

# FERTILIZERS TECHNOLOGY

CHEM 0905554

Spring Semester 22/23

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## CHAPTER 4 POTASH



## INTRODUCTION

- The term potash comes from the English : pot ash, which means ashes pot.
- Two centuries ago, potash was extracted from wood ash in large iron pots.
- First potash mine opened in Germany in the mid- 19<sup>th</sup> century, now potash comes mainly from potash mines of Saskatchewan (Canada) and Urals (Belarus and Russia).
- Virtually all of the economic sources of potassium occur in sedimentary salt beds remaining after the evaporation of ancient seas and lakes.



## INTRODUCTION

- World reserves of such potassium-bearing deposits are immense, and they total about 250 billion tons of  $K_2O$ , of which 9.4 billion tons are considered commercially exploitable.
- With current global consumption of about 25 million tons of  $K_2O$  annually both economical reserves and total resources are sufficient to satisfy world demand for centuries.
- Today, potash deposits are found buried at a depth of 500 to 1 000 meters underground.
- At least 95 percent of world production of potassium fertilizers is in the form of potassium chloride.



## INTRODUCTION

- Potassium sulfate is the next most important source followed by much smaller quantities of specialty materials such as potassium magnesium sulfate, potassium nitrate, potassium thiosulfate, potassium polysulfide, potassium carbonate and potassium bicarbonate.
- Potash is used to 95% by agriculture, the rest is used for detergents, soaps and glass.
- Potash Corp. of Saskatchewan Inc. , the world's largest potash producer, producing 90% of Canada's total output and about one quarter of the world's supplies.

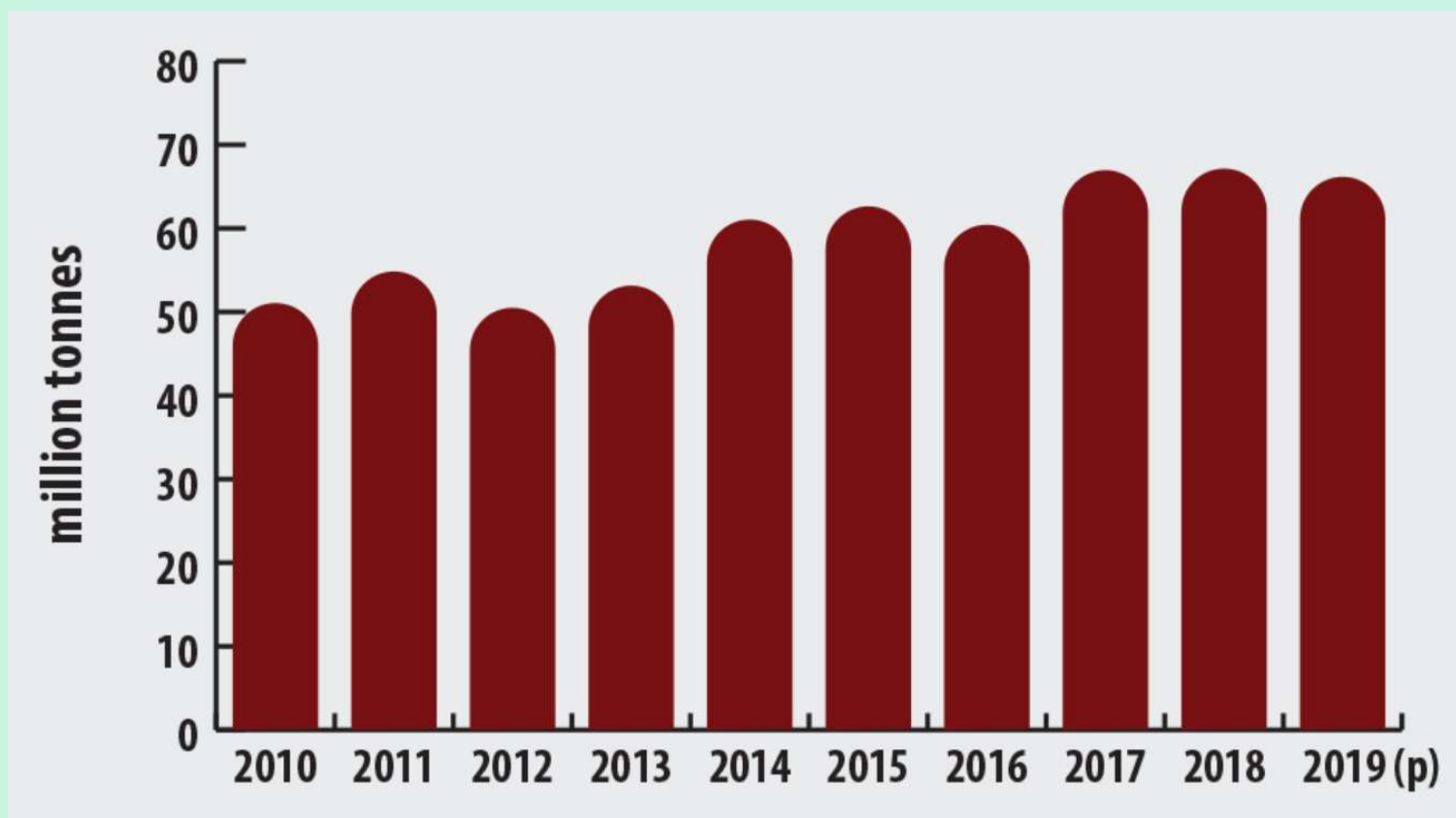


## INTRODUCTION

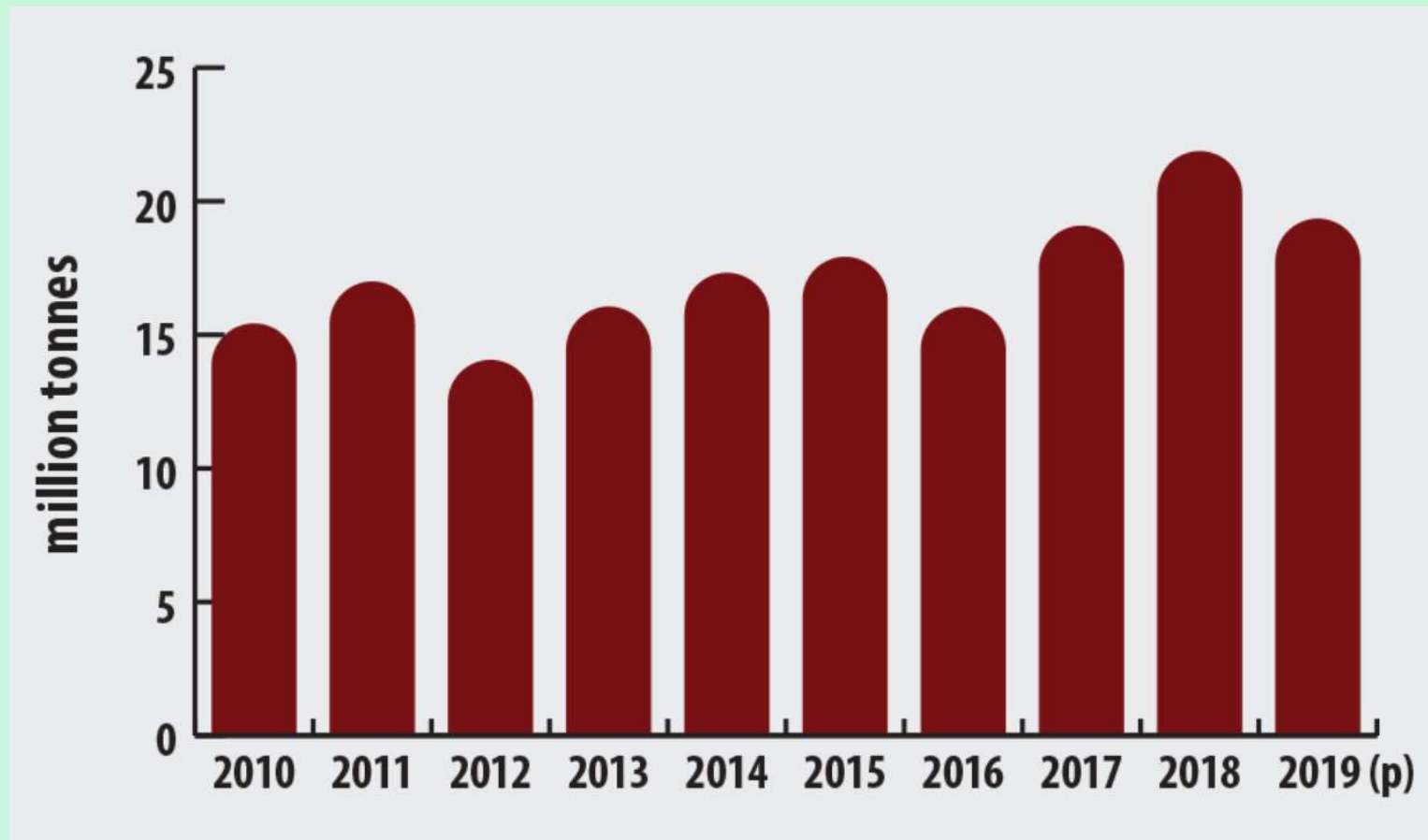
- Saskatchewan cut production by 3.5 million MT in January 2009 in response to decreased demand.
- There are at present over 45 operations producing KCl in 12 countries.
- The worlds total potash output was 62.2 Mt KCl in 2019.
- The global KCl producers operated at 85% of production capacity in 2007.
- The world has many consumers (over 150 nations) but very few producers.
- Canada, Russia and Belarus account for approximately 80% of output.
- Potash ore bodies in Saskatchewan are the world's largest, richest and most economical to mine.



