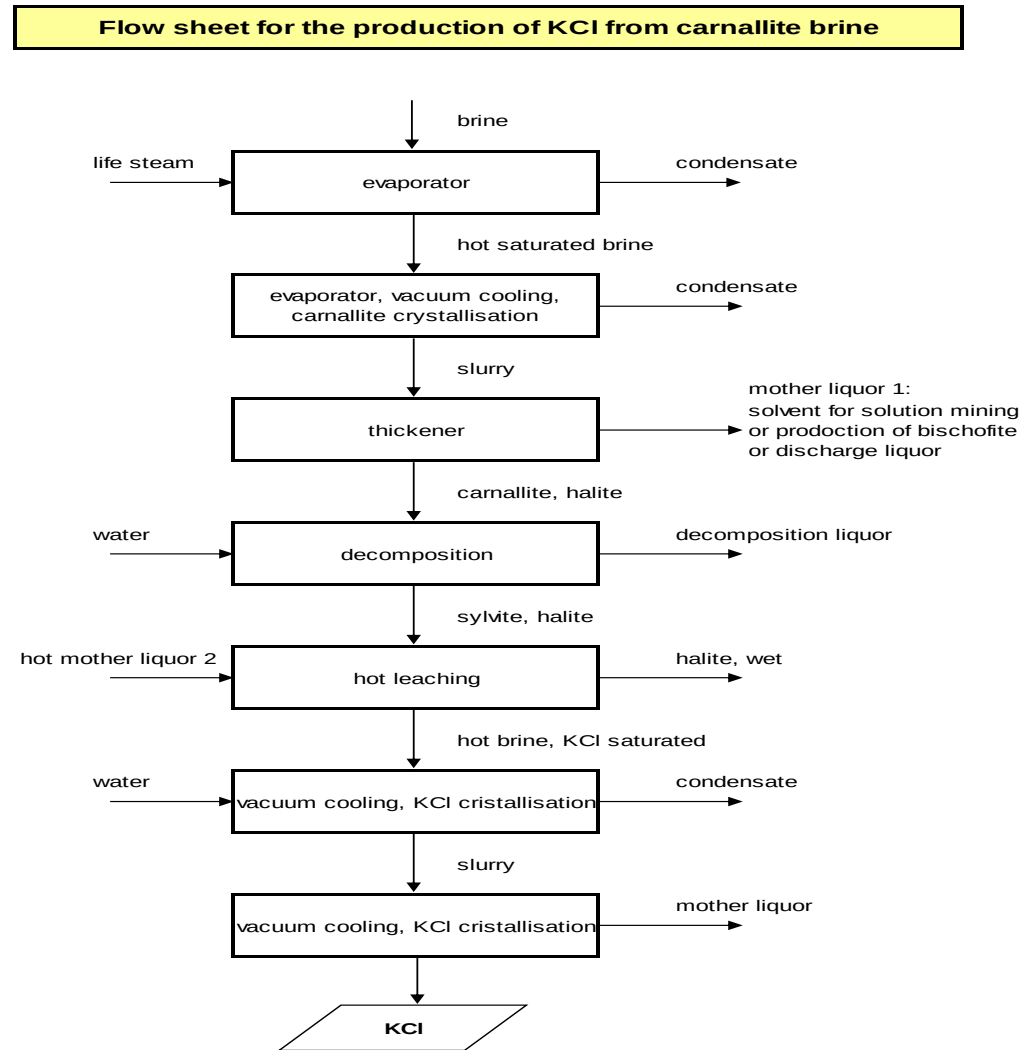
- ❑ How we can see the cold leaching has no efficiency, because:
 - the brine is not high concentrated and many water must evaporated.
 - the losses of KCl by decomposition of carnallite are very high.
- ❑ Therefore the hot leaching technology for solution mining of carnallite must used. This procedure has not the named disadvantages and has the following advantages:
 - The brine is high concentrated. Carnallite can be crystallised by evaporation of a few amount of water and cooling the brine .
 - The solvent is saturated on NaCl. Therefore halite and also kieserite remain in the cavern as residue.
 - In the cavern remains a high concentrated brine, which not worries the environment.
- ❑ Because the solvent has a high temperature, the cavern has two wells as shown in the following picture. In only one well would exchange the heat between the concentric inner and outer tube or casing.

3) Technology of the Carnallite Production



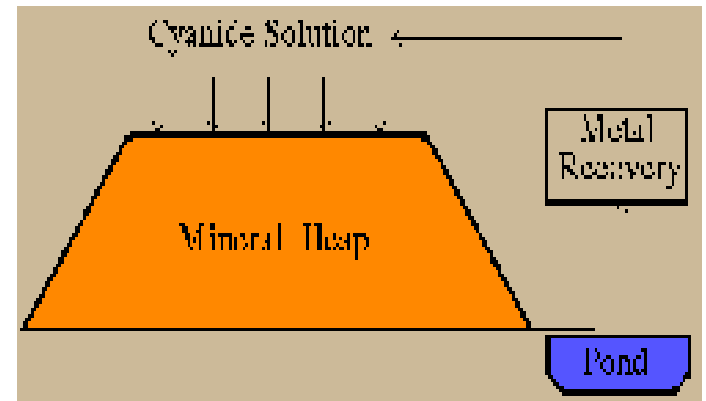
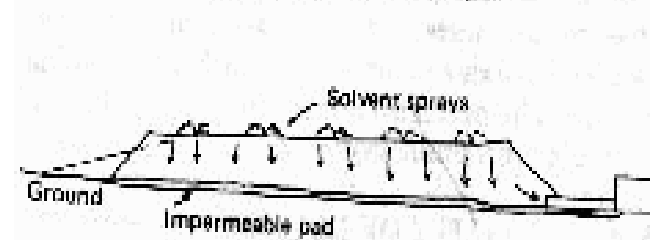
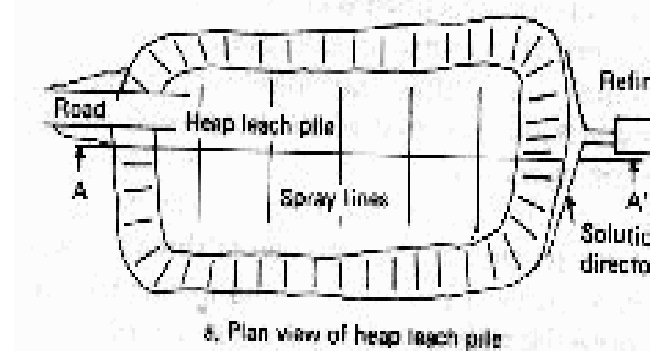
Solution mining of carnallite with:

