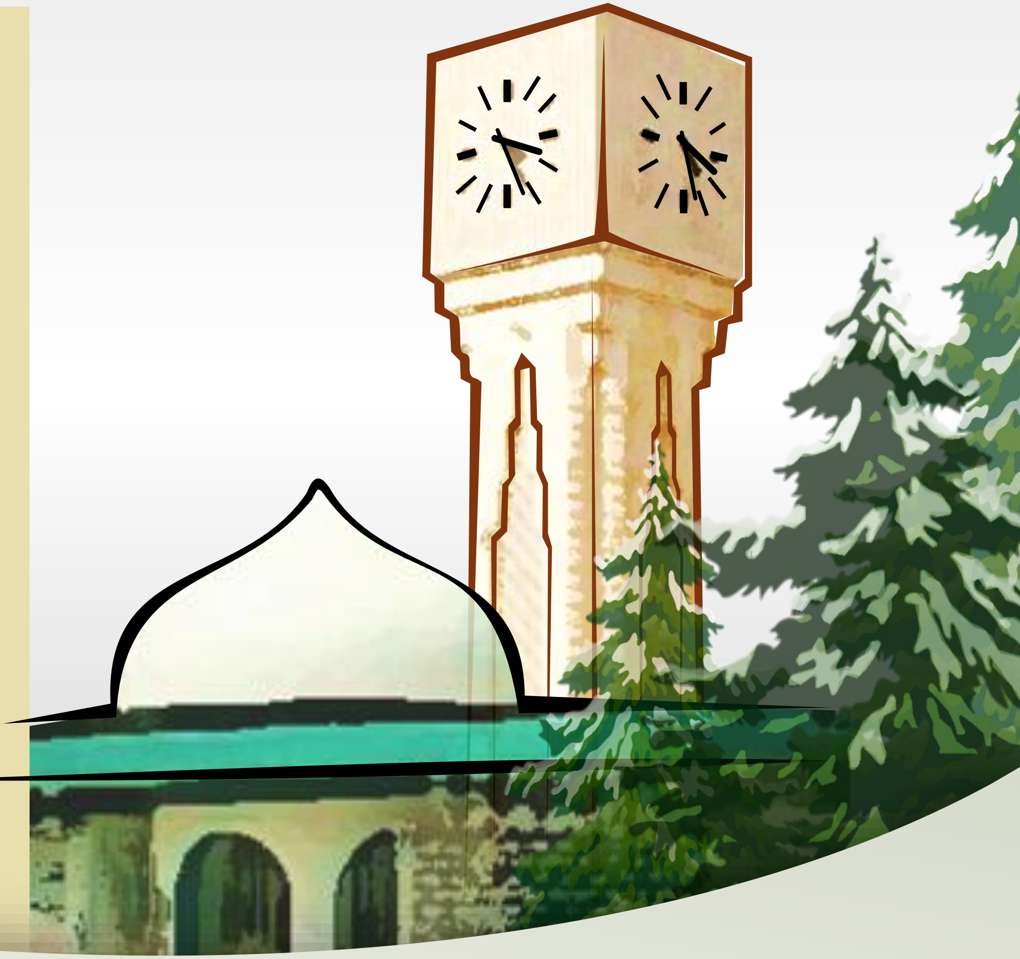
Multiple References are used in this course

CHE 0915481

Chemical Process Technology

Fall 2025

Dr. Hatem Alsyouri	Week 3



The University of Jordan

Chemical Engineering Department

Week 3

Process (1): Potash and Dead Sea Products Industry

Topics	**Lecture 1**	**Industry Overview** **Raw Materials and Feedstock**
	Lecture 2	**Potash Production Process** **Operations** **Processing Plants** **Hot Leach Process**
Learning Outcomes		

Lecture 1

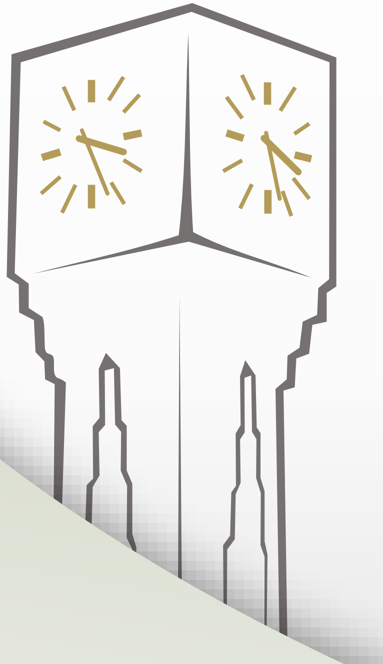
Industry Overview
Raw Materials and Feedstock

Lecture 1

Process (1): Potash and Dead Sea Products Industry

Topics	1. Industry Overview 2. Raw Materials and Feedstock
Learning Outcomes	

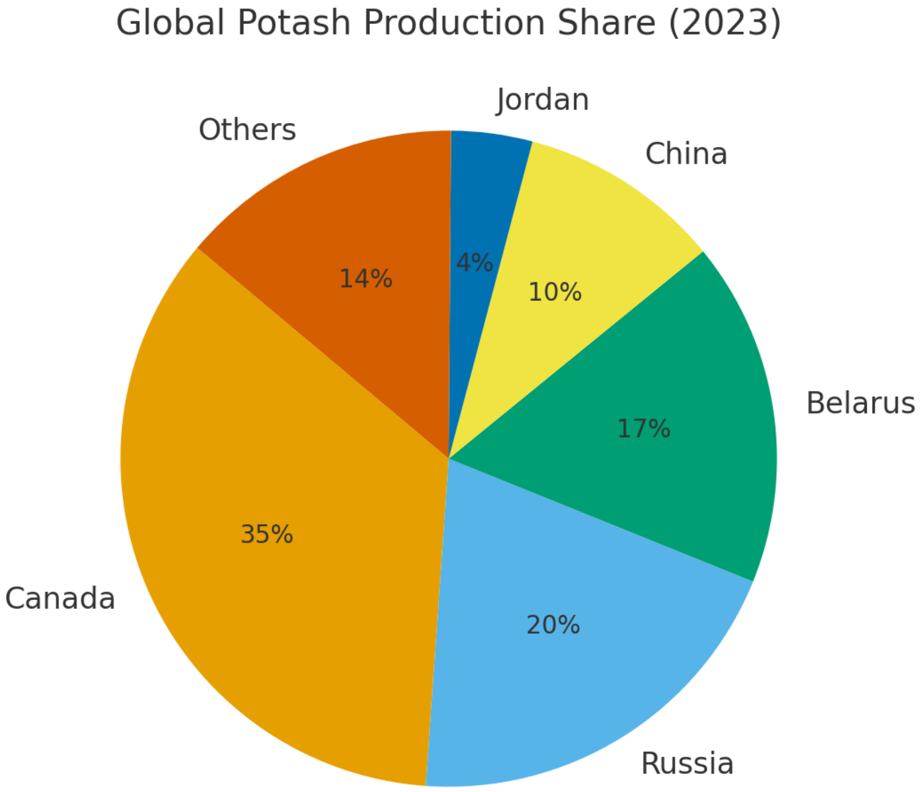
Reacp	1. We discussed course project assignment. 2. Described requirements and evaluation rubrics 3. Defined poster content and provided different samples of posters
Announcements	



Industry Overview

Potash

1. Potash refers to potassium-bearing salts, primarily potassium chloride (KCl).
2. It is a vital source of potassium—one of the three essential plant nutrients (N, P, K).
3. Used mainly as fertilizer to improve crop yield, water retention, and stress resistance.
4. Produced from either ***mined ores*** or ***natural brines***, such as those in the Dead Sea.
5. Jordan accounts for about 4% of global potash production in 2023, from Dead Sea mineral resources. The other major producers are Canada (35%), Russia (20%), and Belarus (17%),



Origin of the name “Potash”

The term '**potash**' is derived from 'pot ash', after the old method of extracting potassium carbonate (K_2CO_3), which consisted of leaching wood ashes and evaporating the resulting solution, leaving a white residue called 'pot ash'.

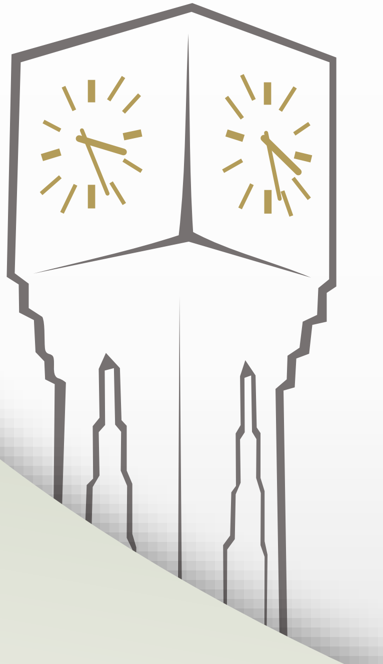
How does potash occur in nature?

1. Potassium is the seventh most common element on earth, which can be found in heavy soils and sea water, which typically contains 390 mg/l K.
2. Large potash-bearing rock deposits occur in many regions of the world deriving from the minerals in ancient seas which dried up millions of years ago.
3. Potash is mined from these deposits in most potash producing countries.
4. The **Dead Sea** is also a natural reservoir of many minerals, including potash, which is found in high enough concentrations for commercial production.

Industry Overview

1. Main producer: **Arab Potash Company (APC)** – established 1956, production started 1982.
2. Production capacity: ~2.6 million tonnes/year of Muriate of Potash (MOP, ≈60% K_2O). MOP is the most common potassium fertilizer used worldwide.
3. Export share: Potash represents around 10% of Jordan’s total exports, shipped to >30 countries (India, China, Indonesia).
4. Location: Southern shore of the Dead Sea, Safi region (110 km south of Amman).
5. Production method: Solar evaporation of Dead Sea brine — unique brine-based potash route vs. rock mining (Canada, Russia).
6. By-products: Magnesium chloride, bromine, and sodium chloride (salt).

- The Dead Sea appears as the large, deep-blue water body in the upper image.
- APC evaporation ponds lie at its southern end, divided into large, geometric basins.
- The distinct colors (blue, green, orange, white) show different salt-concentration stages and microbial activity.
- These ponds use solar energy to concentrate brine and precipitate salts sequentially.
- Causes sequential concentration and selective precipitation of various salts based on their differing solubilities as water evaporates.
- The APC Industrial Complex refines the salts, converting them into final products like potash via chemical processing and finishing operations



Raw Materials and Feedstock

The Dead Sea as Feedstock Source

1. The Dead Sea is the saltiest natural water body on Earth, making it an exceptional source of industrial minerals.
2. Acts as a natural feedstock for several industries producing: Potash (KCl), Bromine (Br_2), Magnesium chloride ($MgCl_2$), Industrial salts ($NaCl$, $CaCl_2$)
3. The unique ionic composition of its brine enables sequential salt precipitation during solar evaporation ($CaSO_4 \cdot 2H_2O \rightarrow NaCl \rightarrow KCl \cdot MgCl_2 \cdot 6H_2O$).
4. Product interconnectivity: The potash mother liquor serves as feedstock for bromine extraction.
5. Provides a renewable, sustainable resource, replenished through controlled brine circulation.

Brine
محلول ملحي

Mother Liquor:
The liquid that remains after crystallization, containing dissolved salts and impurities not yet precipitated.

Key Salts from Evaporation Stages

1. During progressive pond evaporation, three major salts crystallize in sequence from the brine: Gypsum, Halite, and Carnallite.
2. **Gypsum** ($CaSO_4 \cdot 2H_2O$) – First salt to form as water begins to evaporate.
3. **Halite** (NaCl) – Precipitates next after gypsum; most calcium already removed.
4. **Carnallite** ($KCl \cdot MgCl_2 \cdot 6H_2O$) – Forms in the final, most concentrated brine stage. Carnallite Serves as the main feedstock for potash (KCl) production.
5. While carnallite is a potassium source, the final stage often focuses on recovering pure potash (KCl) through further processing or precipitation from the last, highly concentrated brine (often called bitterns), yielding the final salt products.