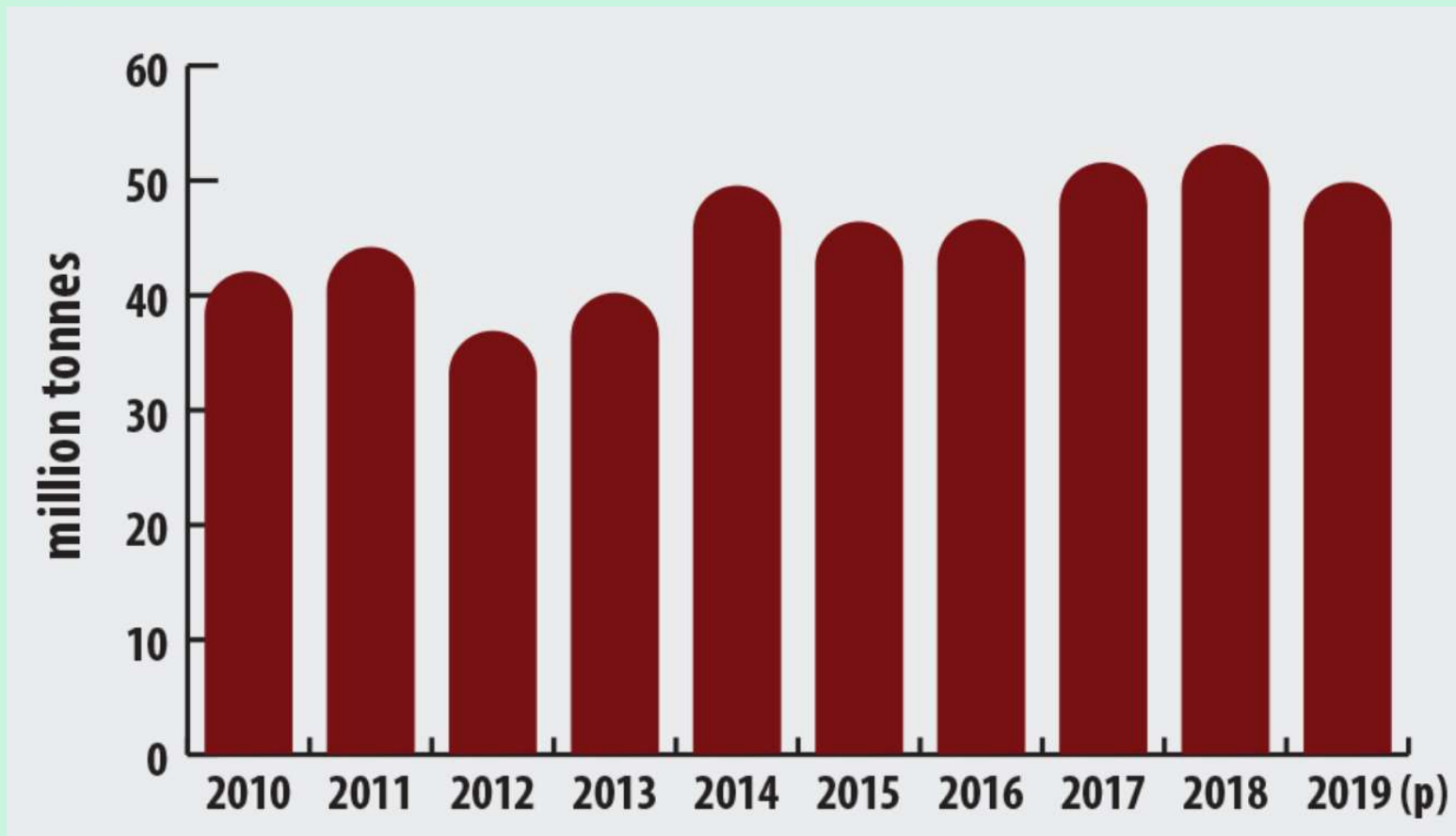
## WORLD PRODUCTION OF POTASH (POTASSIUM CHLORIDE)



## CANADIAN EXPORTS OF POTASH (POTASSIUM CHLORIDE)



## WORLD EXPORTS OF POTASH (POTASSIUM CHLORIDE)





## POTASSIUM CHLORIDE PRICES



## SALT CONCENTRATION IN DIFFERENT WATER SURFACES

Water surface	Total concentration of salts (g/L)
Atlantic Ocean	34.00 – 37.30
Mediterranean Sea	36.00 – 39.50
Read Sea	38.00 – 42.00
Black Sea	18.00
Baltic Sea	6.00 – 11.00
Dead Sea	262.00 – 270.31



## IONIC CONCENTRATION IN DIFFERENT WATER SURFACES

- The concentration of Potassium (K) in the Dead Sea water is 20 times more than that in the Atlantic Ocean and that of Magnesium (Mg) is 34 times more and that of Calcium (Ca) is 42 times more, but that of Bromine (Br) is about 90 times more.
- Yet the concentration of Sodium chloride (NaCl) in the different water areas is about 77% of the total mineral content whereas it is only about 25-30% in the Dead Sea.

Water surface	Na <sup>+1</sup>	K <sup>+1</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Cl <sup>-1</sup>	Br <sup>1</sup>	HCO <sub>3</sub> <sup>-</sup>
Atlantic Ocean	10.770	0.40	0.412	1.300	19.350	0.06	0.04
Black Sea	5.110	0.40	0.250	0.650	9.630	-	0.08
Dead Sea	39.160	7.96	17.130	43.350	22.750	5.36	0.08
River Jordan	0.224	0.03	0.129	0.095	0.762	0.00	0.18

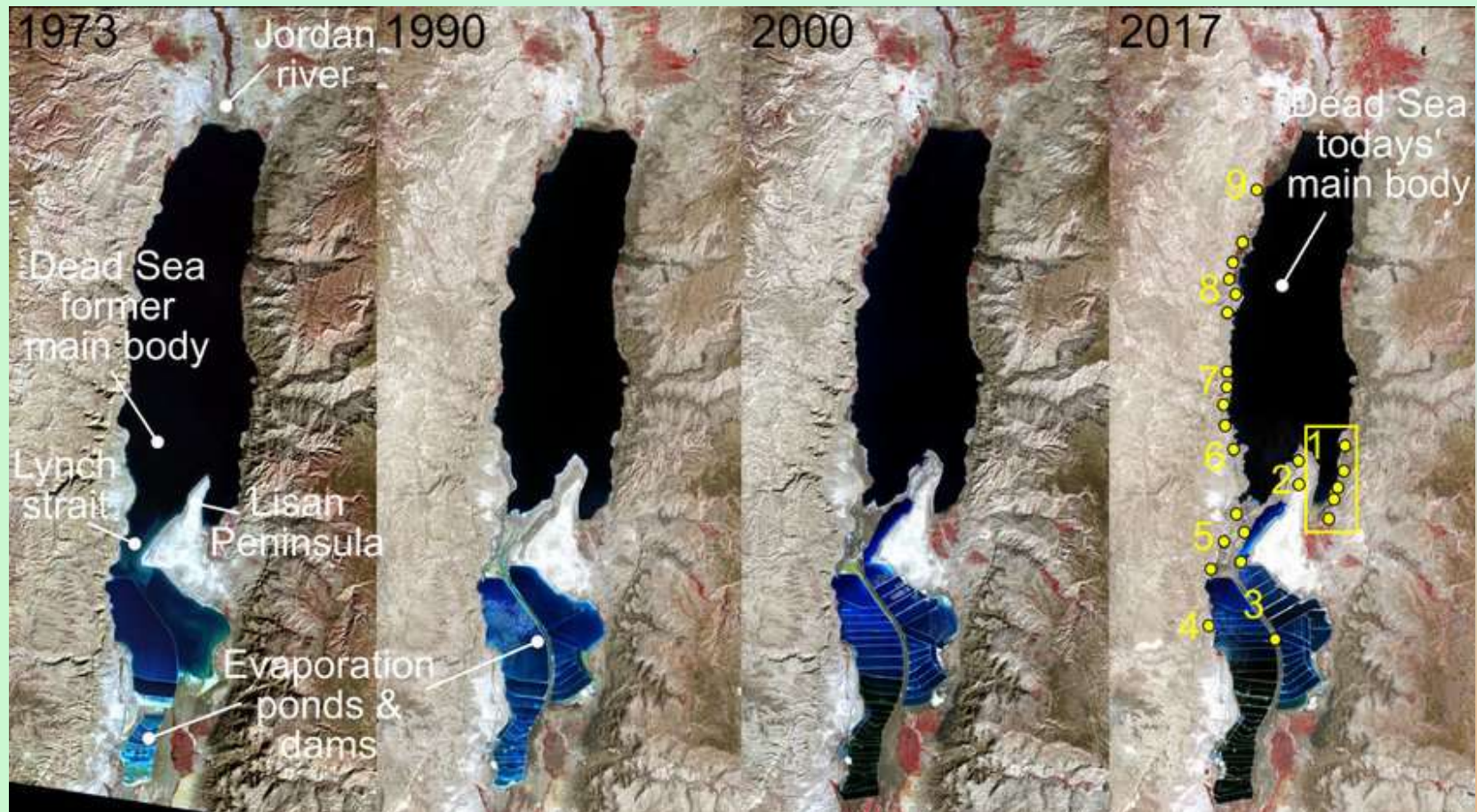


## TYPICAL DEAD SEA SALT MINERAL CONTENT

	g/liter
Mg <sup>+2</sup>	33 - 41
Ca <sup>+2</sup>	14 - 17
Na <sup>+2</sup>	32 - 40
Ratio of Na/K	5.5 in Dead sea 60 in the oceans
K <sup>+</sup>	6 - 7.5
Cl <sup>-</sup>	173 - 217
Br <sup>-</sup>	4 - 5
SO <sub>4</sub> <sup>-2</sup>	0.65 - 0.8
Density	1.18 - 1.215