- two wells
- selective dissolution
- hot leaching



III) HEAP LEACHING

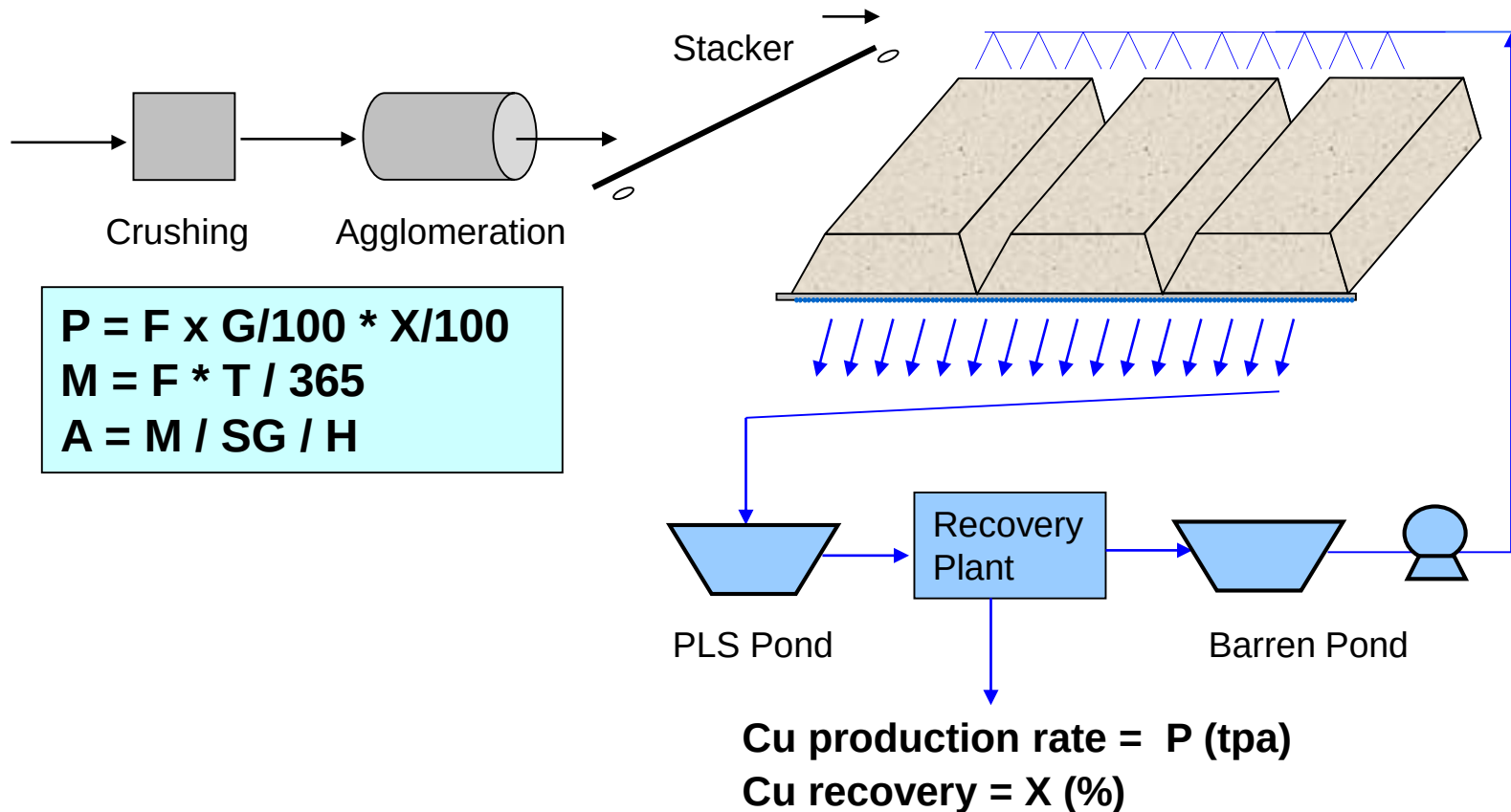
- **'Heap leaching'** is a countercurrent process where the solid is in a stationary heap and the solvent percolates through the solid. An example is a dump or landfill.
- In industrial leaching, solvent and solid are mixed, allowed to approach equilibrium, and the two phases are separated. Liquid and solids move counter currently to the adjacent stages. The solvent phase, called the extract, becomes more concentrated as it contacts in stagewise fashion the increasingly solute-rich solid. The raffinate becomes less concentrated in soluble material as it moves toward the fresh solvent phase.
- Heap leaching is also used in recovering metals from their ores.
- Bacterial leaching is first used to oxidize sulphide minerals. Cyanide solution is then used to leach the metals from the mineral heap.
- Suitability of ore to heap leaching dependent on recoverable value, kinetics, permeability, mineral liberation, reagent consumption.



Heap leach production model

Feed rate = F (tpa)
Head grade = G (%)

Pad Area = A (m²)
Lift Height = H (m)
Leach cycle = T (days)
Mass under leach = M (t)
Stacked density = SG (t/m³)



Important parameters during metallurgical testing

- ☐ Reagent consumption – operating cost
- ☐ Recovery and head grade – ore throughput
- ☐ Leach kinetics – leach cycle (i.e. pad size)
- ☐ Permeability – heap height (i.e. pad size)
- ☐ Effect of lixiviant strength – gangue reactions
- ☐ Effect of bacterial inoculation and forced aeration for sulfides
- ☐ Effect of heat preservation for sulphides
- ☐ Effect of mineralogy (e.g. laterites)
- ☐ Effect of impurity build-up in recycled solutions

Staged Approach to Heap Leach Testwork and Design

Roll Bottles



Stirred tank



1 m columns



6 m columns



Test heap



Commercial heap



Heap Leach Operation



Installing a Plastic Membrane Liner

Uranium Ore Minerals

- ❑ Uranium can be found in a large number of minerals.
- ❑ The most common economic minerals are listed below:

1) Oxides:

- Uraninite (crystalline $\text{UO}_{2-2.6}$)
- Pitchblende **Pitchblende** {an amorphous, poorly crystalline mix of uranium oxides often including triuranium octoxide (U_3O_8)}, though a range of other uranium minerals is found in particular deposits.
- (amorphous $\text{UO}_{2-2.6}$)
- Carnotite $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1-3 \text{H}_2\text{O}$
- Brannerite: $(\text{U,Ca,Y,Ce})(\text{Ti,Fe})_2\text{O}_6$

2) Silicates: Hydrated uranium silicates:

- Uranophane ($\text{CaO}, 2\text{UO}_2, 2\text{SiO}_2, 6\text{H}_2\text{O}$)
- Coffinite ($(\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x})$)

3) Phosphates-Hydrated uranium phosphates of the phosphuranylite type; including:

- Autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$
- Saleeite $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$
- Torbernite $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$

4) Organic complexes & other forms

- ❑ The “primary” uranium minerals weather and break down very easily when exposed to water and oxygen, to produce **numerous “secondary” (oxidized) minerals**, for example **carnotite** and **autunite**, which are often mined, but in significantly lower quantities than uraninite.
- ❑ Uranium is also found in small amounts in other minerals:
- ❑ allanite, xenotime, monazite, zircon, apatite and sphene.