Dead Sea Brine Composition

1. Dead Sea brine refers to the highly concentrated salt solution (saline water) that makes up the Dead Sea.
2. This brine is an extremely concentrated saline solution (TDS ≈ 340 g/L, about 10 times saltier than ocean water).
3. Density: ≈ 1.24 g/cm³ (due to extreme salinity) enabling solar evaporation for mineral recovery.
4. Major ionic composition (g/L): Mg^{2+}: 45 Na^{+}: 36 Ca^{2+}: 17 K^{+}: 7 Cl^{-}: 220 Br^{-}: 5
5. The Dead Sea brine is exceptionally rich in Mg^{2+}, K^{+}, and Br^{-}, making it a valuable source for potash, bromine, and magnesium-based products.
6. This composition drives sequential salt precipitation and defines the process design of evaporation ponds.

Importance of High Density in Dead Sea Brine

1. The Dead Sea brine is extremely dense due to high concentrations of Mg^{2+}, Na^+, K^+, and Cl^- ions — much greater than pure water (1.00 g/mL).
2. **Buoyancy Effect**: According to Archimedes' Principle, a denser fluid exerts a stronger buoyant force, allowing objects and people to float effortlessly on the surface.
3. **Industrial Significance**:
   - **Boosts Efficiency**: High density improves phase separation by enhancing sedimentation and solid–liquid separation.
   - **Ensures Quality Control**: Supports stable brine layering, which is essential for controlled crystallization and the targeted extraction of potash precursor salts.

Industrial Importance of Dead Sea Brine

Dead Sea brine is the raw material (“feedstock”) used by industries such as:

1. Arab Potash Company (APC)

→ Produces potash (KCl) and industrial salts (NaCl, $CaCl_2$) through solar evaporation and refining of brine-derived minerals.

2. Jordan Bromine Company (JBC)

→ Extracts bromine (Br_2) and manufactures bromine-based chemicals (flame retardants, pharmaceuticals, and industrial additives).

3. Other facilities

→ Recover magnesium chloride ($MgCl_2$) and produce industrial and therapeutic products such as:

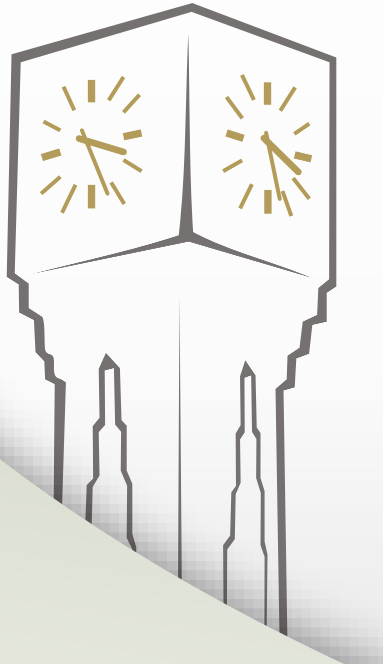
- Cosmetics, mineral salts, and health treatments derived from Dead Sea minerals.
- By-product utilization promotes zero-waste, circular processing between potash and bromine industries.

END.

Lecture 2

Potash Production Process Operations
Processing Plants
Hot Leach Process

Reacp	1. We discussed
Announcements	1. Provide proposed project ideas in the form of a proposal (1 page summary). Submission will be on Moodle ON week 4 (due on Monday 27 Oct 2025). 2. You can submit more than 1 idea (1 page per each idea) but only 1 idea will be selected 3. Project ideas will be discussed 2nd lecture of week 4 (Tue 28 Oct 205)



Potash Production Process

Potash Production Process

Arab Potash Company (APC) has the capacity to produce an approximate total of 2.6 million tons per year of potash via its plants in Jordan:

1. The Hot Leach Plant (HLP).
2. The Cold Crystallization Plant (CCP I).
3. The Industrial Potash Plant (IPP).
4. The Cold Crystallization Plant (CCP II).

Operation

- Arab Potash Company (APC) The site of Arab Potash Company (APC) is located 110 kilometers south of Amman and 200 kilometers north of Aqaba.
- The site is basically a Solar Evaporation Ponds System of an area of 112 km^2 and processing plants.
- APC produces four grades of potash:
  1. **Standard grade** – typical agricultural potash used in fertilizers.
  2. **Fine grade** – smaller particle size, used in applications requiring high solubility.
  3. **Granular grade** – larger, compacted particles suitable for bulk handling and uniform fertilizer blending.
  4. **Industrial grade** – higher purity potash for chemical and industrial uses (e.g., glass, ceramics, and manufacturing of potassium hydroxide).

Process Flow Diagram (PFD): Potash from Dead Sea Brine

1. Brine pumping and pre-concentration in solar evaporation ponds.
2. Sequential precipitation: gypsum → halite → carnallite.
3. Harvesting of carnallite slurry ($KCl \cdot MgCl_2 \cdot 6H_2O$).
4. Refining via Hot Leach Process (HLP) or Cold Crystallization Process (CCP).
5. Crystallization and separation to obtain pure KCl product.
6. Mother liquor recycled for bromine and magnesium recovery.

Solar Evaporation Ponds

1. Dead sea brine is pumped to solar ponds at the Dead Sea Pumping Station, and an initial concentration process is developed.
2. The solids in the brine precipitate to form salts in the ponds.

Operations

- **Solar Ponds**: The process begins at the Brine Intake pumping station where four intake pumps with a capacity of approximately 20 m^3 per second deliver 250 - 300 million tons per year of Dead Sea water.

- As evaporation proceeds, salts crystallize as a mixture of Carnallite ($KCl.MgCl_2.6H_2O$) and NaCl. This is the raw material for producing potash

- This bed is harvested as a slurry from beneath the brine and delivered to booster pumps on the dikes and then to the refinery through floating pipes.

الحواجز Dikes
السدود أو الحواجز الترابية
المرتفعة التي تفصل بين
الأحواض المختلفة في نظام
التبخير الشمسي.
غالبًا ما تُثبَّت المضخات على
هذه الحواجز بين الأحواض.

Operations

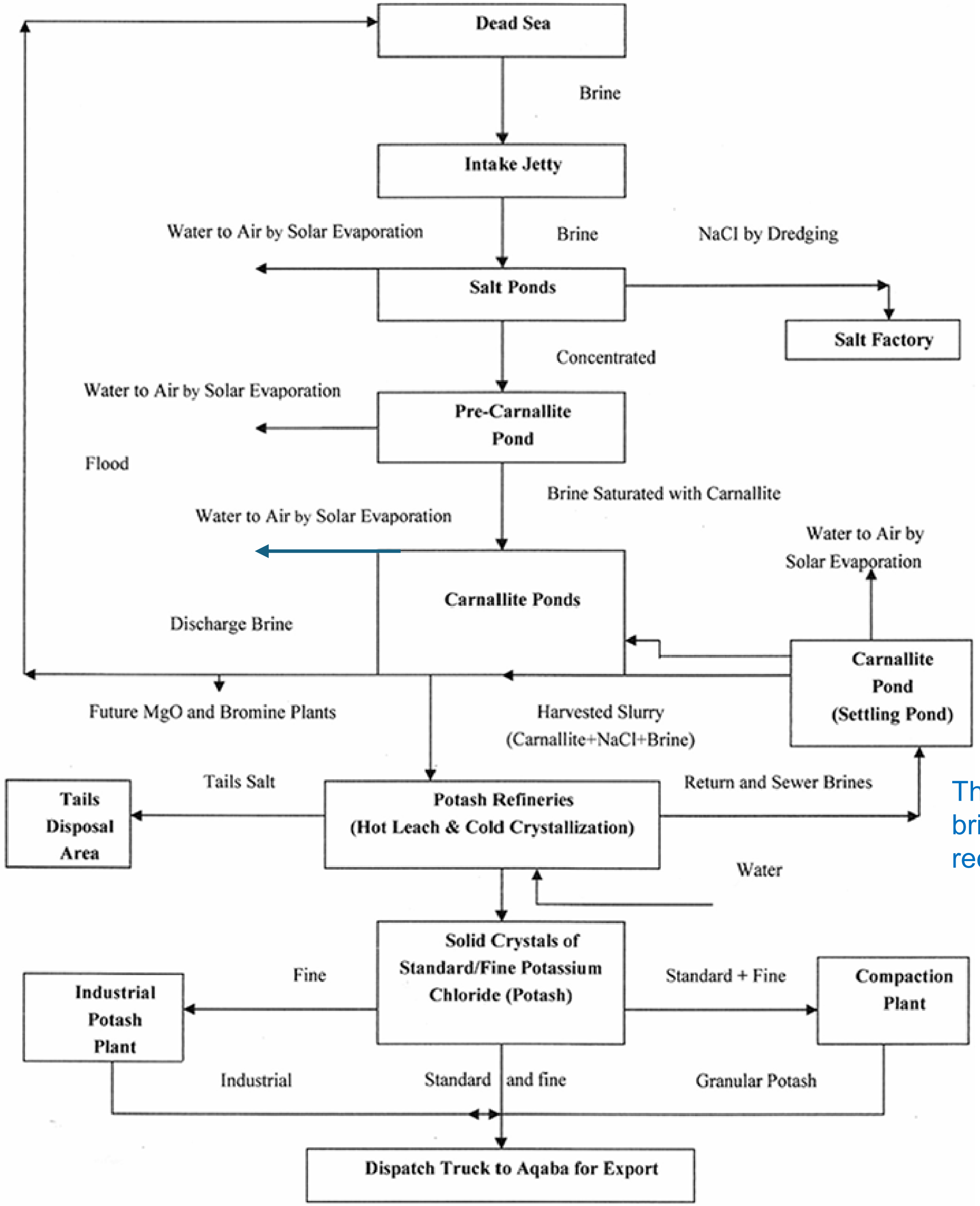
Carnallite harvester

Floating pipes

Processing Plants

Carnallite Loop Flow sheet

Reference:
Abu-Hamatteh, Z., & Al-Amr, A. (2008). *Carnallite froth flotation optimization and cell efficiency in the Arab Potash Company, Dead Sea, Jordan*. *Mineral Processing and Extractive Metallurgy Review*, 29(3), 232–257. https://doi.org/10.1080/08827500801997894



First pond has the highest evaporation rate. Most of NaCl deposits

Pre-carnalite pond acts to control the proper composition of brine feeding the carnallite ponds. KCl composition here is 2%