## SATELLITE IMAGES OF THE DEAD SEA



## DEAD SEA RESOURCES

	1975	2019
Total area (Km <sup>2</sup> )	1000	605
Total volume (Km <sup>3</sup> )	150	114
Max depth (m)	350	304
Evaporation rate (T/y)	1.7×10 <sup>9</sup> (1% of V)	
Water source	65% Jordan river	0 - 10%
	20% local rivers	50%
	5% rain	10%
	10% flooding	30%





## DEAD SEA SINKHOLES

- The Dead Sea region has roughly 7000 sinkholes and will have double that number, 14,000, in the next few years.
- The sinkholes in the Dead Sea region have been proven to be the result of man-made dams and industrial activity which decreased the water volume in the Jordan River and, as a result, the volume of water currently in the Dead Sea.



## TYPICAL DEAD SEA SALT MINERAL CONTENT

- When compared with other oceans and seas, the DS is more abundant in many elements, including chloride (212.4 g/l), magnesium (40.65 g/l), sodium (39.15 g/l), calcium (16.86 g/l), potassium (7.26 g/l), and bromide (5.12 g/l). Conversely, it has a lower concentration of sulfate (0.47 g/l), and bicarbonate (0.22 g/l).
- Heavy metals comprise a well-known group of inorganic chemical hazards. Furthermore, it was proved that chromium (Cr), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), mercury (Hg), nickel (Ni), and arsenic (As) are usually found at contaminated areas.





# CLIMATE CONDITIONS AROUND THE DEAD SEA

Climate data for Dead Sea (390 m below sea level)												
Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Record high °C (°F)	26.4 (79.5)	30.4 (86.7)	33.8 (92.8)	42.5 (108.5)	45.0 (113.0)	46.4 (115.5)	47.0 (116.6)	44.5 (112.1)	43.6 (110.5)	40.0 (104.0)	35.0 (95.0)	28.5 (83.3)
Average high °C (°F)	20.5 (68.9)	21.7 (71.1)	24.8 (76.6)	29.9 (85.8)	34.1 (93.4)	37.6 (99.7)	39.7 (103.5)	39.0 (102.2)	36.5 (97.7)	32.4 (90.3)	26.9 (80.4)	21.7 (71.1)
Daily mean °C (°F)	16.6 (61.9)	17.7 (63.9)	20.8 (69.4)	25.4 (77.7)	29.4 (84.9)	32.6 (90.7)	34.7 (94.5)	34.5 (94.1)	32.4 (90.3)	28.6 (83.5)	23.1 (73.6)	17.9 (64.2)
Average low °C (°F)	12.7 (54.9)	13.7 (56.7)	16.7 (62.1)	20.9 (69.6)	24.7 (76.5)	27.6 (81.7)	29.6 (85.3)	29.9 (85.8)	28.3 (82.9)	24.7 (76.5)	19.3 (66.7)	14.1 (57.4)
Record low °C (°F)	5.4 (41.7)	6.0 (42.8)	8.0 (46.4)	11.5 (52.7)	19.0 (66.2)	23.0 (73.4)	26.0 (78.8)	26.8 (80.2)	24.2 (75.6)	17.0 (62.6)	9.8 (49.6)	6.0 (42.8)
Average precipitation mm (inches)	7.8 (0.31)	9.0 (0.35)	7.6 (0.30)	4.3 (0.17)	0.2 (0.01)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	1.2 (0.05)	3.5 (0.14)	8.3 (0.33)
Average precipitation days	3.3	3.5	2.5	1.3	0.2	0.0	0.0	0.0	0.0	0.4	1.6	2.8
Average relative humidity (%)	41	38	33	27	24	23	24	27	31	33	36	41



## CLIMATE CONDITIONS AROUND THE DEAD SEA

- Air temperature in the Dead Sea district reaches 29 - 39 °C in summer and it exceeds 40 °C in certain years.
- Therefore, the water is exposed to an intensive evaporation process, which leads to the existence of salty sediments on shores similar in different shapes to coral ones.
- The average temperature over the period from November to April is 22 - 29 °C and over the period from May to September and October is 32 - 37 °C and in June July is 38 - 39 °C.
- The humidity level is low 27% in summer and 38% in winter.
- The atmospheric pressure is 800 - 810 mm Hg; while the oxygen concentration in the atmosphere of the Dead Sea is 15% more than of the Atlantic Ocean.



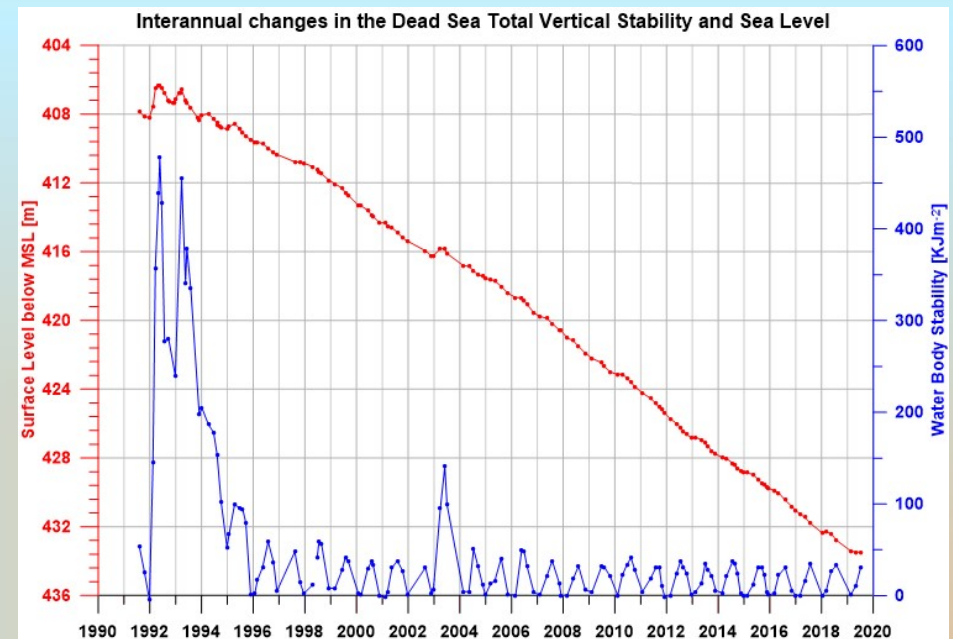
## DEAD SEA DISAPPEARANCE

- Nowadays, the Dead Sea is intensively exploited.
- In addition to the many medical and tourist facilities on its shores there is a group of productive industries to produce minerals, which are used in chemical fertilizers industry.
- Such an intensive exploitation of water and minerals of the Dead Sea began to affect the existence of the Dead Sea itself.
- The river of Jordan after being diverted, it does not provide enough water to the Dead Sea.
- The low level of rainfall and the construction of dams add more to the problem of water evaporation.



## DEAD SEA DISAPPEARANCE

- If the decrease on sea level continues, this decrease is expected to increase within few coming years due to the environmental unbalance around the Dead Sea because of the mentioned reasons.
- The step-by-step disappearance of the Dead Sea will lead to an environmental catastrophe affecting the region around and no one will be able to predict the negative effects of such a catastrophe.



## DEAD SEA FACTORIES

- The Dead Sea brine typically contains 11.5 g/l KCl.
- The concentration of other salts is  $\text{MgCl}_2$  130 g/l NaCl 87g/l  $\text{CaCl}_2$  37 g/l MgBr 5 g/l.
- This concentration encouraged investors to establish different factories on both sides.
- These factories are trying to increase the KCl productive capacity annually. In recent years, new industries such as the Magnesium producing industry, an expensive substance, and the Bromine have been inaugurated.
- These industries utilize solar evaporation systems to extract salts whereby seawater is pumped to special salt ponds that occupy large areas of land extending to more than 120 km<sup>2</sup> only on the Jordanian side.