NAME	CHEMICAL FORMULA
PRIMARY URANIUM MINERALS	
The main “primary” ore in uranium deposits is Uraninite: (UO_2 and UO_3, nominally U_3O_8) . Other important “primary” uranium ore minerals are:	
Uraninite	UO_2
Pitchblende	U_3O_8 rare U_3O_7
Coffinite	$\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$
Brannerite	$(\text{U,Ca,Y,Ce})(\text{Ti,Fe})_2\text{O}_6$
Davidite	$(\text{REE})(\text{Y,U})(\text{Ti,Fe}^{3+})_{20}\text{O}_{38}$
Thucholite	Uranium-bearing pyrobitumen
SECONDARY URANIUM MINERALS	
A large variety of secondary uranium minerals is known, many are brilliantly coloured and fluorescent. The commonest are:	
Autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$
Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1-3 \text{H}_2\text{O}$
Gummite	A general term like limonite for mixtures of various secondary hydrated uranium oxides with impurities. Gum like amorphous mixture of various uranium minerals
Saleeite	$\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$
Torbernite	$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$
Tyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5-8\text{H}_2\text{O}$
Uranocircite	$\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8-10\text{H}_2\text{O}$
Uranophane	$\text{Ca}(\text{UO}_2)_2(\text{HSiO}_4)_2 \cdot 5\text{H}_2\text{O}$
Zeunerite	$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8-10\text{H}_2\text{O}$

Uranium Minerals

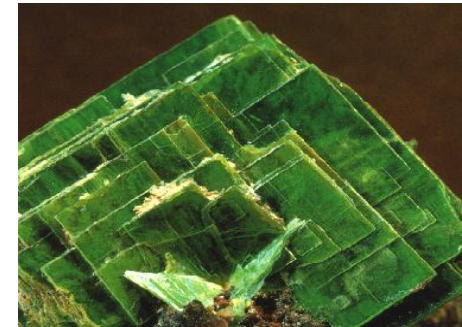
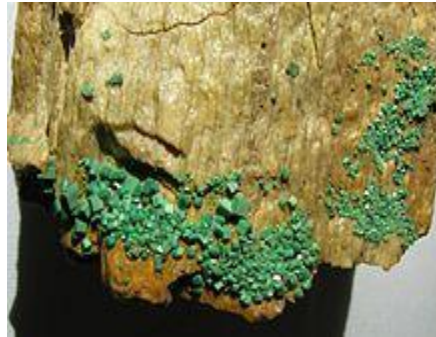


Autunite

a secondary uranium mineral named after the town of Autun in France

Torbernite

an important secondary uranium mineral



Uraninite (Pitchblende) UO_2



Carnotite



An important “secondary” uranium-vanadium bearing mineral, from Happy Jack Mine, White Canyon District, Utah, USA. Credit: Andrew Silver.

Basic Geochemistry of Uranium Minerals

Uranium normally occurs in 2 valence states:

U⁺⁴ (reduced-insoluble) and U⁺⁶ (oxidized-soluble)



Uraninite

1) Uranous ion: U⁺⁴ is quite insoluble.

- Uraninite: UO_2 [U_3O_8 and Th & REE]
- Pitchblende (UO_2) if fine-grained, massive, Density 6.5-8.5
- Coffinite: $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$
- Brannerite: $(\text{U,Ca,Y,Ce})(\text{Ti,Fe})_2\text{O}_6$, Density 4.5-5.4

2) Uranyl ion: U⁺⁶ is quite soluble and forms many stable aqueous complexes and then minerals when additional cations become available.

- Carnotite: $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1-3 \text{H}_2\text{O}$
- Tyuymunitite: $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5-8\text{H}_2\text{O}$
- Autunite: $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$
- Tobernite: $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$
- Uranophane: $\text{Ca}(\text{UO}_2)_2\text{SiO}_3(\text{OH})_2 \cdot 5\text{H}_2\text{O}$

3) Complexes with: $(\text{CO}_3)^{2-}$, OH^- , H^- , $(\text{PO}_4)^{2-}$, F^- , Cl

Uranium Leaching

- ❑ Uranium minerals are soluble in acidic or alkaline solutions.
- ❑ The production (“pregnant”) fluid consisting of the **water soluble** uranyl oxyanion (UO_2^{2+}) is subject to further processing on surface to precipitate the concentrated mineral product U_3O_8 or UO_3 (yellowcake).

Acid leaching fluid:

sulphuric acid + oxidant (Nitric acid, hydrogen peroxide or dissolved oxygen)
or

Alkali leaching fluid:

ammonia, ammonium carbonate/bicarbonate, or sodium carbonate/bicarbonate

The hydrology of the aquifer is irreversibly changed: its porosity, permeability and water quality. It is regarded as being easier to “Restore” an aquifer after alkali leaching.