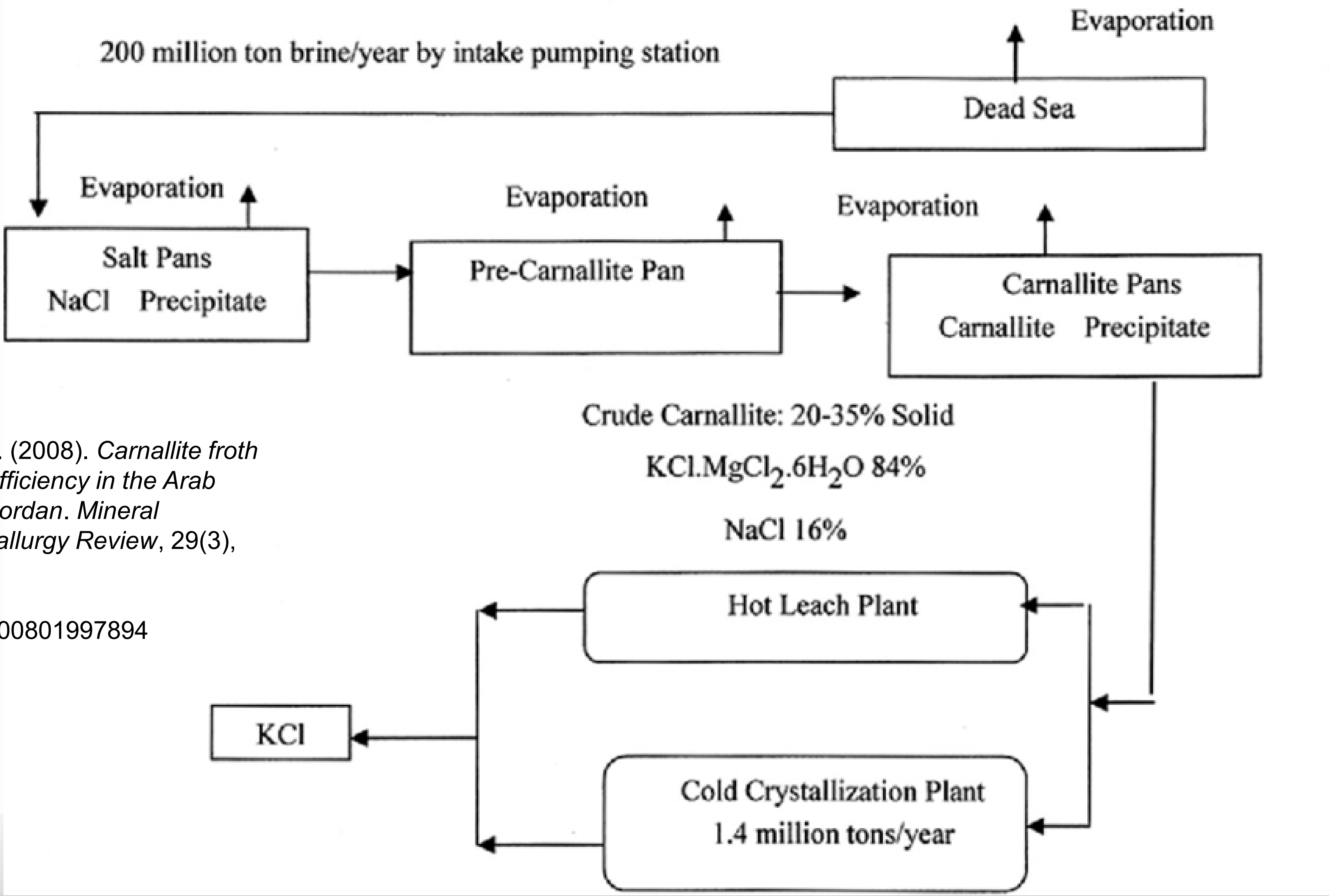
7 carnalite ponds in series. Evaporation leads to carnalite precipitation

Tails are the **residual solids** that remain after the valuable product (KCl) is separated from the feed carnallite

The C-4 pond is fed by refinery return brine in order to improve the overall recovery of the pond system.

The evaporation ponds produce 10-11 million metric ton/year carnallite, which is harvested and sent to both plants: the hot leaching plant and the cold crystallization plant

General Process Flow Diagram



Reference:
Abu-Hamatteh, Z., & Al-Amr, A. (2008). *Carnallite froth flotation optimization and cell efficiency in the Arab Potash Company, Dead Sea, Jordan*. *Mineral Processing and Extractive Metallurgy Review*, 29(3), 232–257.

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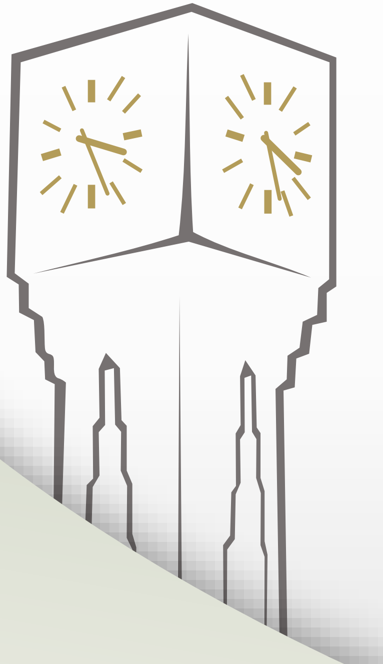


1. The Hot Leach Plant

1. The Hot Leach Plant

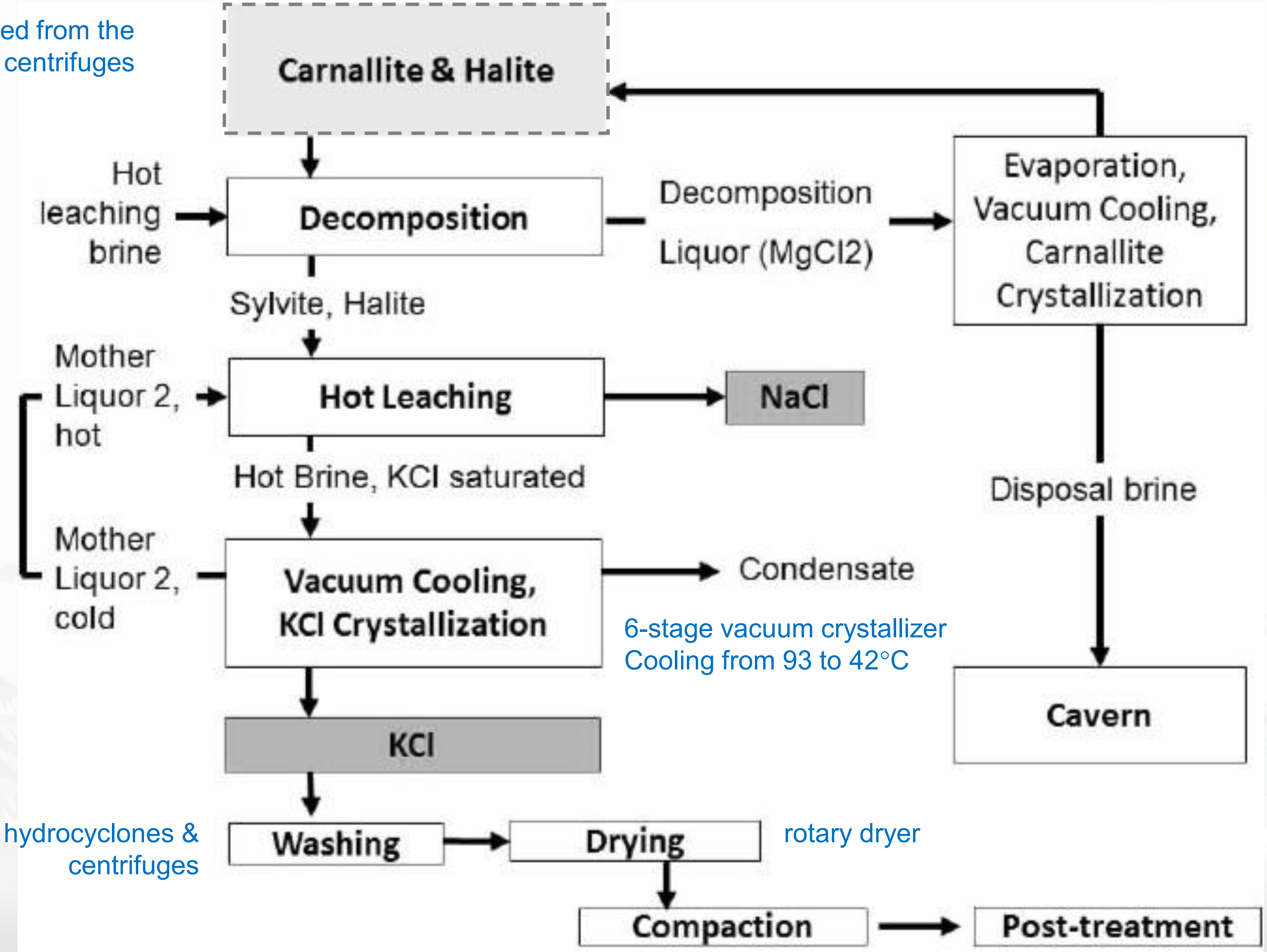
APC utilizes the **hot leach process** technology to produce high grade standard and fine potash, which includes the following units of operation:

- □ Carnallite Processing
- □ Sylvinite Processing
- □ Crystallization
- □ Product Dewatering
- □ Drying
- □ Screening

Carnallite
($KCl.MgCl_2.6H2O$)

Sylvinite : KCl+ NaCl

The Hot Leach Process



cake is separated from the liquid by centrifuges

Carnallite & Halite

Hot leaching brine

Decomposition

Decomposition Liquor (MgCl2)

Evaporation, Vacuum Cooling, Carnallite Crystallization

Sylvite, Halite

Mother Liquor 2, hot

Hot Leaching

NaCl

Hot Brine, KCl saturated

Disposal brine

Mother Liquor 2, cold

Vacuum Cooling, KCl Crystallization

Condensate

6-stage vacuum crystallizer
Cooling from 93 to 42°C

Cavern

KCl

hydrocyclones & centrifuges

Washing

Drying

rotary dryer

Compaction

Post-treatment

Leaching
is the process of using a liquid (usually water or brine) to dissolve and extract specific soluble components from a solid mixture.

Carnallite: $KCl.MgCl_2.6H_2O$

Sylvinite: KCl+ NaCl

Halite: NaCl

Two products:
Standard and Fine.
Granular is produced by compaction

The Hot Leaching Process

- A process first used in 1860 for the extraction of potash from sylvinite ore based on the differing solubilities of sodium and potassium chloride.
- The ore, which is a mixture of sodium and potassium chloride, is crushed and mixed with saturated sodium chloride.
- It is heated to boiling in which the potassium chloride dissolves but the sodium chloride does not.
- On cooling, the potassium chloride crystallizes and is separated.

Plant Processing/ Hot Leach Plant

Carnallite Processing

- Carnallite ($KCl.MgCl_2.6H_2O$) slurry is received,
- Dewatered and decomposed with water.
- The resulting solids mixture (Sylvinite: KCl+ NaCl) is dewatered and washed, creating a cake-like material.

Plant Processing/ Hot Leach Plant

Sylvinite Processing

- Sylvinite cake is leached. Heated brine returned from the crystallization stage is used for leaching the potassium chloride (KCl) solids.
- The hot KCl-saturated brine is clarified in a thickener, and then the overflow is pumped to the crystallization stage.
- The underflow slurry containing sodium chloride crystals is dewatered, repulped with waste brine and pumped to tailings.

Plant Processing/ Hot Leach Plant

Crystallization

- Hot brine is cooled successively in a six-stage vacuum crystallizer system.
- Upon cooling, the KCl decreases in solubility and crystallizes under controlled conditions.

Plant Processing/ Hot Leach Plant

- **Product Dewatering** – Potash slurry from the crystallization stage is dewatered using hydro- cyclones and centrifuges.

- **Drying** – Cake from the centrifuges is conveyed to the rotary dryer to remove the last traces of moisture entrained with the crystals. The product is then sent to the screening unit, while the dust is collected using high-efficiency cyclones..

Plant Processing/ Hot Leach Plant

- **Screening –** The product is segregated into **standard** and **fine** grades, and an anti-caking agent is added to both products in controlled amounts to minimize potash's natural tendency to agglomerate during storage and shipment.

- **De-dusting Systems** – Specially installed systems, such as bag filtration units and high-efficiency cyclones minimize environmental impact and potash losses as dust.

END.