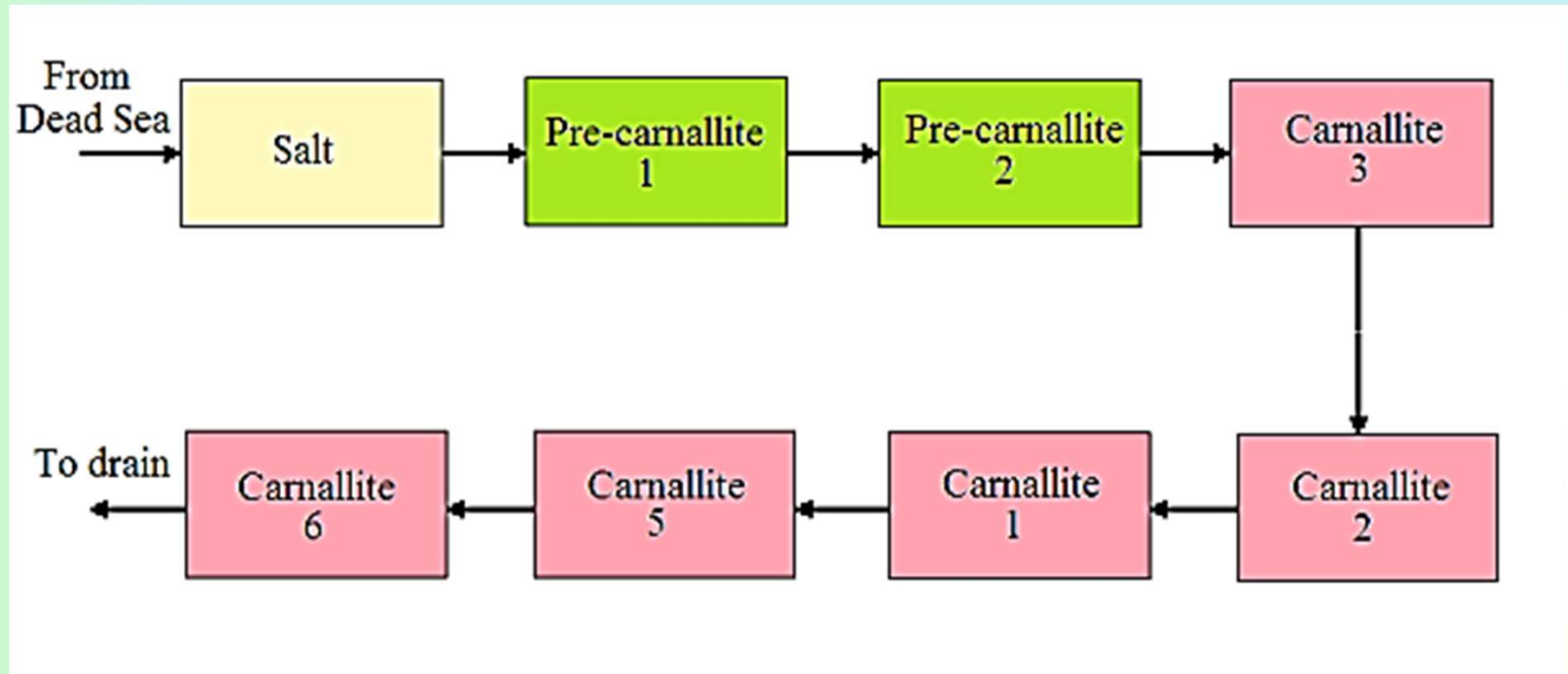


- In Jordan to produce KCl from dead sea brine, the first step is to concentrate the Dead Sea brine naturally in large ponds, there are 3 types of ponds: salt, precarnallite, and carnallite ponds.
- These ponds are working in series, NaCl is precipitated in the first step then the solution is transported to other ponds where the carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), which is the key product is crystallized and precipitated, after which the remaining solution is returned to the sea.





## DEAD SEA EVAPORATION PONDS



## SALT PONDS

- At 30°C sodium chloride has a solubility of approximately 36.09 g/100 g H<sub>2</sub>O
- Maximum solubility of potassium chloride, KCl, at 30 °C is 37.2 g/100 g H<sub>2</sub>O.
- At 40 °C the solubilities are 36.37 and 40.1 g/100 g H<sub>2</sub>O, respectively.
- As temperature increases, its solubility increases as well.
- Dead sea brine is pumped from the Dead sea to the first NaCl pond.
- There are 4 pumps with a capacity of 4m<sup>3</sup>/sec.
- About 1×10<sup>6</sup> m<sup>3</sup> of Dead Sea brine is pumped to the salt pond.
- There are 2 pipelines with a diameter of 1.6 m and a length of 900 m.





## SALT PONDS

- These 2 pipelines deliver the Dead Sea brine to a 10.6 km canal which is connected to the salt pond at its end.
- Large solar ponds, in series (100 km<sup>2</sup> total area) serve to evaporate water and settle NaCl.
- Dead Sea brine enters the salt pond with a percentage of water of 74.7 %.
- As a result of water evaporation, the percentage of water reduces to 70%.
- The level of the brine in the salt pond is kept approximately 1 m.
- As a result of the continuous evaporation more and more NaCl will be precipitated and so, it is necessary to increase the height of the pond's walls after years.



## PRE-CARNALLITE PONDS

- There are 2 pre-carnallite ponds, the first one has an area of 4.5 km<sup>2</sup> and the second has an area of 2.5 km<sup>2</sup>.
- The main purpose of the first one is the continuation of concentrating the brine and precipitation of NaCl.
- The brine flows from the first to the second pond by gravity, where the percentage of water within the brine reduced further to 68%.
- At this percentage, the carnallite will start to precipitate.



## PRE-CARNALLITE PONDS

- The percentage of the KCl will increased from 1.1% for Dead Sea brine to 1.8% at the second pre-carnallite pond.
- The carnallite point is an important point and needs more attention and control.
- Samples should be taken on a daily basis from the second pre-carnallite pond to check if the brine reaches the carnallite point.
- It will not be profitable if carnallite is allowed to precipitate in this pond.



## CARNALLITE PONDS

- There are 5 carnallite ponds with an area of 22.5 km<sup>2</sup>.
- The main function of these ponds is to precipitate the carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ).
- As a result of the evaporation process, the carnallite will precipitate and this process will continue till the height of the carnallite reaches 35 to 50 cm.
- After precipitation, the carnallite will be harvested and pumped to the plant.



## CARNALLITE PONDS

- Since the harvesting of the carnallite is carried out using very heavy machines, a solid ground is prepared before the actual operation is started.
- NaCl is used as a mattress for the carnallite ponds with a thickness of 20 to 40 cm.
- The height of the brine in the carnallite ponds is kept at 1 to 2 m.
- The height of the walls in the carnallite ponds remains constant.



## FACTORS AFFECTING THE CARNALLITE PRECIPITATION

1. Wind speed.
2. Temperature.
3. Relative humidity.
  - Increasing the wind speed and the temperature will increase the evaporation rate.
  - In the meantime, increasing the temperature will increase the solubility of the salts specially the carnallite.



## FLOATING-TRACK HARVESTERS

- The harvesters used in the Arab Potash company are specially designed to be used by the company.
- They consist of the following:
  1. The cutting head.
  2. Moving system.
  3. Pumping system.
  4. Control room.
- Length: 26 m, width: 9 m, and weight: 270 Ton









- The precipitated salt is harvested by harvesting machines, which float on the pond's surface.
- The carnallite slurry (20% - 25% solids) is cyclone to reduce the water content and pumped at 30 to 40% solids to the processing plant.
- The carnallite in the slurry contains 85% carnallite and 15% NaCl.
- Some seasonal rainfall in summer leads to diluting the solution in the ponds leading to a change in water solution-crystal phase equilibrium, as well to slow the crystallization process where the formed crystals may begin to dissolve in the solution again.
- The solution may stay for a long period of time in these ponds, which leads to mushroom-type sediments covering the ponds bottom and appearing on the surface.





## KCl PLANT

- The building and construction of the buildings and equipment started in 1980.
- The plant started production on 18/3/1982.
- To produce KCl from the carnallite, the following steps are used:
  - 1- Treatment of carnallite.
  - 2- Treatment of sylvinite.
  - 3- Crystallization of KCl.
  - 4- Drying.
  - 5- Screening.
  - 6- Store and transport.