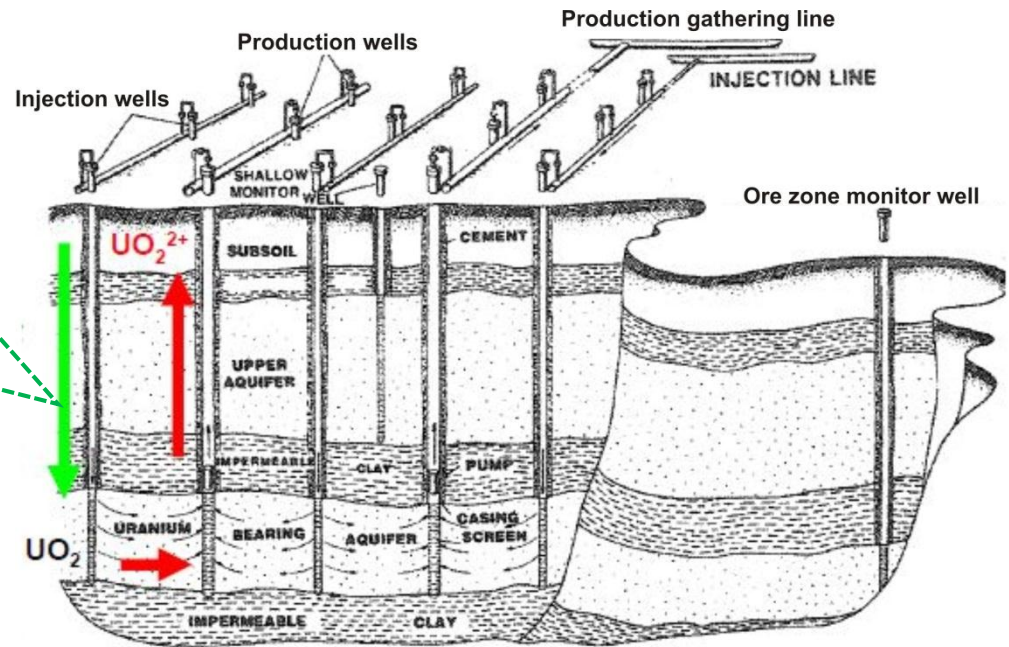
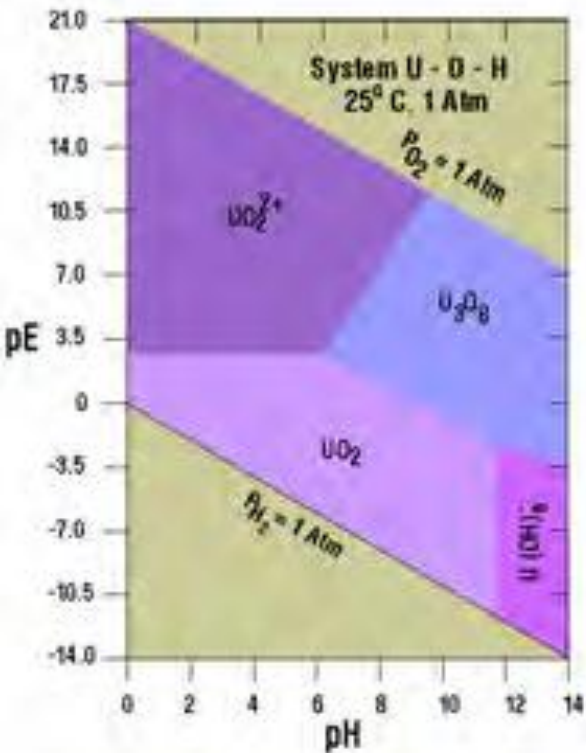
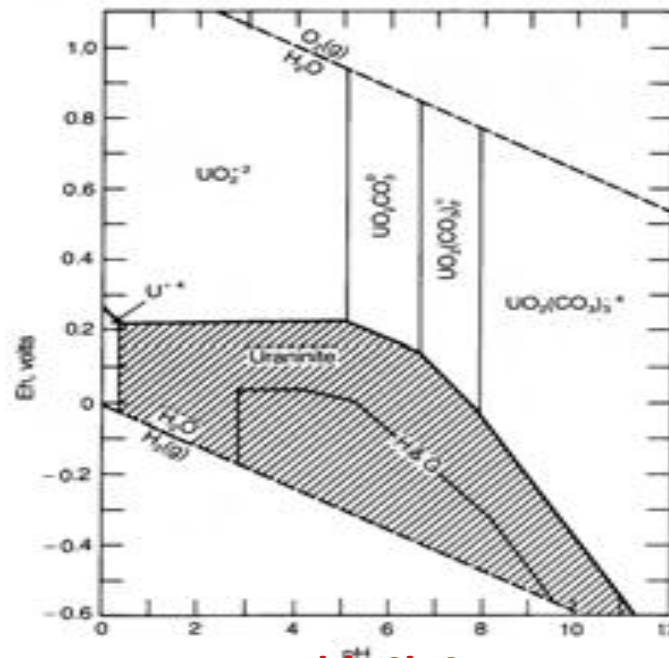


Figure from Hartman and Mutmanský, 2002.

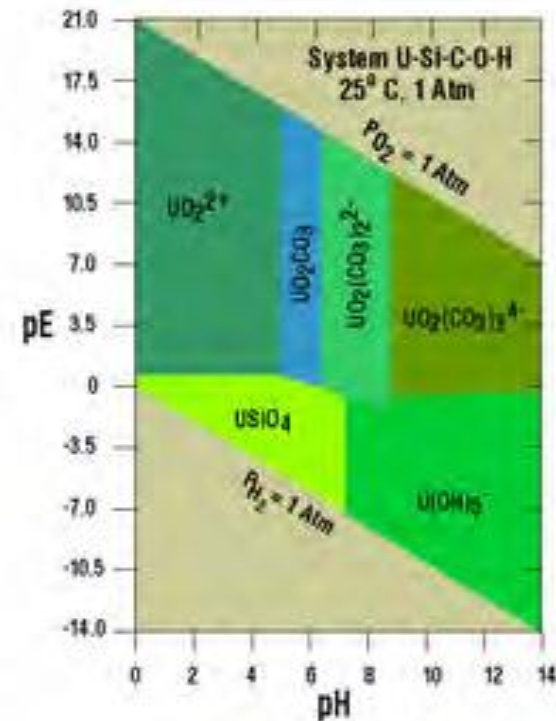
Eh-pH and Uranium Solubility



Reduced
Uranous Ion
 U^{+4} (reduced-insoluble)



Now add: Cl, S, P, F, ...
 $(CO_3)^{2-}$, OH^- , H^+ , $(PO_4)^{2-}$, F^- , Cl^-

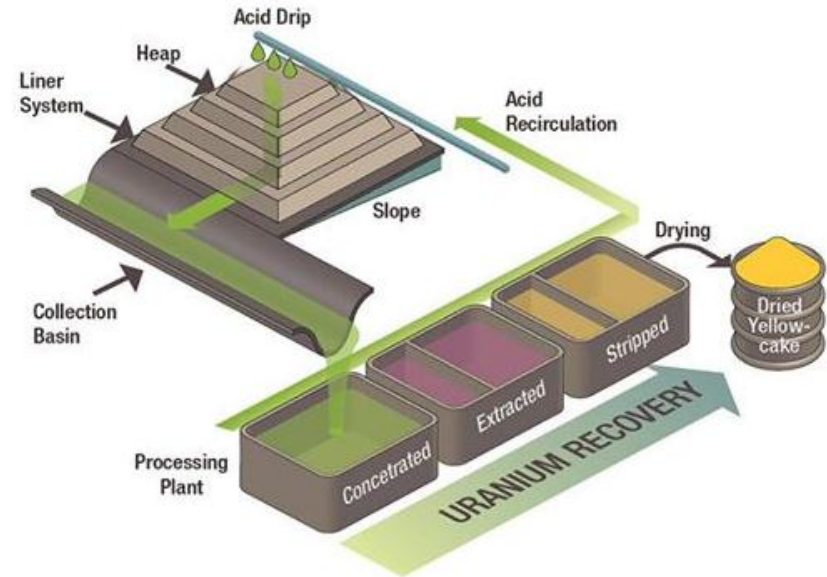


Oxidized
Uranyl Ion
 U^{+6} (oxidized-soluble)

Uranium Heap Leaching

- ❑ Occurs in tetravalent and hexavalent forms
- ❑ Tetravalent uranium requires oxidation during leaching.
- ❑ Leaching in acid or carbonate medium, depending on gangue acid consumption. Lower recoveries in carbonate medium.
- ❑ Addition of suitable oxidising agent such as, H_2O_2 , MnO_2 , NaClO_3 for regeneration of Fe^{3+} , or by bacterial oxidation. Typically 0.5g/L Fe, ORP 475-425 mV, which may be produced from gangue dissolution.
- ❑ **Bacterial leaching** offers advantage of reduced oxidising agent cost and generation of acid from sulphide minerals such as pyrite, as well as liberation of mineral from sulphide host.
- ❑ **“Readily leachable”** minerals are acid leached at pH 1.5-2.0 and 35-60°C, which are suitable conditions for bioleaching. “Refractory” minerals require higher temperature (60-80°C) and stronger acid (up to 50g/L).
- ❑ Uranium heap leaching dependent on mineralogy, uranium price determines cut-off grade of suitable waste rock. Bacterial leaching offers advantage for reducing oxidising agent and acid cost.