Multiple References are used in this course

CHE 0915481

Chemical Process Technology

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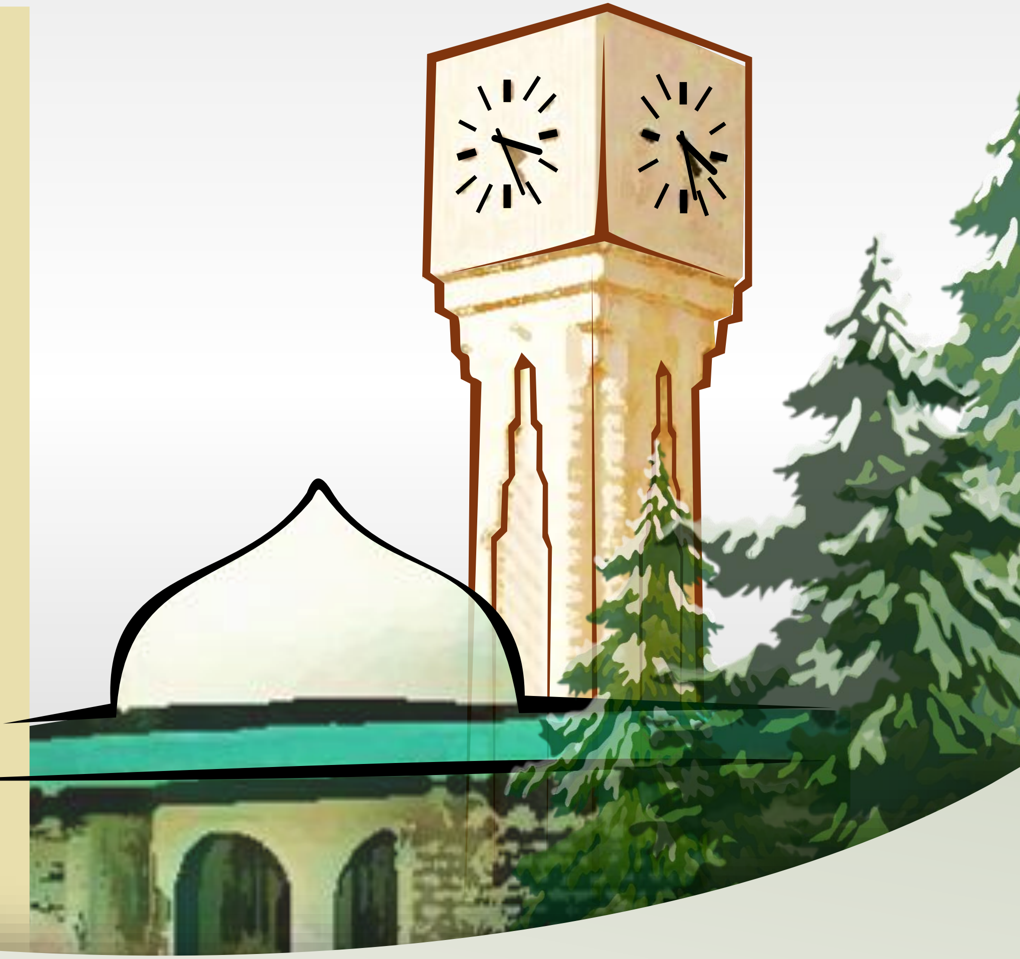
Dr. Hatem Alsyouri	Week 4



The University of Jordan
Chemical Engineering Department

Week 4

Process (1): Potash and Dead Sea Products Industry

Topics	**Lecture 3**	**Industrial Potash Plant** **Cold Crystallization Plant**
	Lecture 4	**Integrating Sustainability and AI Practices in the Potash Industry**
Learning Outcomes	**LO1.** Describe the production of potash from Dead Sea raw materials by explaining the hot leach process and the cold crystallization process, including major raw materials, process steps, and products. (SO7) **LO7.** Assess the application of modern trends such as sustainability practices, environmental protection, and the integration of artificial intelligence (AI) in process design and optimization. (SO7)	

Lecture 3

Industrial Potash Plant
Cold Crystallization Plant

Reacp	In previous lecture we covered the following topics: 1. Discussed operations and process diagram of potash production. 2. Described the hot leaching plant operations
Announcements	1. Provide proposed project ideas in the form of a proposal (1 page summary). Submission will be on Moodle due week 4 (Monday 26 Oct 2025). 2. You can submit more than 1 idea (1 page per each idea) but only 1 idea will be selected 3. Project ideas will be discussed 2nd lecture of week 4 (Tue 28 Oct 205)

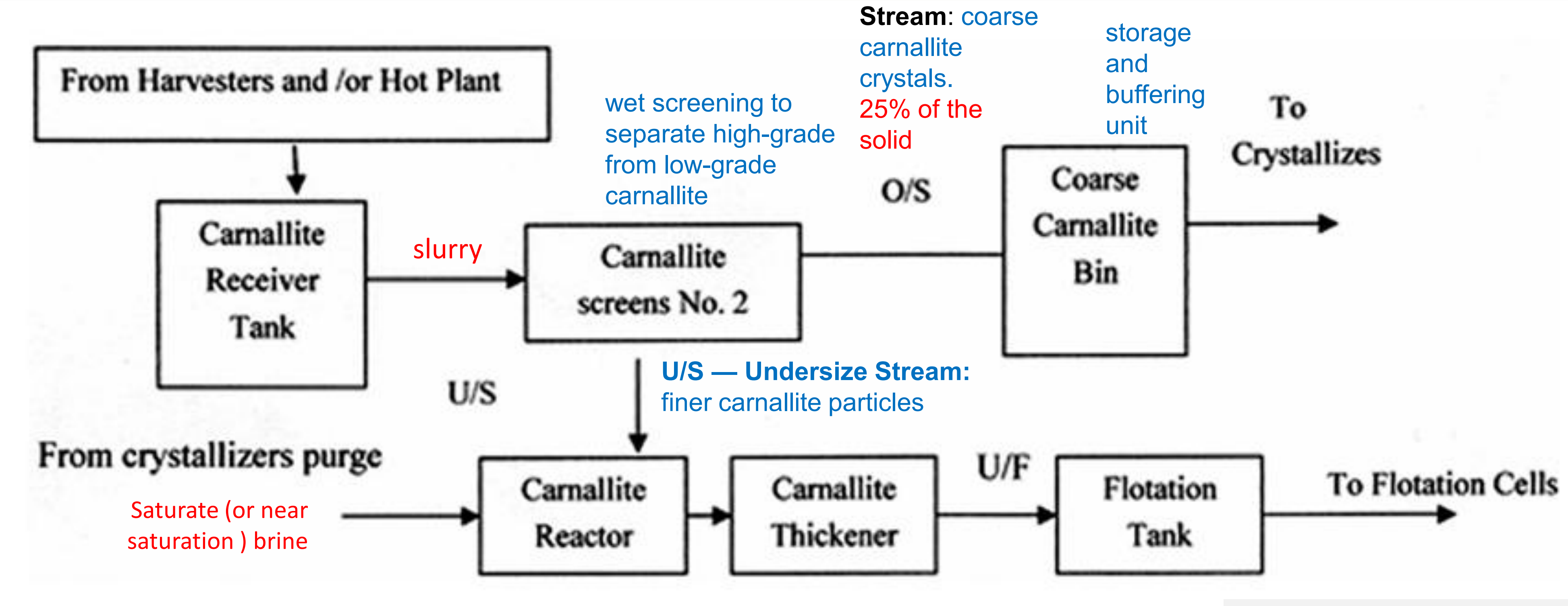
2. Industrial Potash Plant:

Industrial grade Potash (KCl) is the premium form of Potassium Chloride (99.2% KCl min.) that is produced to meet the needs of the non-fertilizer sector.

Cold Crystallization Plant I

- The Cold crystallization plant is operating at a design production capacity of 0.5 million metric ton per year (mmtpy).
- The cold crystallization plant is independent of the hot leach facility.
- It is operated under ambient temperature and therefore requires less energy.
- It includes the following processes: Carnallite Receiving; Flotation; Crystallization; Cold Leaching; Drying.

Carnallite Processing in Cold Crystallization



O/S: Oversize Stream: coarse carnallite crystals. 25% of the solid

storage and buffering unit

wet screening to separate high-grade from low-grade carnallite

slurry

U/S — Undersize Stream: finer carnallite particles

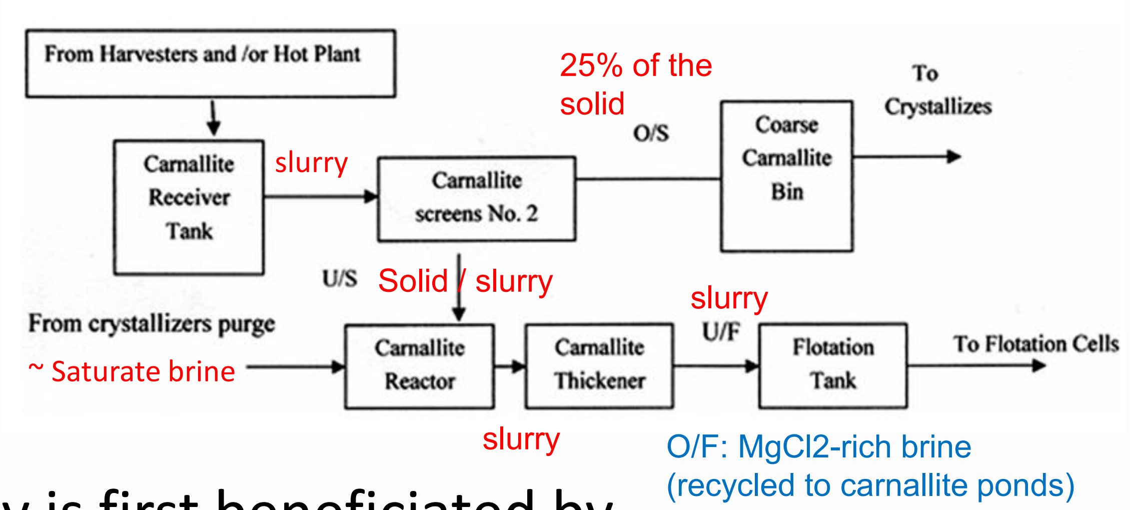
Saturate (or near saturation) brine

The Carnallite Reactor acts as a conditioning and partial dissolution vessel, where fine carnallite is equilibrated with recycle brine to achieve the proper composition for efficient thickening, flotation, and subsequent crystallization of potash (KCl).

The **Carnallite Thickener** concentrates the reactor slurry by settling out solids. Its **underflow (U/F)** is the **feed to the flotation tank**, where the valuable **KCl** is recovered from the thickened salt mixture.

The Flotation Tank is used to selectively separate KCl from NaCl by froth flotation. It is the key purification step in the potash process that produces a KCl-rich stream for cold crystallization and a NaCl-rich waste stream for disposal.

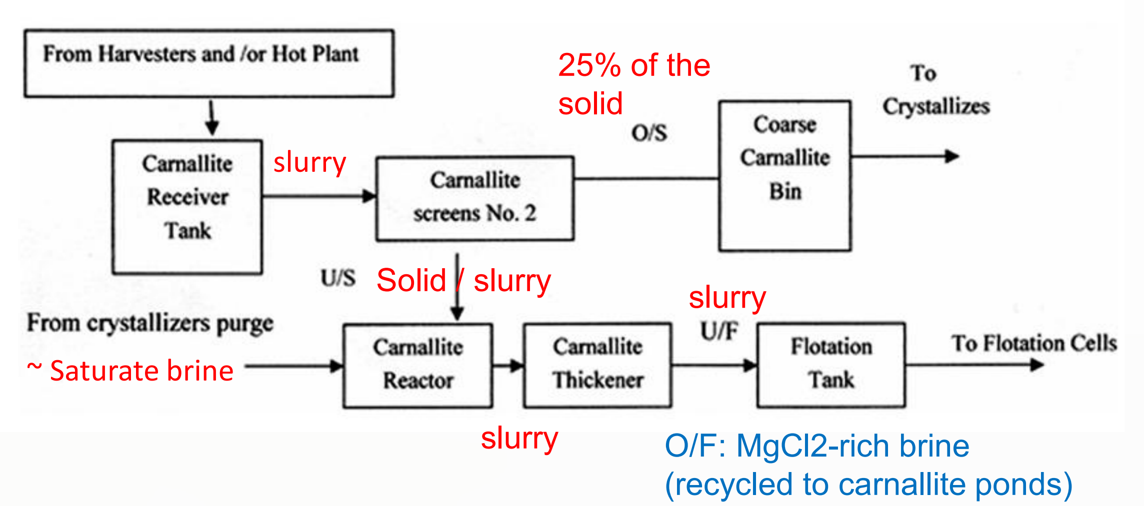
Cold Crystallization Plant



Carnallite Receiving

- ☐ **Carnallite screening**: Crude carnallite slurry is first beneficiated by wet screening to separate the high-grade carnallite fraction, which is about one quarter of the solids.
- ☐ This high-grade carnallite (coarse carnallite: oversize fraction) is fed directly to the cold crystallizers.
- ☐ **Carnallite Reactor**: The screen undersize slurry (undersize fraction) is mixed with brine discharge from the cold crystallizers overflow, which is at or near saturation, in a draft tube reactor.
- ☐ When solar pond brine mixes with crystallizer brine in the **reactor**, precipitation of carnallite occurs as the brine mixture equilibrates.