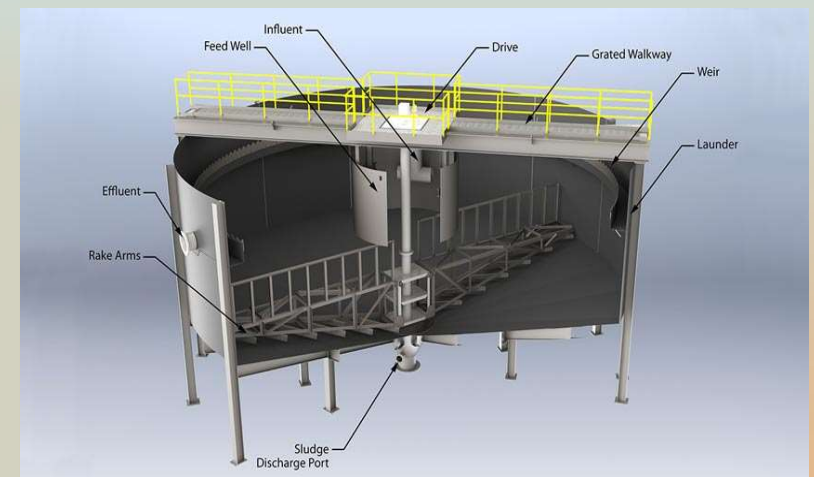
## CARNALLITE TREATMENT

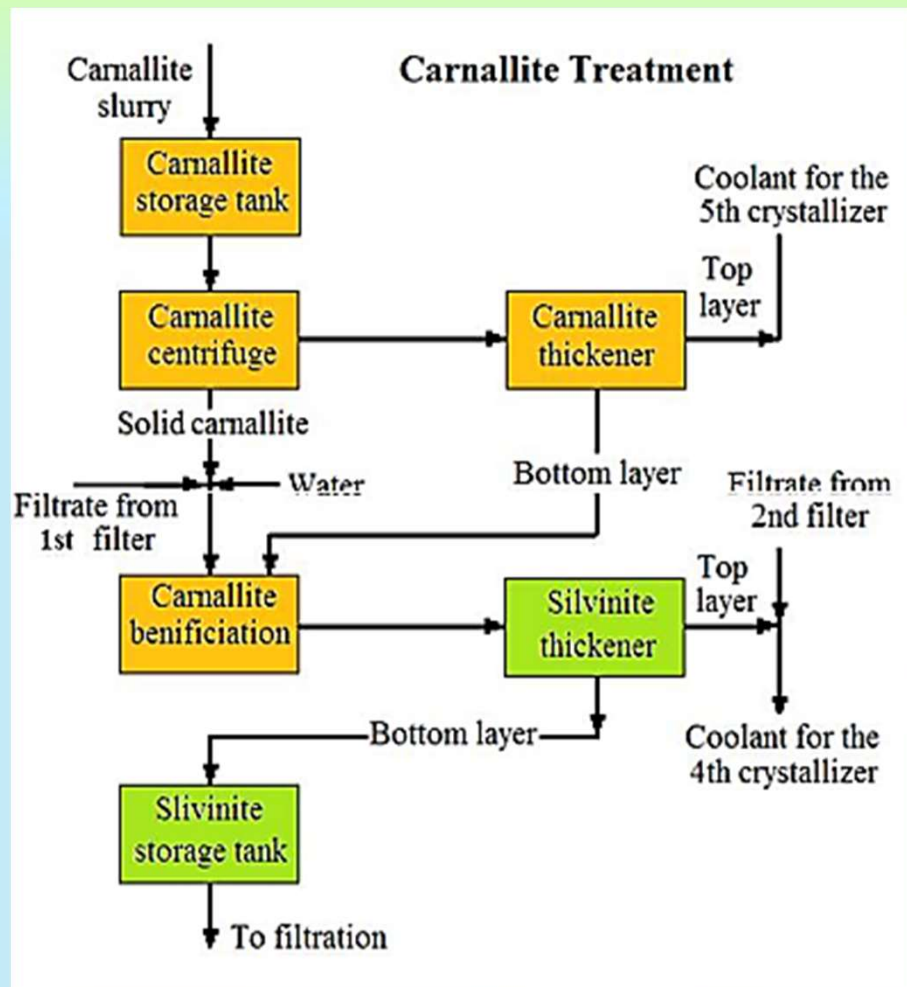
- The pumped carnallite slurry is stored in 3 large storage tanks each with a 5000 m<sup>3</sup> capacity.
- Continuous agitation is required to prevent precipitation of solid materials at the bottom of the storage tank.
- The first step is to separate the solid materials from the liquid which carried out using 11 centrifuges.
- The liquid flows out of these centrifuges is sent to one of the 3 carnallite thickeners.
- The main function of the thickener is to collect any solid materials remain in the liquid after centrifugation.



## CARNALLITE TREATMENT

- The solid materials will be collected at the bottom of the thickener.
- An arm at the bottom of the thickener moves with a continuous slow speed will prevent the solid material from precipitation.
- The collected solid materials from both the centrifuges and the thickeners will be sent to the carnallite beneficiation tanks.







## SYLVINITE TREATMENT

- Fresh water is added to the beneficiation tanks to separate the potassium chloride from magnesium chloride.
- Magnesium chloride will dissolve in addition to small amount of potassium chloride (3 to 4 %). 72.7 g/100 ml water @ 100 °C.
- Most of the potassium chloride remains in its solid phase as well as sodium chloride.
- Potassium chloride and sodium chloride in a solid form known as Sylvinite.



## SYLVINITE TREATMENT

- Sylvinite can be found in nature in some countries and is used as a raw material for potash.
- Fresh water is added with a constant ratio of 425 g/1 kg solid
- Usually, it takes 90 minutes to dissolve the carnallite in the beneficiation tanks.
- The exit from the beneficiation tanks flows to the sylvinite thickeners.
- Two layers are formed in the sylvinite thickener; the bottom layer which contains most of the solid materials and the top layer contains the saturated solution of magnesium chloride.





## SYLVINITE TREATMENT

- The saturated solution ( $\text{MgCl}_2$ ) is sent to the ponds because it contains 3 to 4% KCl.
- The bottom layer which contains 30% sylvinite is pumped to sylvinite storage tank.
- Three steps are carried out for sylvinite treatment:
  1. Filtration.
  2. Hot leaching.
  3. Removal of NaCl.