The Heap Leach Recovery Process



Common Uranium minerals

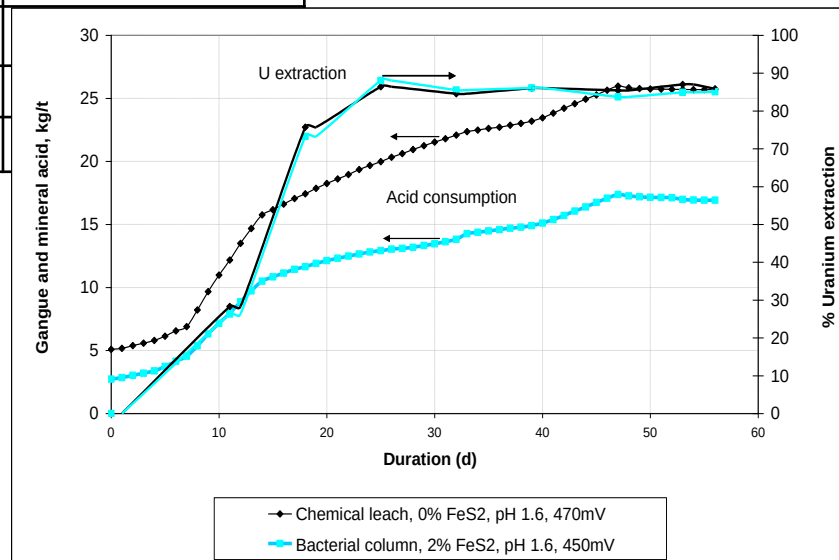
Type	Mineral	Formula	Operation
Leachable oxides	Uraninite ^{TL}	$U^{+4}_{1-x}U^{+6}_xO_{2+x}$	Rossing, Dominion Reefs, Ezulwini
	Pitchblende ^{TL}	UO_2 to $UO_{2.25}$	Narbalek, Kintyre
Leachable silicates	Coffinite ^{TL}	$U(SiO_4)_{1-x}(OH)_{4x}$	Rystkuil
Refractory complex oxides	Brannerite ^{TR}	$(U,Ca,Fe,Th,Y)(Ti,Fe)_2O_6$	Elliot Lake
	Davidite ^{TR}	$(La,Ce,Ca)(Y,U)(Ti,Fe^{3+})_{20}O_{38}$	Radium Hill
Hydrated oxides	Becquerelite ^{HL}	$7UO_2 \cdot 11H_2O$	
	Gummite ^{HL}	$UO_3 \cdot nH_2O$	
Silicates	Uranophane ^{HL}	$Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$	Rossing
	Uranothorite ^{TL}	$(UTh)SiO_4$	Dominion Reefs
	Sklodowskite ^{HL}	$(H_3O_2)Mg(UO_2)_2(SiO_4)_2 \cdot 2H_2O$	
Vanadates	Carnotite ^{HL}	$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$	Langer Heinrich
	Tyuyamunite ^{HL}	$Ca(UO_2)_2(VO_4)_2 \cdot 8H_2O$	
Phosphates	Torbernite ^{HL}	$Cu(UO_2)_2(PO_4)_2 \cdot 10H_2O$	Rum Jungle
	Autunite ^{HL}	$Ca(UO_2)_2(PO_4)_2 \cdot 11H_2O$	Rum Jungle
Carbonates	Schroekingerite ^{HL}	$NaCa_3(UO)_2(CO_3)_3(SO_4)F \cdot 10H_2O$	
Arsenates	Zeunarite ^{HL}	$Cu(UO_2)_2(AsO_4)_2 \cdot 10-12H_2O$	
Hydrocarbons	Thucholite ^{TL}		

HL- hexavalent readily acid leachable without oxidation

TL - tetravalent readily acid leachable with oxidation

TR - tetravalent refractory

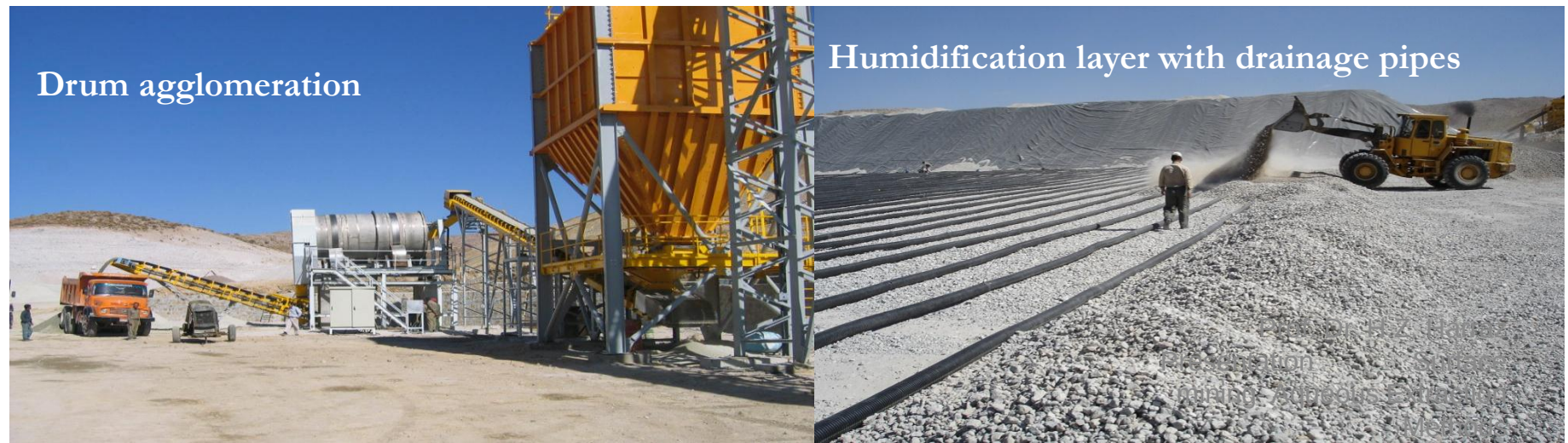
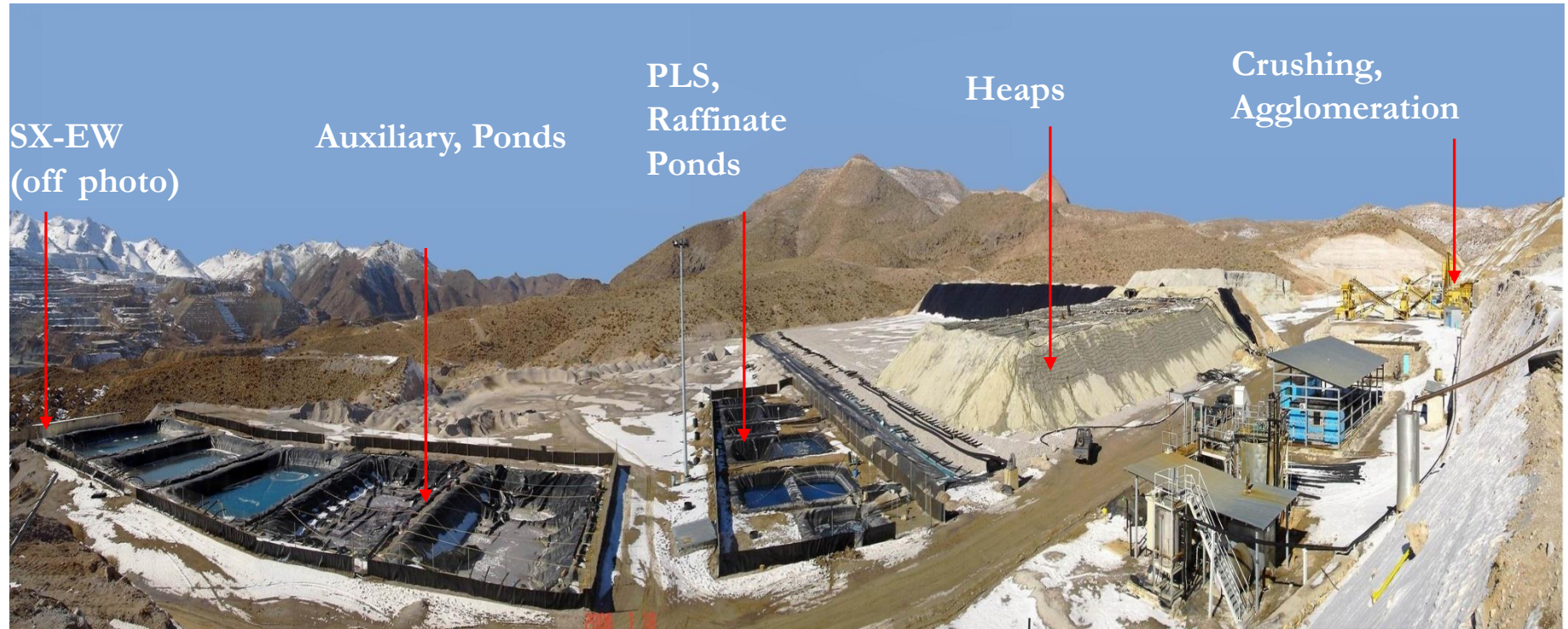
Bacterial versus Chemical Leaching of Uranium Ore