Cold Crystallization Plant



Carnallite Thickener

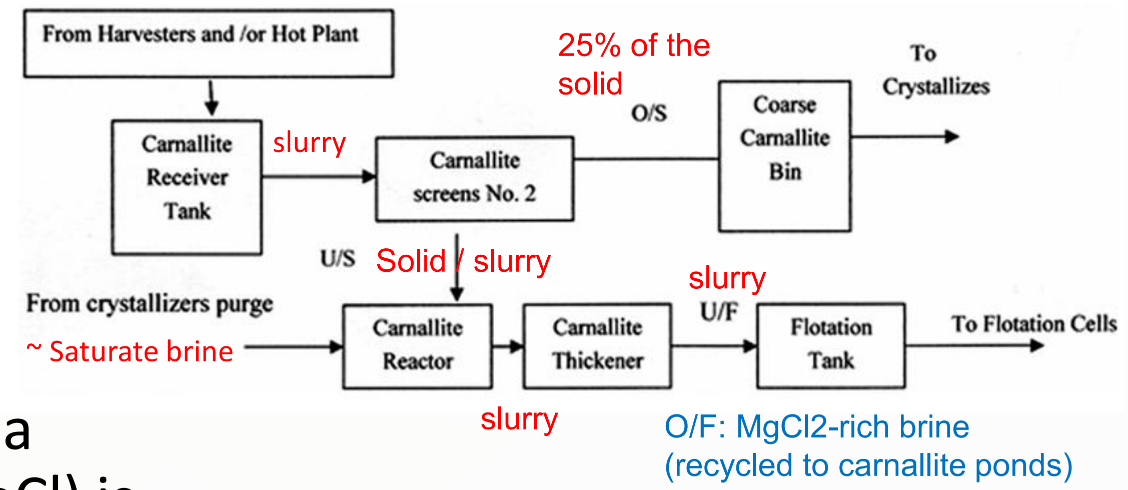
- ☐ Slurry from the reactor is densified in the <u>**carnallite thickener**</u> and the overflow (O/F) is returned to the evaporation ponds.

A **thickener** is a large, circular settling tank used to **separate solids from liquid** in a slurry by gravity settling. It produces two output streams:

Overflow (O/F): The **clarified liquid (brine)** that rises to the top and flows over a weir. Usually recycled back into the process (e.g., to ponds). Contains minimal suspended solids.

Underflow (U/F):
The **concentrated slurry (thickened solids)** that settles at the bottom. It is sent to the next process step, such as flotation or crystallization. Contains most of the suspended solids (KCl-rich or carnallite-rich material).

Cold Crystallization Plant



Flotation

- Carnallite thickener underflow is beneficiated by a flotation technique, in which sodium chloride (NaCl) is floated and pumped to the tailings area.
- Sink slurry is settled in a flotation thickener, the overflow of which is used as make-up brine to the flotation cells and the excess is pumped to the carnallite thickener.
- Flotation thickener underflow is dewatered in centrifuges.
- Centrifuge cake (fine carnallite) is conveyed to the cold crystallizers and the effluent is recycled to the flotation thickener.

The **Flotation Tank** separates sodium chloride (NaCl) from the carnallite thickener underflow using selective flotation. Chemical reagents are added so that NaCl attaches to air bubbles and rises as froth, while the heavier carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) remains as sink slurry. Outputs are:

Froth (float product): NaCl-rich material sent to the tailings area.
Overflow brine: (top liquid discharge):This is $MgCl_2$-rich brine that does not carry solids.
Underflow (sink slurry): Carnallite-rich slurry directed to the flotation thickener for further separation and dewatering.

Cold Crystallization Plant

Crystallization

- Coarse carnallite and fine carnallite are decomposed in a two-stage crystallizer system in the presence of water. Potassium chloride (KCl) crystals are formed in the crystallizers.

- Crystallizer discharge slurry is wet screened to remove large particles of carnallite and/or sodium chloride.

- Screen oversize is pumped to the tailings area along with flotation overflow slurry. Screen undersize is directed to the leaching area.

Cold Crystallization Plant

Cold Leaching

In order to remove adhering high magnesium chloride brine from the crystallizer product, two-stage leaching and dewatering centrifuges are used to reduce the magnesium chloride content in the product down to the allowable limit.

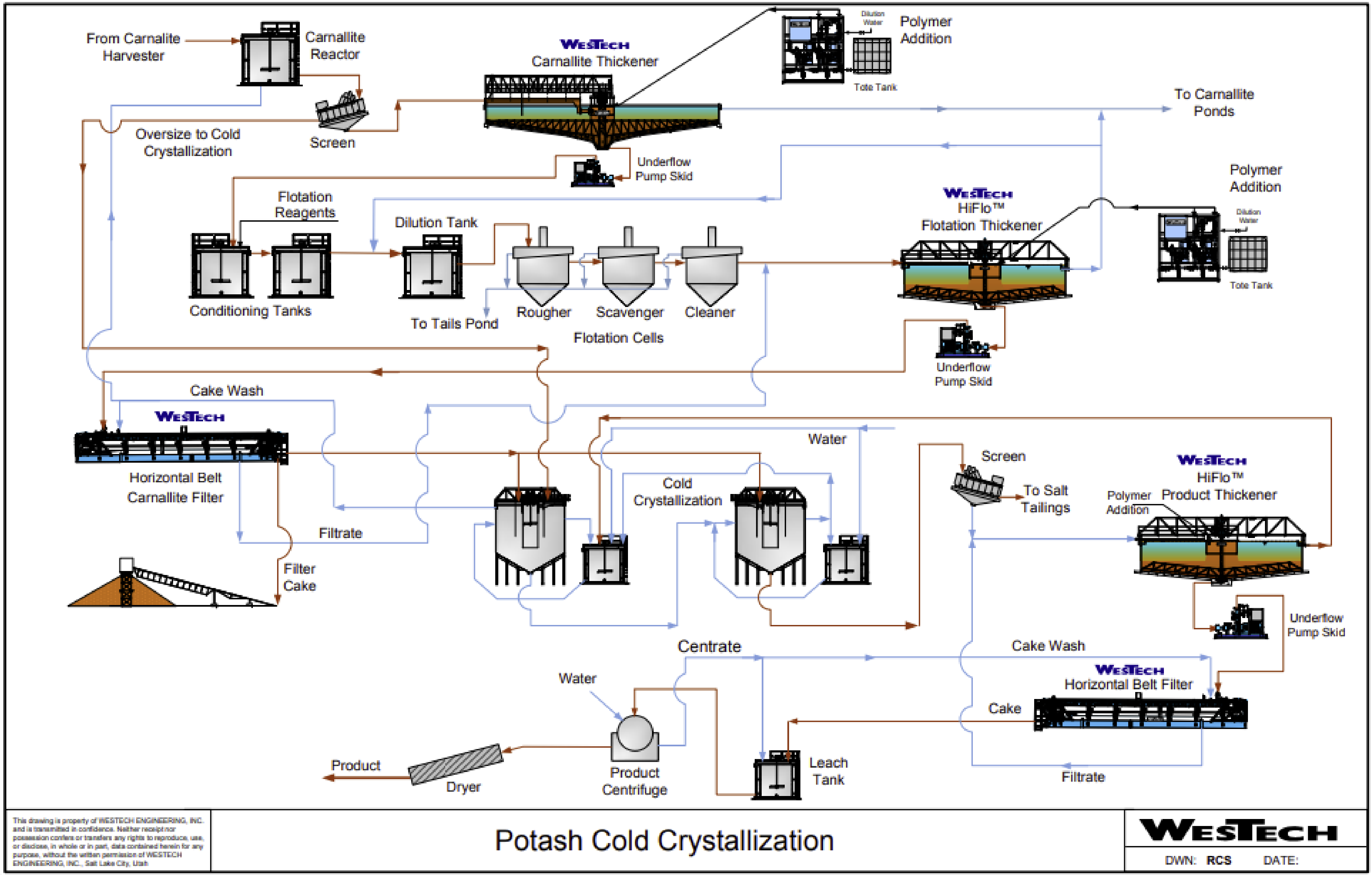
Drying

Second-stage centrifuge cake is dried to 0.1% moisture content in a co-current, rotary dryer. The product is then cooled in a rotary cooler by a counter-current air stream.

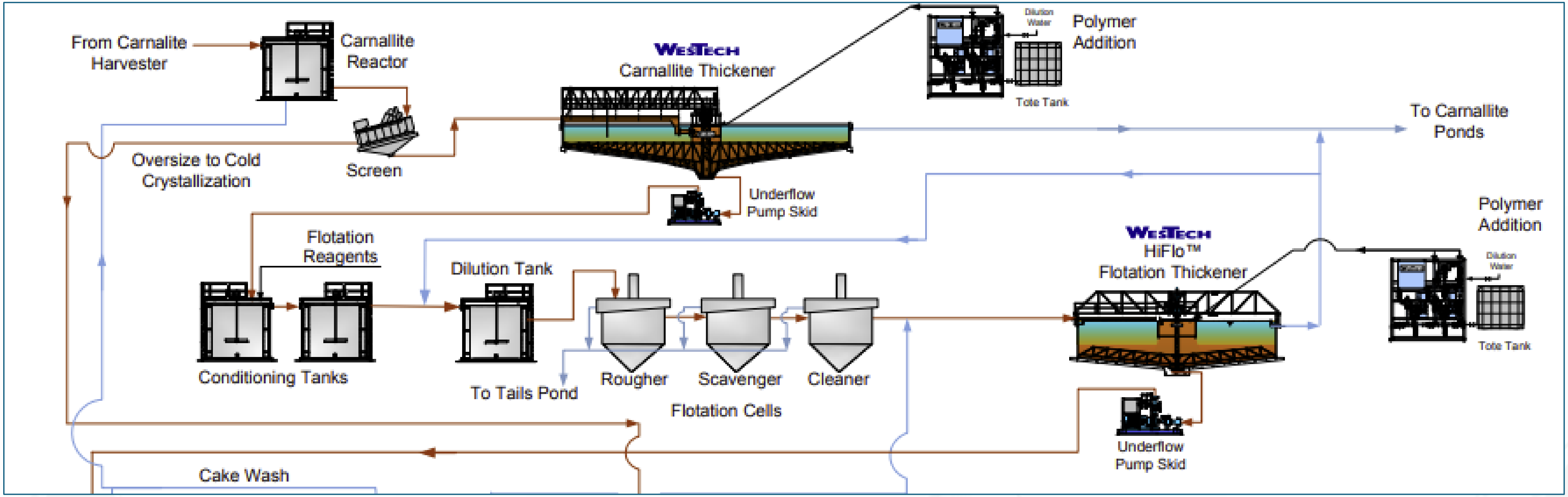
Cold Crystallization Process Flow Diagram

The Cold Crystallization Process is a refining stage used to recover potassium chloride (KCl) from the carnallite slurry after initial leaching and flotation. It takes advantage of solubility differences between KCl and NaCl at low temperatures to crystallize pure KCl.

Note: this process is slightly different from the block flow diagram described earlier.



Reference: WesTech Water. (n.d.). *Mineral Processing — Potash Cold Crystallization flow sheet*. Retrieved from https://www.westechwater.com/markets/mining-minerals/mineral-processing



1. Carnallite Reactor

Feed: Carnallite slurry from the harvesting ponds (contains $KCl \cdot MgCl_2 \cdot 6H_2O$, NaCl, and brine) and/or U/S slurry from prior screen.

Operation: The carnallite is decomposed with water or process brine to release $MgCl_2$ into the solution.