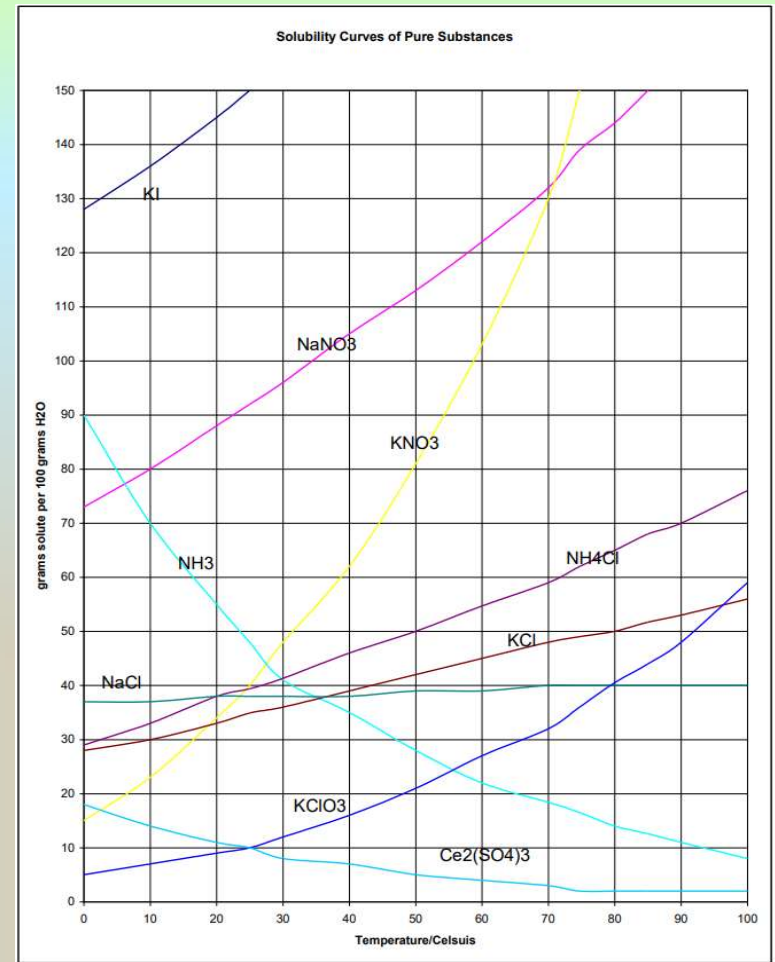
## SYLVINITE FILTRATION

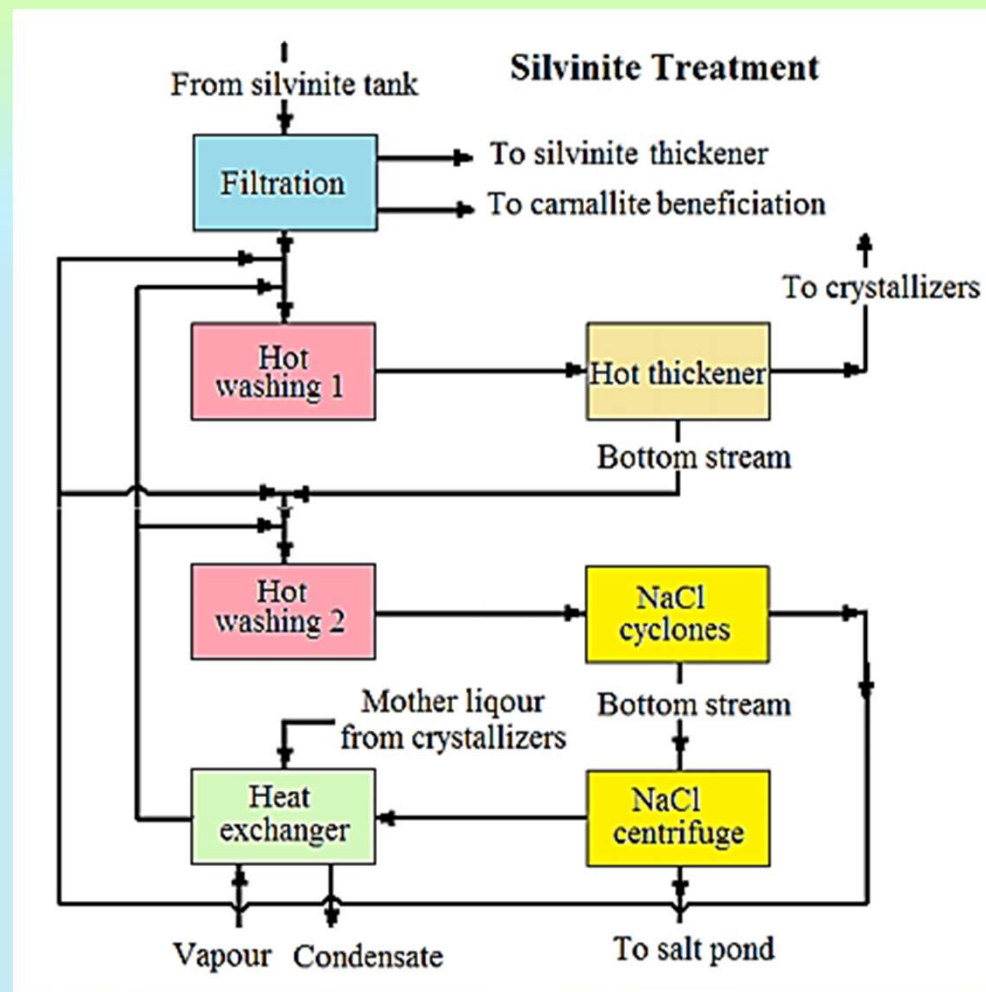
- The sylvinite slurry is pumped from the storage tanks to 2 filtration units.
- These filters are belts made from rubber covered with special cloth and operates under vacuum.
- The filtrate is collected in tanks and used in other processes.
- The cake (sylvinite) which contains 45 – 55 % KCl is transferred to the hot leaching step using belt conveyor.



## HOT LEACHING

- The main purpose of this step is to separate the KCl from NaCl by dissolving the KCl in a saturated solution at 104°C.
- The saturated solution at this temperature will only dissolve KCl while the NaCl remains in its solid phase.
- The process is carried out in two stages, in the first stage and after dissolving the KCl, the solution is sent to the hot thickener where the KCl rich solution is collected in the top layer.



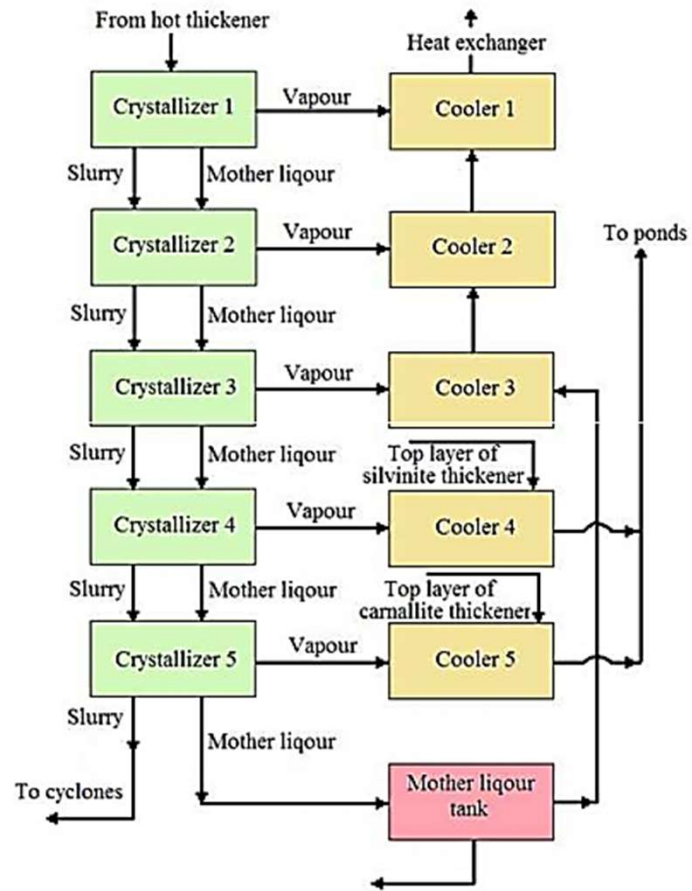


## KCl CRYSTALLIZATION

- The KCl saturated solution is pumped to the crystallizers to crystallize the potassium chloride.
- There are 5 crystallizers work in series.
- There are 2 streams exit from each crystallizer, the first one exit from the bottom of the crystallizer and contains the crystals formed and the second stream exits from the top layer of the slurry which contains not more than 1wt% KCl.
- The KCl crystals formed as a result of cooling the saturated solution.



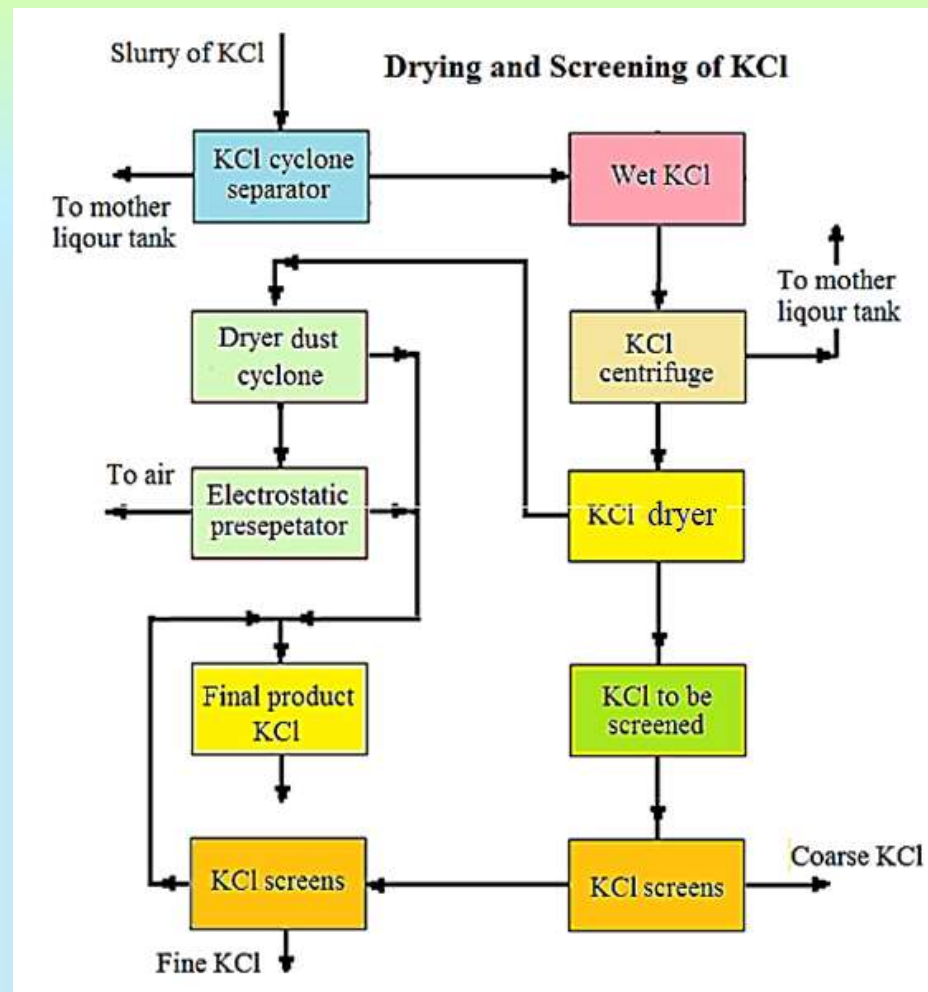
### Crystallization Unit



- It is necessary to keep the amount of water within the crystallizer at a point which will not allow NaCl to crystallize.
- The discharge from the 5th crystallizer contains 15 to 25 % KCl crystals.
- Crystallizer discharge slurry is cycloned to remove part of the liquid present with the KCl crystals.
- 3 centrifuges are used to get rid of most of the liquid before KCl crystals are fed to the rotary dryer using a belt conveyor.
- KCl crystals exit the rotary dryer with at most 0.1% moisture content.
- The dried potassium chloride product passes through screens to be separated into two fractions, standard, and fines, according to the required size specifications.







## BY-PRODUCTS OF KCl INDUSTRY

1. Solid material, sodium chloride (NaCl).

2. Final solution that contains:

$\text{MgCl}_2$ ,  $\text{MgBr}_2$ , and  $\text{CaCl}_2$

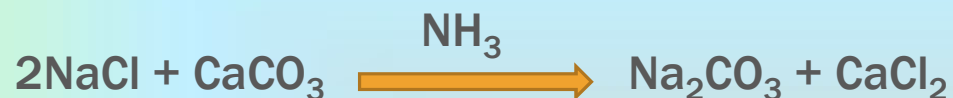
➤ **Future plans to produce:**

1. Bromine: used to produce chemical compounds for industrial and agricultural purposes, calcium bromide and sodium bromide.