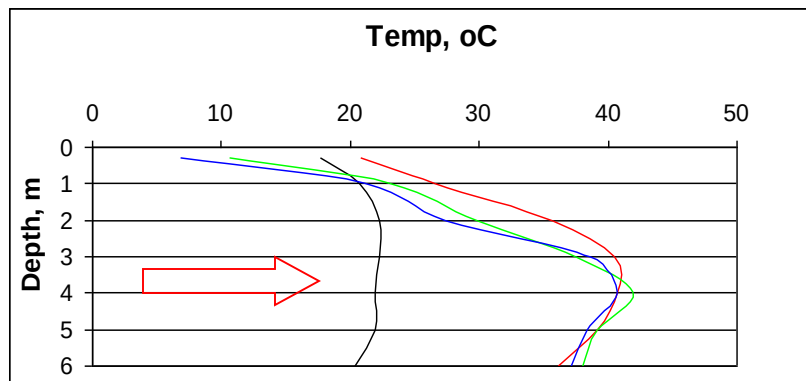
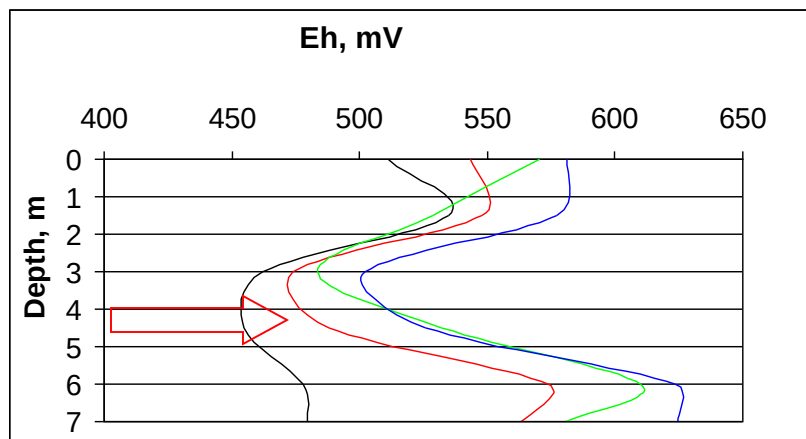
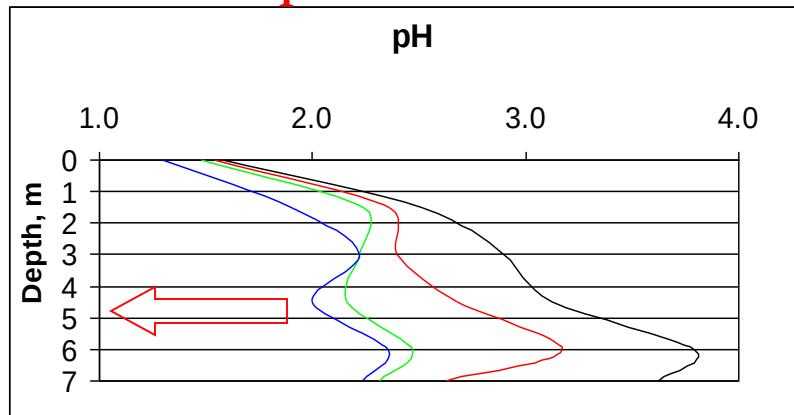
Copper Heap Leaching

- ❑ Common for oxides and low-grade secondary sulphides (<0.6% Cu) which are unsuitable for flotation.
- ❑ Bacterial-assisted heap leaching common for chalcocite (Cu_2S) and covellite (CuS) where bacterial activity assist in ferrous to ferric oxidation and direct conversion of sulphur.
- ❑ Ores containing high levels of acid-consuming carbonate gangue may be uneconomical.
- ❑ Presence of clay minerals may result in poor percolation.
- ❑ Chalcopyrite gives poor leach kinetics, but rate increases with temperature. Irrigation and aeration rates can be manipulated to maintain temperatures of around 40°C in bioheap.
- ❑ Longer leach cycles (~1 year) and lower extractions (~50-60%) associated with chalcopyrite will result in larger pad and larger crushing plant capital costs.
- ❑ Chalcopyrite heap leaching will require larger pad size and throughput due to lower extractions and longer leach cycles compared with secondary sulphides.