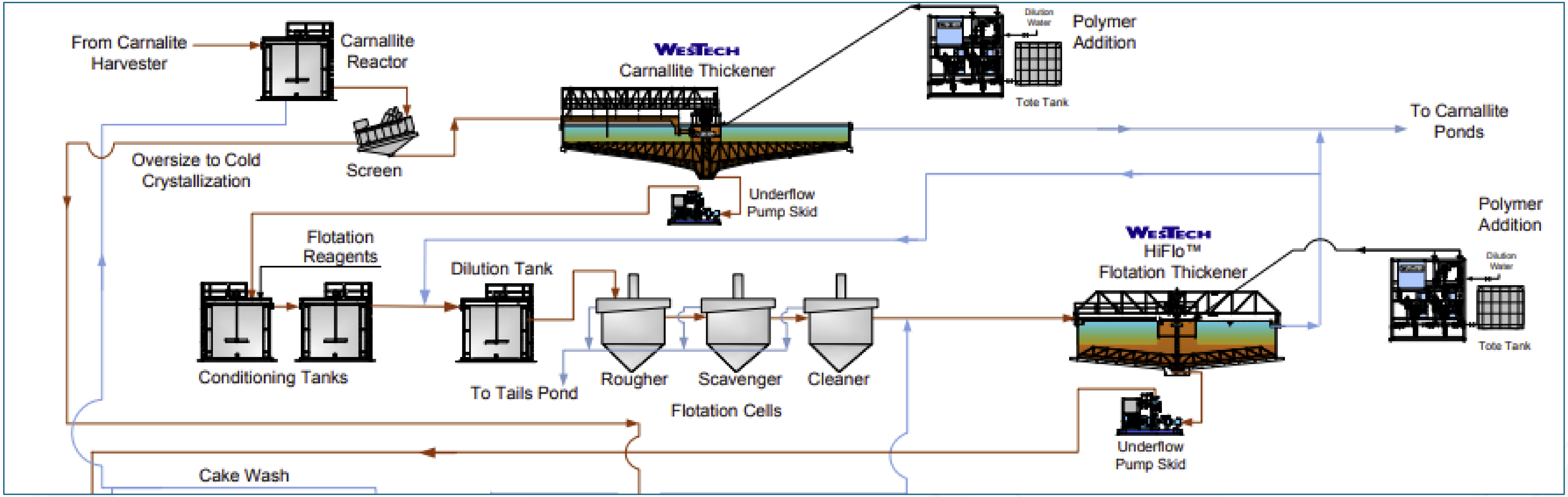
Output: Slurry containing solid KCl/NaCl and dissolved $MgCl_2$

2. Screen

Purpose: Separates the slurry into coarse and fine fractions.
Oversize (O/S): Sent to **Cold Crystallization** for further recovery of KCl.
Undersize (U/S): Sent to the **Carnallite Thickener** for settling and brine recovery.

3. Carnallite Thickener

Purpose: Concentrates the fine solids from the screen undersize using polymer addition.
Overflow: Recycled to **Carnallite Ponds** as clarified $MgCl_2$-rich brine.
Underflow: Pumped to the **Conditioning Tanks** for further processing.



4. Conditioning Tanks

Operation: Mix flotation reagents (collectors, frothers) with the thickened slurry to prepare it for separation.
Output: Conditioned slurry sent to the **Flotation Cells**.

5. Flotation Cells

(Rougher – Scavenger – Cleaner)
Purpose: Separate KCl from NaCl based on surface hydrophobicity.

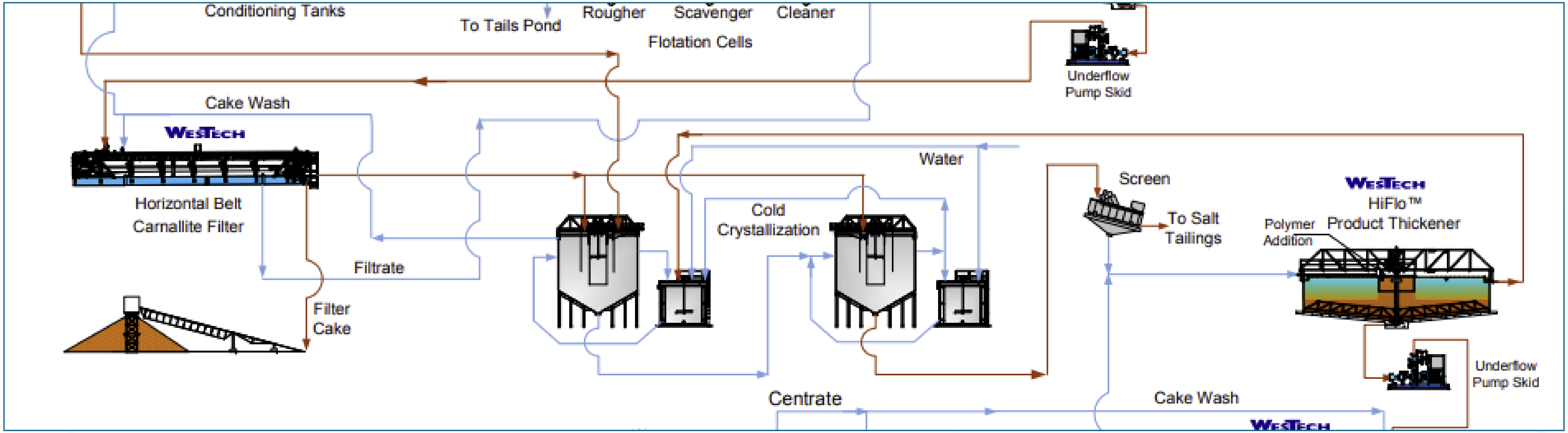
- **Rougher:** Recovers most of the KCl.
- **Scavenger:** Captures remaining KCl from tailings.
- **Cleaner:** Produces high-purity KCl froth.

Outputs:

- Froth → **Flotation Thickener**.
- Tailings → **Tails Pond**.

6. Flotation Thickener

Purpose: Settles and thickens the KCl-rich froth slurry coming from the flotation cells.
Additives: Polymer solution is added to accelerate settling and improve separation of solids and liquid. **Outputs:**
Underflow (UF): Concentrated KCl slurry → sent to the **Product Thickener** for further thickening.
Overflow (OF): Clarified brine → recycled to the process as **dilution water** or returned to ponds.



8. Horizontal Belt Filter (Product)

Purpose: Filters and washes KCl cake to remove brine.

Outputs:

- **Cake:** Moist KCl crystals → **Dryer**.
- **Filtrate:** Recycled to process.

9. Cold Crystallization

Feed: Oversize solids from Screen and recycled brine.

Operation: KCl is crystallized from brine by cooling (using solubility difference at low temperature).

Outputs:

- **KCl crystals:** Sent to **Product Thickener or Filter**.
- **Concentrate:** Recycled to process (e.g., to Leach Tank or dilution).

10. Wet screen

Purpose: remove large particles of carnallite and/or NaCl. Outputs:

Oversize: Pumped to tailing area along with flotation overflow.

Undersize: is directed to product thickener.

11. Product Thickener

Settles and concentrates the KCl crystals before filtration. Outputs:

Underflow: Thick KCl slurry sent to the belt filter and dryer to produce MOP potash.

Overflow: Brine recycled to the process.

Cold Crystallization Operation

The **cold crystallizer** is the main unit in the **cold crystallization stage**, which separates **potassium chloride (KCl)** from the brine based on **temperature-dependent solubility**.

Principle:

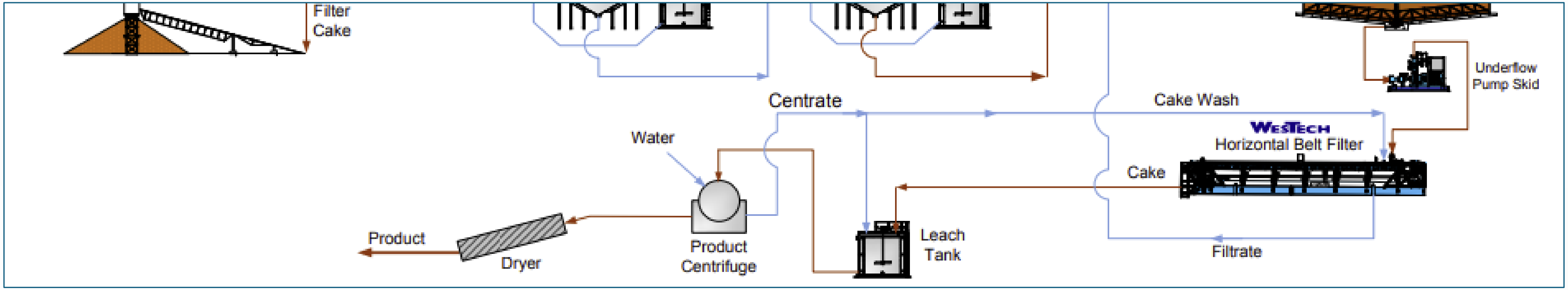
As temperature decreases, **KCl solubility decreases** more than NaCl or $MgCl_2$.
Therefore, cooling the saturated brine leads to **selective crystallization of KCl**, while other salts remain dissolved.

Operation Steps:

- The feed solution (KCl-rich brine from flotation) enters the crystallizer.
- The solution is **cooled gradually** using chilled water or air heat exchangers.
- **KCl crystals form and grow** as supersaturation develops.
- The resulting slurry (crystals + mother liquor) is sent to filters for solid-liquid separation.
- The **centrate (mother liquor)** is recycled, while solid KCl is washed, dried, and compacted.

Purpose:

To recover high-purity KCl crystals with minimal NaCl or Mg contamination and to enhance overall process yield while reducing energy demand compared to hot crystallization.



12. Horizontal Belt Carnallite Filter

Purpose: Dewaters solids from the Carnallite Thickener underflow.

Outputs:

- **Filter Cake:** Sent for disposal or reprocessing.
- **Filtrate:** Reused in process as wash or dilution water.

13. Leach Tank (optional stage)

Purpose: Further purifies KCl by dissolving residual NaCl.

Output:

Purified slurry → **Filter** → **Dryer**.

14. Product Centrifuge

Purpose: Removes remaining moisture to produce dry potash(muriate of potash, >95% KCl).

Outputs:

- Final **Product** ready for storage or shipment.
- Concentrate: brine recycled to the process or leach tank.

15. Drying and Product Handling:

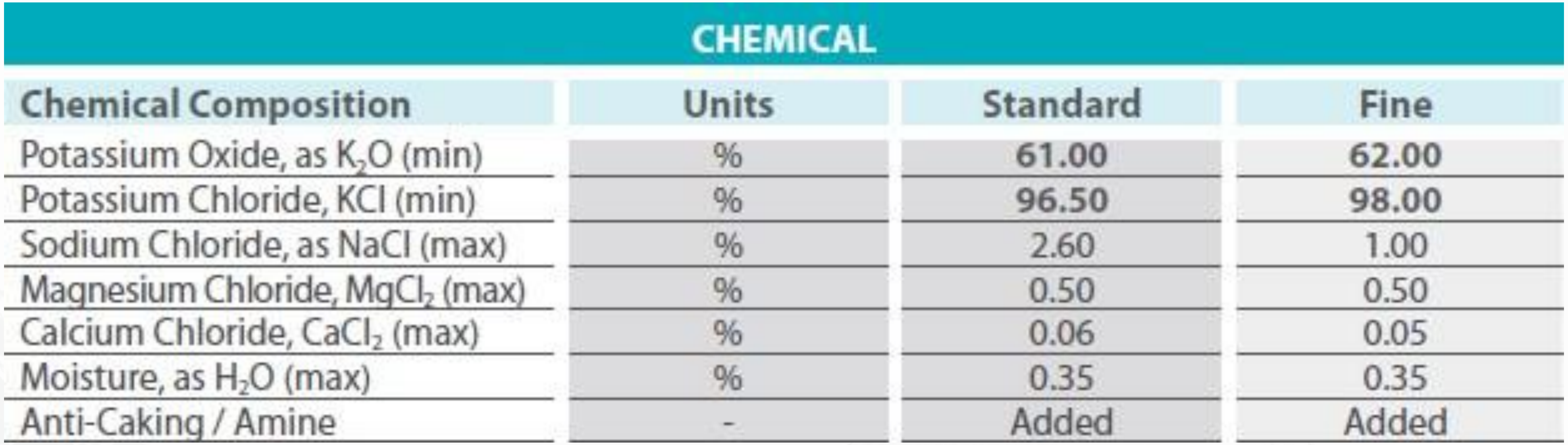
The washed crystals are dried in a rotary dryer, producing standard or fine-grade KCl ready for compaction or direct export.