## BY-PRODUCTS OF KCl INDUSTRY

2. Sodium carbonate: used mainly in glass industry, papers, water treatment, detergents.



3. Magnesium Oxide: used in thermal bricks industry where this can be used as a lining for furnaces.



4. Sodium hydroxide:



# BENEFICIATION AND PROCESSING OF POTASH ORES

- Four basic beneficiation techniques have been applied in the potash industry:
  1. Flotation
  2. Heavy Media Separation
  3. Electrostatic Separation
  4. Thermal Dissolution Crystallization
- Most potash processing plants practice a combination of beneficiation techniques.



# CRUSHING AND GRINDING

- The first step in the beneficiation of a solid potash ore is to reduce the ore to a size where the potash is liberated from the other ore constituents and can be separated from them.
- A prime consideration in crushing and grinding is that a minimum number of fines be produced.
- Any fines produced by grinding must be processed by more costly methods.

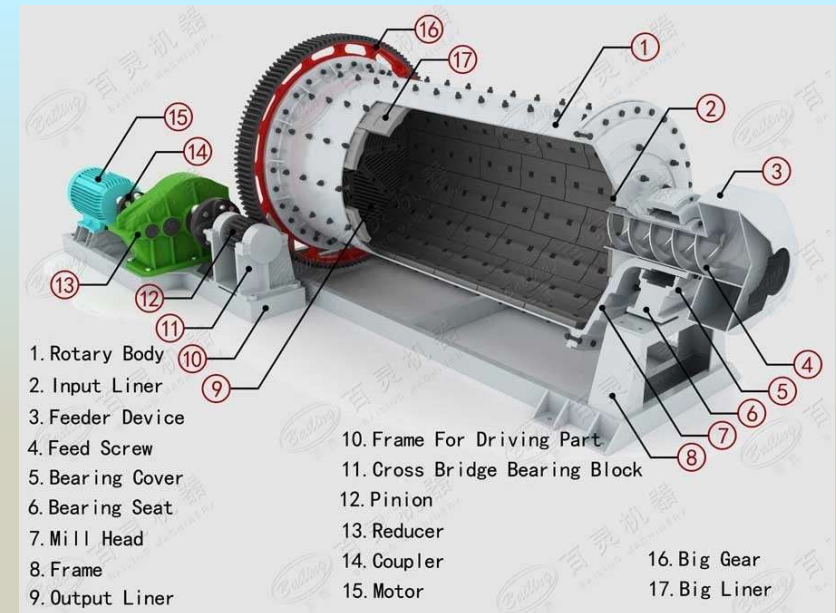


Client: Metso  
www.metso.com  
Photo: Peter James Hume  
www.miningphotos.com



## CRUSHING AND GRINDING

- Larger and closely sized product is more valuable, and less energy is spent on grinding.
- Another prime consideration is that both the capital costs involved in establishing the operation and the production costs be minimized.
- To accomplish these goals, processing usually begins with various size reduction equipment and coarse (0.6 - 1.2 cm) screens working in closed circuit.



## DESLIMING

- Fine particles, both ore minerals and insoluble, are always removed to the greatest extent possible before the potash separation step.
- In flotation, fine particles with high surface areas tend to adsorb excessive quantities of flotation reagents.
- Excessive amounts of fines can significantly raise reagent costs and cause contamination of the product.
- Most plants deslime by using one or more stages of cyclones and hydro separators.