Layout of copper bio-heap pilot plant

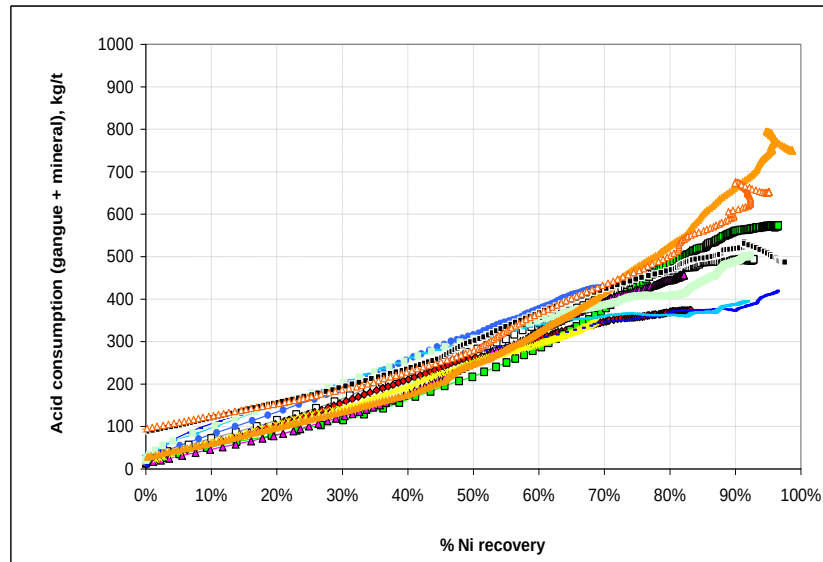


Development of axial profiles in bacterial test heap



Laterite Heap Leaching

- ❑ Acid consumptions are high (~500-700kg/t), so on-site acid plant required
- ❑ Saprolitic and nontronitic mineralogies give good nickel leach kinetics and extractions, but limonites give poor extractions
- ❑ Nontronite clays may inhibit percolation
- ❑ Leach rate limited by supply of acid, hence kinetics may be improved by increasing acid strength or irrigation rate
- ❑ Irrigation rate limited by permeability
- ❑ Acid strength limited by need to minimise residual acid reporting to recovery plant
- ❑ Counter-current operation is proposed to meet both requirements of high acid strength and low residual acid
- ❑ Need to determine acid neutralisation potential of ore in order to maximise acid strength
- ❑ Laterite heap leaching dependent on cheap acid source, mineralogy, permeability and counter-current operation to minimise residual acid to recovery plant.

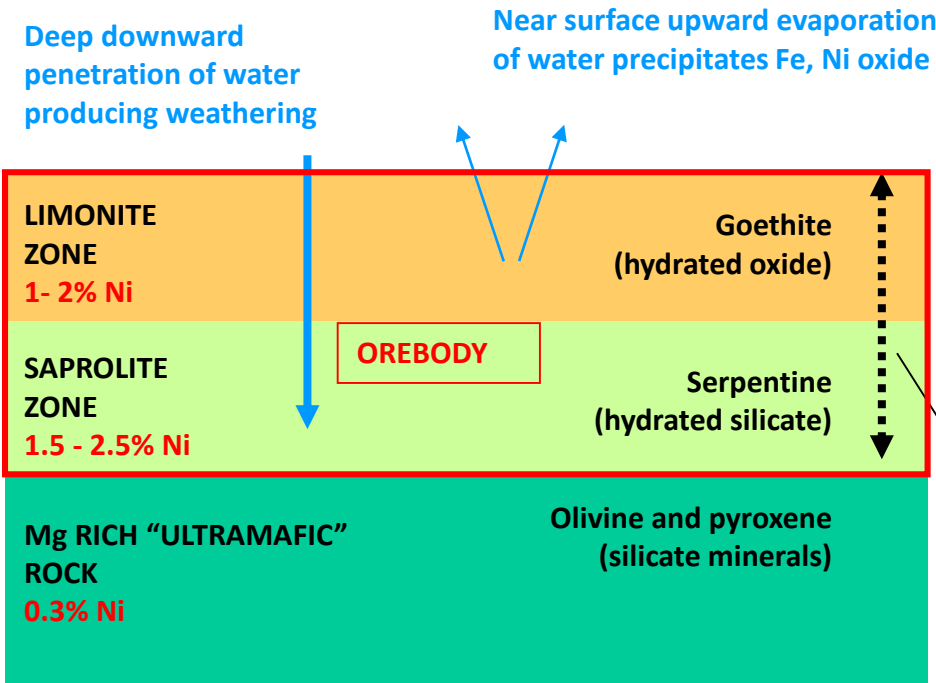


Acid consumption vs Ni recovery for laterites

Nickel Laterite Deposits

Nickel laterite ore deposits are the surficial, deeply weathered residues formed on top of ultramafic rocks that are exposed at surface in tropical climates. They are found widely in New Caledonia, Cuba, Australia, Papua New Guinea, the Philippines, and Indonesia, and are estimated to **comprise about 73% of the world continental nickel resource**.

Two kinds of lateritic nickel ore can be distinguished: limonite (oxide) types and saprolite (silicate) types.