Cold Crystallization Plant II

- A second Cold Crystallization Plant (II) came into service in late 2010 to give a total production of 450,000 tpy.
- The new plant is similar to the Cold Crystallization Plant I, but it has certain modified processes and more advanced technology, mainly in crystallization, flotation, screening, leaching and other areas.
- An advanced control system (DCS) was incorporated to facilitate control of various processes.
- Highly efficient dust collection systems were included in the new plant to ensure minimum dust emissions into the surrounding environment.
- A new compaction plant was also installed to produce more than 260,000 tpy of high quality granular potash. The new compaction plant comprises a post-treatment unit intended for enhancing the quality of granular potash.

Reference: https://alchetron.com/Arab-Potash

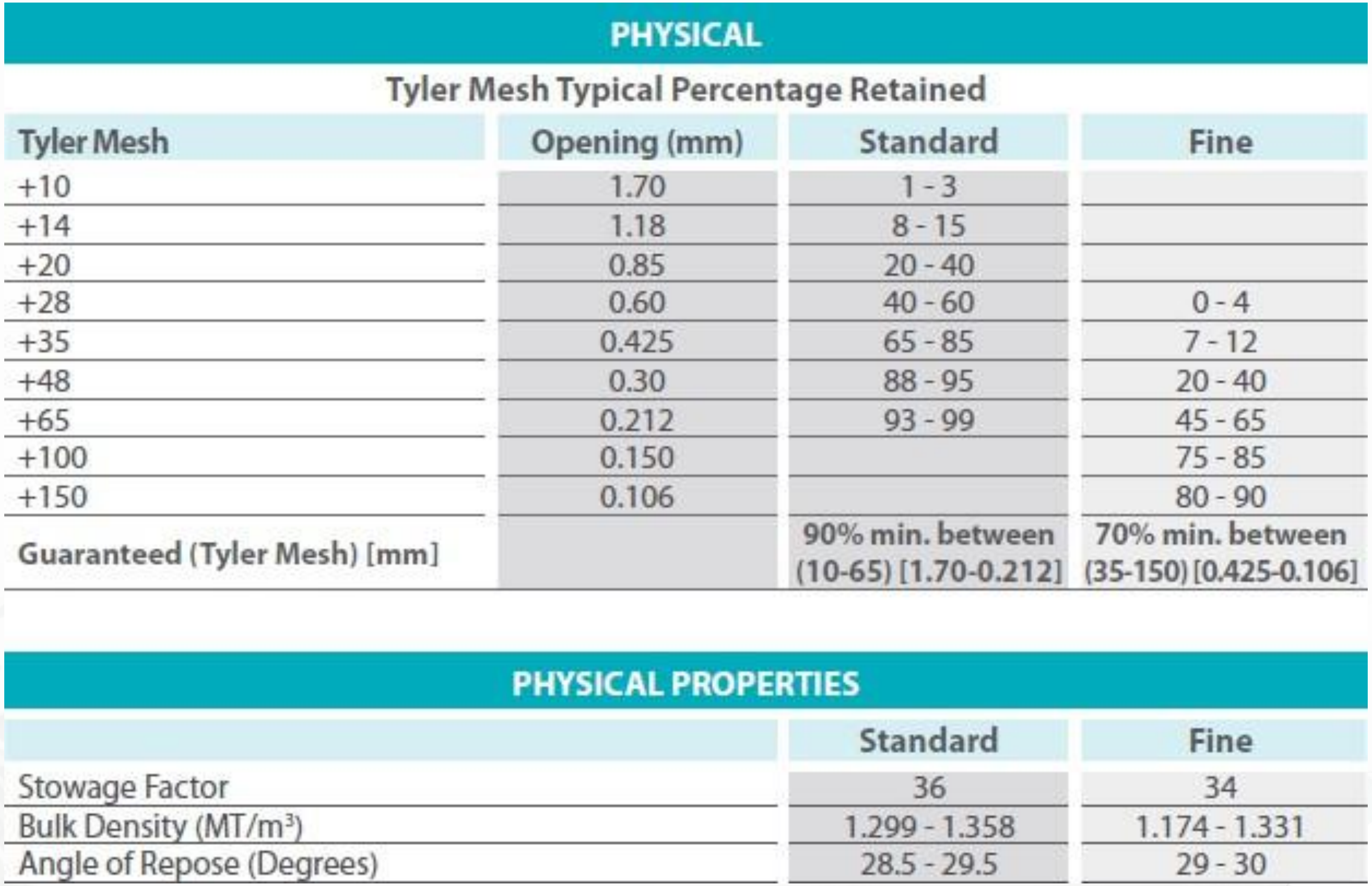
Product Standard and Fine Grades



CHEMICAL

Chemical Composition	Units	Standard	Fine
Potassium Oxide, as K_2O (min)	%	**61.00**	**62.00**
Potassium Chloride, KCl (min)	%	**96.50**	**98.00**
Sodium Chloride, as NaCl (max)	%	2.60	1.00
Magnesium Chloride, $MgCl_2$ (max)	%	0.50	0.50
Calcium Chloride, $CaCl_2$ (max)	%	0.06	0.05
Moisture, as H_2O (max)	%	0.35	0.35
Anti-Caking / Amine	-	Added	Added

Product Properties



PHYSICAL

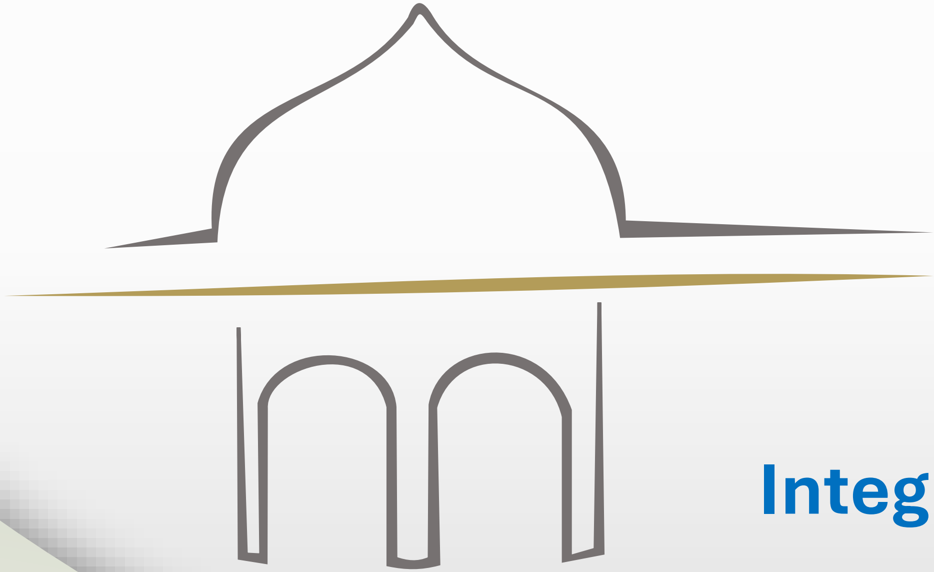
Tyler Mesh Typical Percentage Retained

Tyler Mesh	Opening (mm)	Standard	Fine
+10	1.70	1 - 3	
+14	1.18	8 - 15	
+20	0.85	20 - 40	
+28	0.60	40 - 60	0 - 4
+35	0.425	65 - 85	7 - 12
+48	0.30	88 - 95	20 - 40
+65	0.212	93 - 99	45 - 65
+100	0.150		75 - 85
+150	0.106		80 - 90
Guaranteed (Tyler Mesh) [mm]		90% min. between (10-65) [1.70-0.212]	70% min. between (35-150) [0.425-0.106]

PHYSICAL PROPERTIES

	Standard	Fine
Stowage Factor	36	34
Bulk Density (MT/m³)	1.299 - 1.358	1.174 - 1.331
Angle of Repose (Degrees)	28.5 - 29.5	29 - 30

END.



Lecture 4

Integrating Sustainability and AI Practices in the Potash Industry

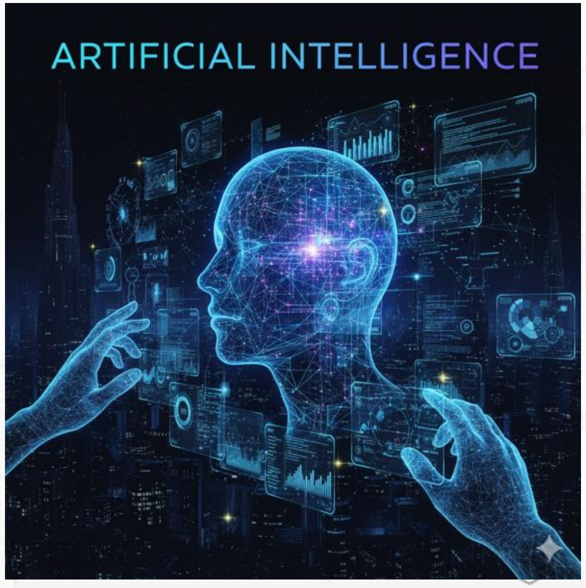
Definitions

Sustainability:

The practice of meeting current industrial and societal needs without compromising the ability of future generations to meet theirs by balancing economic growth, environmental protection, and social responsibility.

Artificial Intelligence (AI):

The use of computer systems and algorithms that can analyze data, learn from patterns, and make decisions or predictions, helping industries optimize processes, improve efficiency, and reduce resource consumption.



Why Sustainability & AI in Jordan’s Potash?

1. **Dead Sea resource stewardship: hypersaline ecosystem, finite brine inflow**
   The Dead Sea is a unique, delicate natural system with limited water inflow. Sustainable operation means managing brine extraction and evaporation carefully to preserve this strategic and environmentally sensitive resource.

2. **Energy-intensive refining (hot-leach / cold crystallization, drying, compaction)**
   Both potash extraction routes consume large amounts of heat and power. Improving energy efficiency and recovering waste heat can significantly cut fuel use and carbon emissions.

Why Sustainability & AI in Jordan’s Potash?

3. **Competitive pressure on water, energy, and reagent costs → efficiency = margin**
   In Jordan’s arid climate, water and energy are costly, and reagent prices impact profitability. Increasing process efficiency directly improves both sustainability and economic margins.

4. **AI can turn plant/pond data into better recovery, lower emissions, safer operations**
   Using AI tools to analyze production and pond data allows smarter control of crystallizers, pumps, and dryers—raising KCl recovery, reducing waste and emissions, and enhancing safety through predictive monitoring.

Core Sustainability Practices (Process & Energy)

1. **Heat integration:** Recover waste heat from dryers to preheat process brine or slurries, reducing fuel consumption and improving thermal efficiency.
2. **High-efficiency drives:** Install variable-frequency drives (VFDs) on pond intake pumps, booster pumps, and thickeners to optimize power use according to load demand.
3. **Low-carbon energy:** Utilize solar photovoltaic (PV) and thermal salt-loop systems to supply low-grade process heat, and explore green-power purchase agreements (PPAs) to lower CO_2 emissions.
4. **Fuel switching and electrification:** Replace diesel-powered pumps with electric units and electrify mobile harvesters where feasible to reduce air pollution and maintenance costs.
5. **Advanced process control (APC/MPC):** Apply model-based control to crystallizers and dryers for more stable operation, fewer off-spec cycles, and higher product yield.

APC: Advanced Process Control; MPC: Model Predictive Control

Water & Brine Management

1. **Closed-loop process water:** Recycle mother liquors and process water wherever purity allows to reduce freshwater demand.
2. **Brine recirculation & bleed optimization**: Control brine recycles to maintain a stable $K^+/Na^+/Mg^{2+}$ balance and consistent crystallization conditions.
3. **Zero-Liquid-Discharge (ZLD) mindset**: Segregate brine streams, evaporate residues, and reuse water to minimize liquid waste.
4. **Leak minimization**: Use corrosion-resistant materials, online leak detection, and secondary containment to prevent brine losses.
5. **Rain-runoff handling**: Design dikes and drainage systems to collect and divert rainwater, preventing pond dilution and overflow incidents.