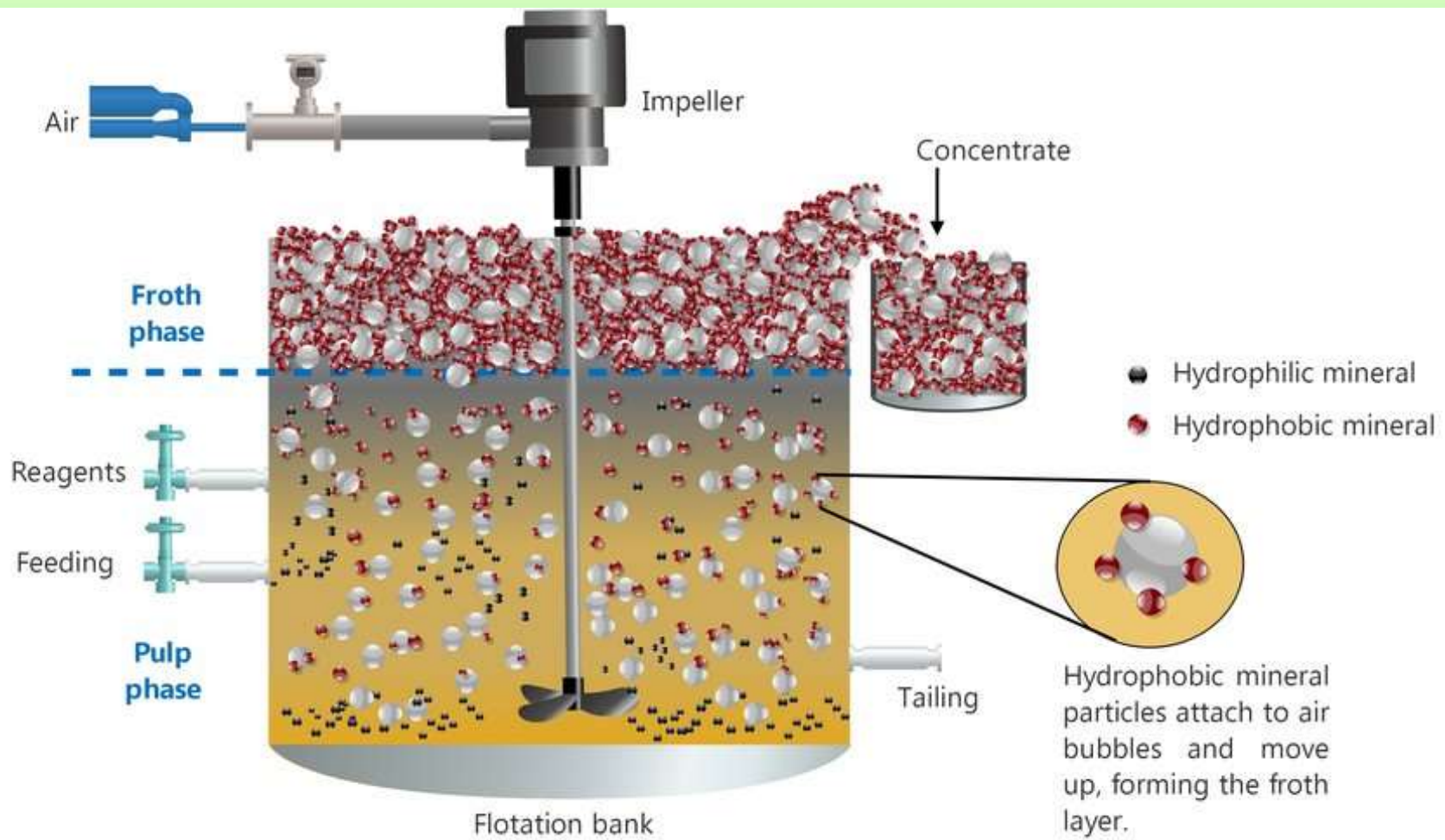


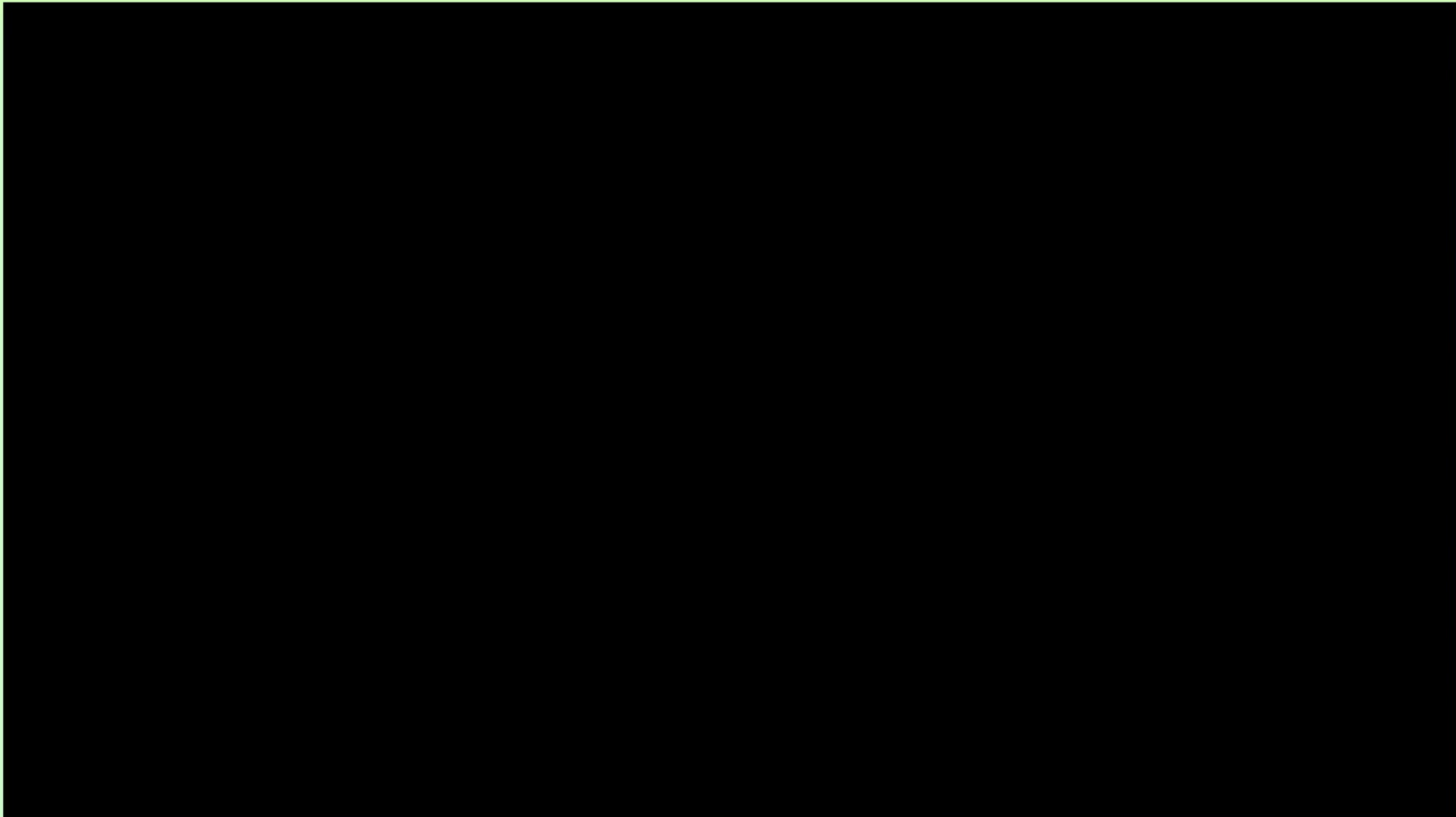


# FLOTATION

- Flotation is a selective beneficiation process that utilizes the differences in surface properties of various minerals.
- By conditioning ores with specific reagents, selected minerals can be induced to become either hydrophobic (water repellent) or hydrophilic (water attracting) in solutions.
- If a solution is then agitated and aerated by introducing air bubbles, mineral particles that are hydrophobic will attach themselves to the air bubbles and float to the surface where they can be removed.







## FLOTATION

- This type of flotation, where the valuable minerals are removed in the froth, is termed direct flotation and is the most common flotation technique employed in the potash industry.
- The most important reagents used in flotation are collectors.
- These collectors are mostly straight chain aliphatic primary amines derived from natural fats and oils that are neutralized by acetic or hydrochloric acid before use.
- Another category of reagents that is commonly used is known as frothier.



## HEAVY MEDIA SEPARATION

- The process utilizes the difference in specific gravity of sylvite (KCl) and halite (NaCl).
- Halite is the denser mineral (specific gravity 2.13 versus 1.9 for sylvite).
- In a liquid of intermediate specific gravity, halite will sink and sylvite will float.
- Commercial heavy media operations use a very finely divided weighting agent, typically ferrosilicon or magnetite of minus 200-mesh, which is slurred to create an artificial heavy medium at the specific gravity required for separation.
- After separation, the magnetite or ferrosilicon is recovered by magnetic separation and recirculated to the system.





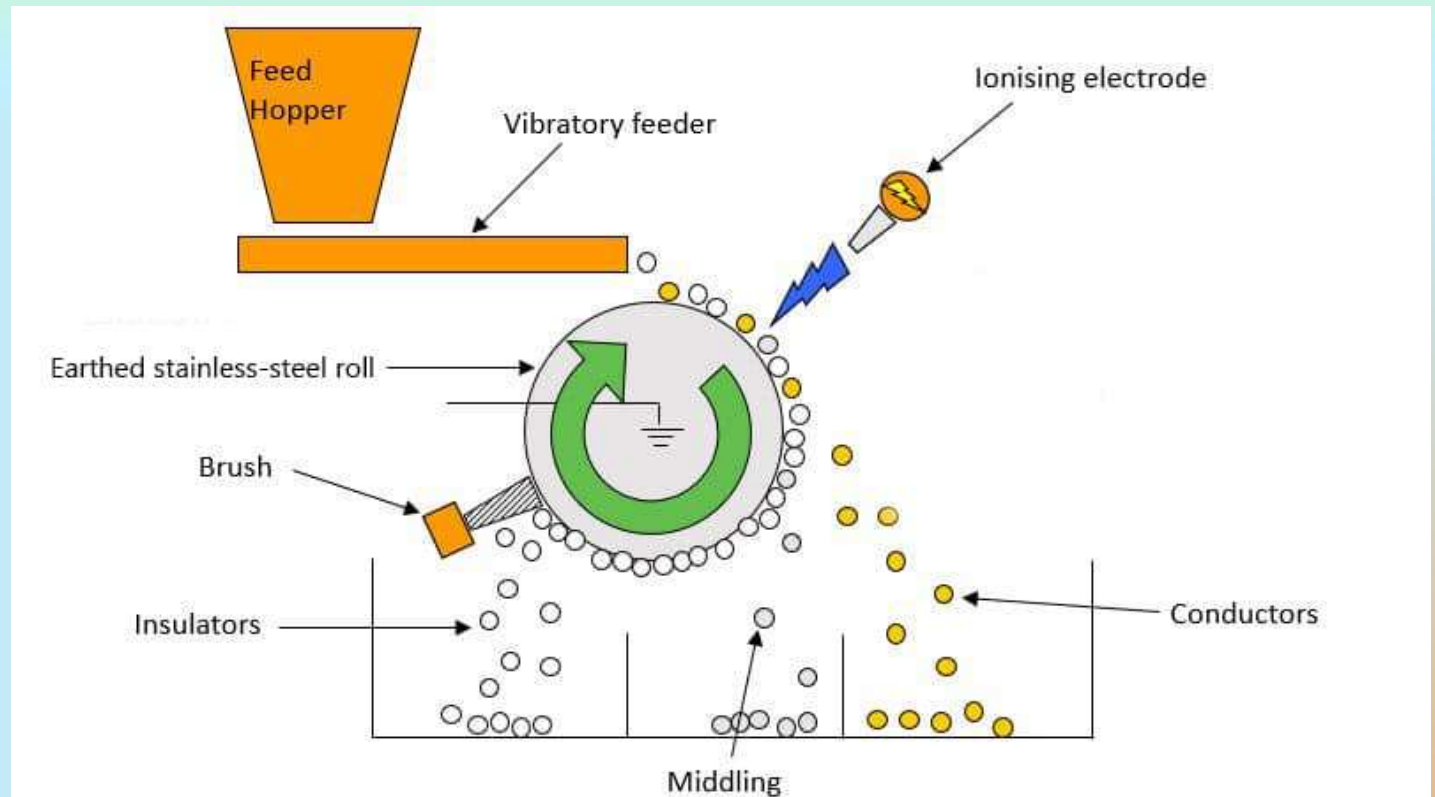
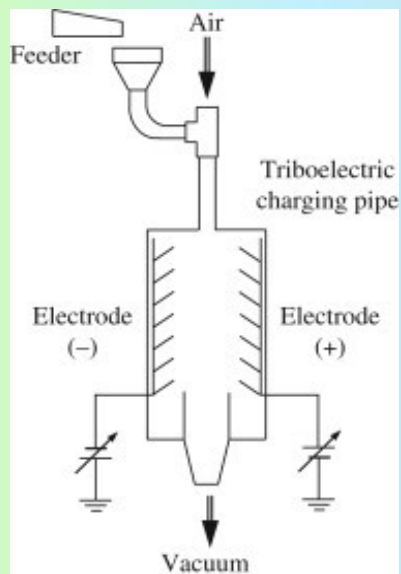
## ELECTROSTATIC SEPARATION

- Electrostatic separation is a dry technique in which a mixture of minerals may be differentiated according to their electrical conductivity.
- For potash minerals, which are not naturally conductive, the separation must be preceded by a conditioning step that induces the minerals to carry electrostatic charges of different magnitudes and different polarities.
- For potash, fractional or triboelectric charging is used; the charges are induced through repeated physical contact between the different minerals.





# ELECTROSTATIC SEPARATION



## ELECTROSTATIC SEPARATION

- In Germany, the potash ore is ground to between minus 1 and 2 mm.
- The ground ore is conditioned with one or more reagents, preferably aromatic and aliphatic monocarboxylic acids.
- The mixture is then heated in a fluidized bed, and the relative humidity is adjusted to enhance charging of the particles.
- The ore is then fed into the electrostatic separator, to yield three fractions: product, residue, and middling.
- The middling, after further grinding, are recycled to the conditioning stage.





## THERMAL DISSOLUTION-CRYSTALLIZATION

- Thermal dissolution-crystallization is possible because potassium chloride is much more soluble in hot water than in cold and sodium chloride is only slightly more soluble at 100 °C than at 20 °C.
- In saturated solutions containing both salts, sodium chloride is actually less soluble at higher temperatures.
- When a brine that is saturated with both salts at 20 °C is heated to 100 °C, it is capable of dissolving substantial amounts of KCl but not NaCl.