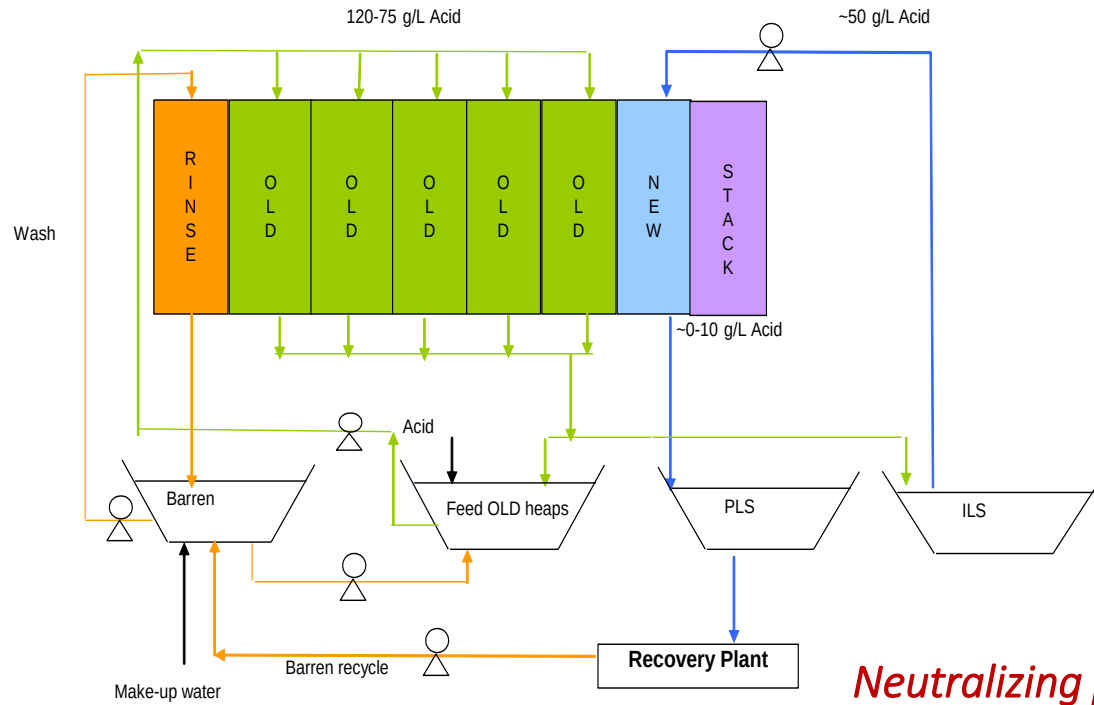


Classificat ion	Approximate composition of tropical laterite*	Minerals	Process
Limonite	MgO < 5%, Fe >40%, Ni <1.5%	Goethite, Hematite	Pressure leaching
Nontronite	MgO 5-15%, Fe 25-40% Ni 1.4-4%	Smectite clays, chalcedony, sepiolite	Ammonia leach (Caron)
Saprolite	MgO 15-35%, Fe 10-25%, Ni 1.8-3%	Garnierite, serpentine, chlorite, talc	Atmospheric tank leaching, heap leaching, smelting

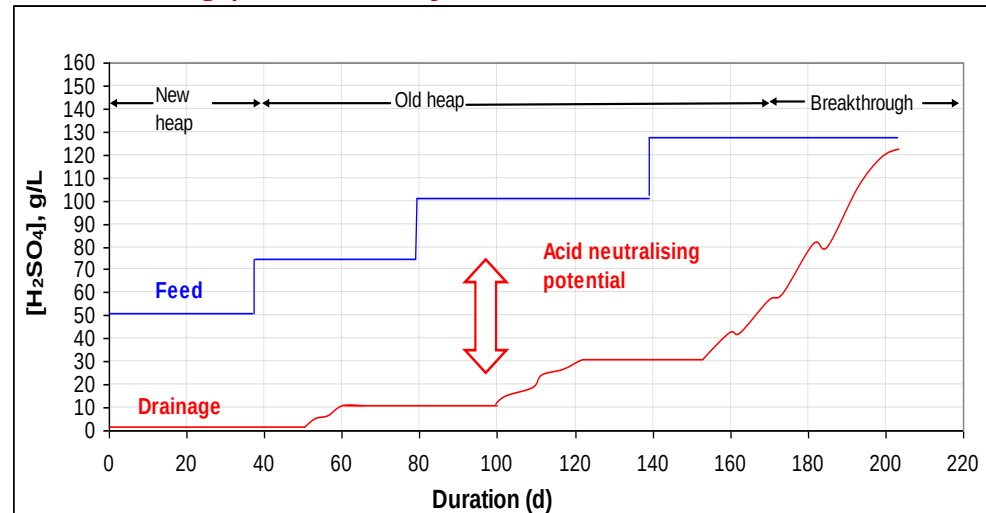
* Elias, CSA Australia, Giant ore deposits workshop, 2002

The process of oxidation and weathering depletes the original mafic rock of Mg and Si, and concentrates Fe and Ni in the weathered zone.

Proposed counter-current heap leach arrangement

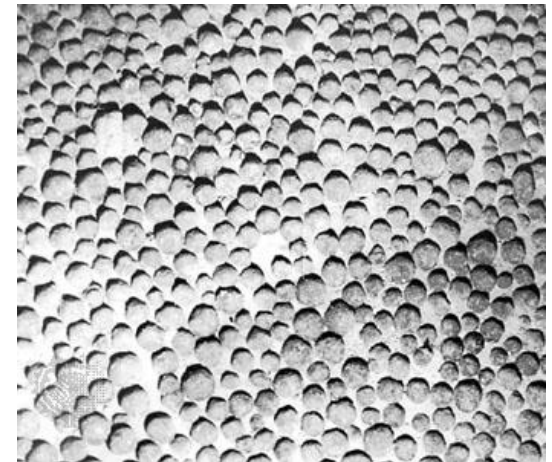


Neutralizing potential of laterites in 6 meter column



IV) UNDERSEA MINING (or Mining Oceans)

- ❑ We extract minerals (e.g., magnesium) from seawater
- ❑ Minerals are dredged from the ocean floor
 - Sulfur, phosphate, calcium carbonate (for cement), silica (insulation and glass), copper, zinc, silver, gold
- ❑ Manganese nodules = small, ball-shaped ores scattered across the ocean floor
 - Mining them is currently uneconomical
 - **Manganese Nodules (pacific ocean)**– ore nodules crystallized from hot solutions arising from volcanic activity. Contain manganese, iron copper and nickel.
- ❑ Hydrothermal vents may have gold, silver, zinc
- ❑ Mining would destroy habitats and organisms and release toxic metals that could enter the food chain.
- ❑ **Note:**
 - 1) Minerals are found in seawater, but occur in too low of a concentration
 - 2) Continental shelf can be mined
 - 3) Deep Ocean are extremely expensive to extract (not currently viable)



Advantages of Solution Mining :

- Less environmental impact than other methods:
- Less surface area is disturbed.
- Acids, heavy metals, uranium can accidentally leak.
- No solid wastes.
- Liquid wastes (low concentration brines with no market value) can be re-injected into the stratum being leached. Also reported that wastes are sometimes injected into a separate aquifer (*not good practice*).

Problems of Solution Mining :

- Little control of the solution underground and difficulty in ensuring the process solutions do not migrate away from the immediate area of leaching.
- Main impact of evaporite ISL is derived from surface or shallow groundwater contamination in the vicinity of evaporation ponds. Pregnant solutions can be highly corrosive and phyto-toxic, and can react with the soil materials used in pond construction, and may migrate to surrounding areas through seepage, overflow (*both bad practice*), and windblown spray.
- Surface subsidence and the development of sink-holes may also occur after prolonged solution mining if inadequate un-mined material is left to support the overburden (*bad practice*).

Advantages/disadvantages of heap leaching

Advantages

- ☐ Low capital and operating costs
- ☐ Absence of milling step, may require crushing and agglomeration
- ☐ Simplicity of atmospheric leach processes
- ☐ Can be used to treat low-grade ores, wastes and small deposits
- ☐ Absence of liquid-solid separation step allows counter-current operation
- ☐ Metal tenor may be built up by recycling solution over heaps

Disadvantages

- ☐ Lower recoveries than mill/float or mill/leach
- ☐ Long leach cycles and hold-up
- ☐ Lengthy experimental programmes
- ☐ Large footprint
- ☐ Acid-mine drainage of wastes

Conclusions

- ❑ In the most cases solution mining has a very high economic efficiency because:
 - The investment costs are low. (We don't need a mine).
 - The drilling of the bore holes are running costs.
 - The demand of manpower is low.
 - Solution mining can also used by difficult hydrogeological conditions.
 - The first step of the potash mill (hot leaching) is in the underground. There are no costs for this equipment.
 - Residue and high concentrated brine stays in the cavern, therefore there environmental burdens are low.
- ❑ If the geological and technical conditions are very difficult, the solution mining is not usable.

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