Materials, By-products & Circularity

1. **Valorize bittern/mother liquor** (leftover brine)**:** Extract valuable by-products such as bromine, magnesium chloride, or specialty salts to add economic value.
2. **Tailings management**: Reduce KCl losses by re-flotation or scavenger cells and adopt dry stacking for safer and smaller waste storage.
3. **Reagent optimization**: Use low-toxicity flotation reagents and adjust dosages precisely to achieve the target product grade.
4. **Dust & noise controls**: Enclose conveyors, use bag filters, and apply misting systems to reduce dust and noise around operating units.

Circularity means designing industrial processes and resource use so that materials are reused, recycled, or recovered instead of being wasted — forming a "closed loop."

Emissions & Environmental Management

1. **Dryer/calciner upgrades:** Install low-NOx burners and heat recovery units to lower emissions and improve energy efficiency.
2. **Fugitive dust (الغبار المتطاير) controls**: Map dust sources in storage and compaction areas and apply enclosed handling or suppression systems.
3. **Real-time monitoring**: Implement air-quality and saline-spill sensors near ponds and dikes to detect leaks or emissions quickly.
4. **Biodiversity & visual footprint**: Use saline-tolerant vegetation and wildlife-safe lighting to reduce visual and ecological impact.

AI Use Cases: Ponds & Upstream

1. **Evaporation forecasting:** Machine learning (ML) models predict pond levels and harvest timing using weather and process data.
2. **Pond health imaging**: Drones or satellite images with computer vision detect color or texture changes indicating salt-phase shifts.
3. **Pumping optimization**: AI schedules and controls intake and booster pumps to cut energy use and avoid equipment stress.
4. **Brine chemistry soft-sensors**: Predict $K^+/Na^+/Mg^{2+}$ composition from limited lab data, enabling faster process decisions.

AI Use Cases: Refinery & Recovery

1. **Crystallizer set-points:** ML models recommend operating parameters (temperature, vacuum, seeding) for optimal KCl purity.
2. **Flotation dosing:** AI tunes collector and depressant dosages automatically to maintain target product grade with minimal reagent use.
3. **Thickener performance:** Predictive models estimate underflow density and overflow clarity to adjust polymer dosing in real time.
4. **Predictive maintenance:** Vibration and current data are analyzed to detect faults early in pumps, centrifuges, and conveyors.
5. **Quality prediction:** Real-time models forecast MOP grade and moisture content to minimize reprocessing.

Digital Foundation (What Plants Need First)

What digital systems a potash plant needs before applying AI (such as reliable instruments, organized data, and secure control systems.)

1. **Instrumentation:** Reliable sensors for flow, density, conductivity, and pH ensure accurate data collection.
2. **Clean historian**: Store high-frequency time-series data with batch tags to support AI analysis and troubleshooting.
3. **Data governance**: Maintain a single source of verified plant data with version control and audit trails.
4. **OT-IT security & safety**: Integrate cybersecurity and safety checks; all model updates go through formal management-of-change reviews.

OT–IT stands for Operational Technology and Information Technology integration

Key Performance Indicators (KPIs) to Track

KPIs: key indicators used to measure how well the plant performs in terms of energy, water use, product quality, and reliability.

1. **Energy and water use:** Track kWh per ton of MOP and cubic meters of water per ton of product.
2. **Recovery and yield**: Monitor KCl recovery (%) and daily yield versus production plan.
3. **Product quality**: Measure product moisture, dust loss, and stack emissions (NOx, PM).
4. **Reliability**: Record equipment availability and mean time between failures (MTBF).
5. **AI benefit**: Compare model-based operation versus manual control for energy, reagent, and downtime savings.

Implementation Pitfalls (Teach the Limits)

AI tools are not perfect and must be applied carefully in industrial settings

1. **Data drift**: Models must be retrained periodically to adapt to seasonal and feed variations.
2. **Overfitting**: Ensure models are validated across different feed grades and plant conditions.
3. **Human factors**: Build operator trust with clear, explainable AI interfaces and training.
4. **Safety integration**: AI controls must respect all interlocks and fail-safe procedures.

So What? (For Jordan's Potash Context)

The real-world benefits of integrating sustainability and AI in potash production for Jordan,

1. **Higher recovery**: Achieve more KCl from the same pond area, improving national resource efficiency.
2. **Lower costs**: Reduce energy and reagent expenses, strengthening competitiveness.
3. **Environmental gains**: Cut brine losses, emissions, and waste, improving sustainability credentials.
4. **Skill development**: Train local engineers in process optimization and AI for long-term industrial growth.

END.

CEMENT INDUSTRY

REFERENCE: SHREVE’S BOOK CH. 10, PP. 171-186
HTTPS://WWW.UNDERSTANDING-CEMENT.COM/ARTICLE-DIRECTORY.HTML (UP TO “CEMENT ANALYSIS”)

Week 6

Process (2): Cement Industry

Topics	**Lecture 1**	**Introduction** **Basic Definitions and Terminology**
	Lecture 2	**Types of Hydraulic Cements**
Learning Outcomes	**LO1.** Describe the production of potash from Dead Sea raw materials by explaining the hot leach process and the cold crystallization process, including major raw materials, process steps, and products. (SO7)	

Lecture 1

Introduction
Basic Definitions and Terminology

What is common among these?

- Reinforced-concrete walls
- Reinforced-concrete girders
- Tunnels
- Dams
- Roads

Concrete and Cement

- Concrete is composite material, meaning that it is made up of more than one type of material at the macroscopic scale.
- In its simplest view, concrete is divided into two components: the filler and the binder.
  - Cement is the binder component of concrete, the glue that holds the filler together to create a uniform, strong material.
  - The filler in concrete consists primarily of aggregate particles. The vast majority of aggregate is just sand, gravel, and rocks.

Basic Ingredients of Concrete

From left to right:
fine aggregate (sand),
coarse aggregate,
water, and cement.

Typical Concrete Mix Design

Ingredient	Percent by Volume	Percent by Weight
Water	19.5	8.1
Cement	11.3	14.7
Coarse aggregate (1 inch max)	42	46.5
Fine aggregate	27.2	30.7
Total	**100**	**100**

Basic Definitions and Terminology

- Cement: The dry unreacted powder that comes in a sack
- Cement paste: Cement that has been mixed with water.
- Concrete: A mixture of sand, gravel, and rocks held together by cement paste.
- Aggregate: The inert filler material that makes up the bulk of concrete. Usually sand, gravel, and rocks.
- Mortar: A mixture of cement paste and sand used in thin layers to hold together bricks or stones. Technically, mortar is just a specific type of concrete with a small maximum aggregate size.

Basic Definitions and Terminology

- Fresh: Cement paste or concrete that has been recently mixed and is still fluid. This is what those big trucks with the rotating container on the back are full of. (These are often called "cement mixers" but now you know why they should be called "concrete mixers").
- Hardened: Cement paste or concrete that has gained enough strength to bear some load.
- Set: The transition from fresh cement paste to hardened cement paste. The terms "initial set" and "final set" refer to specific times when the paste becomes no longer workable and completely rigid, respectively. "Setting" is the process by which this occurs.

Basic Definitions and Terminology

- Curing/Hardening: Essentially interchangeable terms that mean the process of continued strength gain after the cement paste has set due to chemical reactions between cement and water.
- Young: Cement paste or concrete that has recently set and is now actively hardening. What constitutes "young" in terms of time is variable; the term implies that the paste has undergone only a fraction of its full reaction and is thus weak and vulnerable to damage. This could be anywhere from a few hours to weeks depending on the mix design and the temperature.
- Mature: Cement paste or concrete that has reached close to its full strength and is reacting very slowly, if at all. An age of 28 days is a very rough rule of thumb for reaching maturity.

Basic Definitions and Terminology

- Hydration: The chemical reactions between cement and water. Hydration is what causes cement paste to first set and then harden.
- Hydration products: The new solid phases that are formed by hydration.
- Heat of hydration: The hydration reactions between cement and water are exothermic. Large volumes of concrete can warm up considerably during the first few days after mixing when hydration is rapid. This is generally a bad thing, for reasons that will be discussed.

Basic Definitions and Terminology

- Placing: The process of transferring fresh concrete from the mixer to the formwork that defines its final location and shape.
- Segregation: An undesirable process of the aggregate particles becoming unevenly distributed within the fresh cement paste while the concrete is being placed or consolidated.
- Bleeding: An undesirable process of mix water separating from the fresh cement paste or concrete while it is being placed or consolidated.

What is Special about Cement?

Easy to mix, use, and shape on site.

Convenient

Low-cost due to abundant raw materials.

Cheap

Can form any shape or structure.

Adaptible

Strong

Provides high compressive strength.

Durable

Long-lasting and weather-resistant.

Lecture 2

Types of Hydraulic Cements

Types of Hydraulic Cements

1. **Hydraulic lime**
   Only used in specialized mortars. Made from calcination of clay-rich limestones (calcium carbonate, $CaCO_3$).
   الحجر الجيري
2. **Natural cement**
   Misleadingly called Roman cement. It is made from argillaceous limestones or interbedded limestone and clay or shale, with few raw materials. Because they were found to be inferior to Portland.
   الطيني
3. **Portland cement**
   Artificial cement. Made by the mixing clinker with gypsum in a 95:5 ratio.

Why is it called “lime”? Because it is made by burning limestone ($CaCO_3$) to produce quicklime (CaO).

The term **Calcination** comes from calx (Latin for lime) because it originally referred to heating calcium carbonate ($CaCO_3$) to form calcium oxide (CaO) and CO_2. Today, it broadly means heating solids to cause decomposition or removal of volatile components.

Types of Hydraulic Cements

4. **Portland-limestone cement**

   Large amounts (6% to 35%) of ground limestone have been added as a filler to a Portland cement base.

5. **Pozzolan-lime cement**

   Original Roman cements. Mix of pozzolans (2 to 4 parts) with hydrated lime (1 part). Resist corrosive action of saline solution and seawater better than Portland cement.

6. **Blended cement**

   Mix of Portland cement with one or more supplementary cementitious materials (SCM) like pozzolanic additives.

Hydrated Lime is calcium hydroxide, with the chemical formula $Ca(OH)_2$, produced by adding water to quicklime (CaO) in a process called slaking. Used as a binding and plasticizing material in mortars, plasters, and pozzolanic cements. When combined with pozzolans, it contributes to slow but durable hardening.

Pozzolans are siliceous or aluminosiliceous materials that themselves have little or no cementing property, but when mixed with lime and water, they form compounds with cementitious properties.

Types of Hydraulic Cements

7. **Aluminous cement**

   Limestone and bauxite (aluminum oxide) are the main raw materials. Used for refractory applications (such as cementing furnace bricks) and certain applications where very rapid hardening is required. More expensive than Portland. Superior resistance to seawater and sulfate-bearing water.

8. **Masonry cement**

   A type of Portland cement blended with materials like limestone, hydrated lime, or plasticizers to improve workability, water retention, and plasticity.

   It is mainly used for bricklaying, plastering, and mortar work, not for structural concrete.

   البناء بالطوب التلييس

Bauxite is the main ore of aluminum, consisting mainly of hydrated aluminum oxides such as gibbsite ($Al(OH)_3$), boehmite (γ-$AlO(OH)$), and diaspore (α-$AlO(OH)$), along with impurities like iron oxides and silica.

Refractory applications: Uses of heat-resistant materials (like alumina or bauxite) to line furnaces, kilns, and reactors that operate at very high temperatures.

Abbreviations Used in Cement Industry

The **oxide notation system** used in cement chemistry.
Each oxide is represented by a single letter — for example, **CaO = C**, and **SiO_2 = S.**
These abbreviations make it easier to write complex compounds like **$3CaO \cdot SiO_2$** as **C_3S,**
which is commonly used in cement formulas and discussions.

$CaO = C$	$MgO = M$	$CO_2 = \bar{C}$
$SiO_2 = S$	$SO_3 = \bar{S}$	$H_2O = H$
$Al_2O_3 = A$	$Na_2O = N$	
$Fe_2O_3 = F$	$K_2O = K$	

$Ca_3SiO_5 = 3CaO.SiO_2 = C_3S$ tricalcium silicate

Cement Minerals and Products

- Different ways to represent some cement minerals and products:

These abbreviations are applied to identify **major cement minerals** and their products.

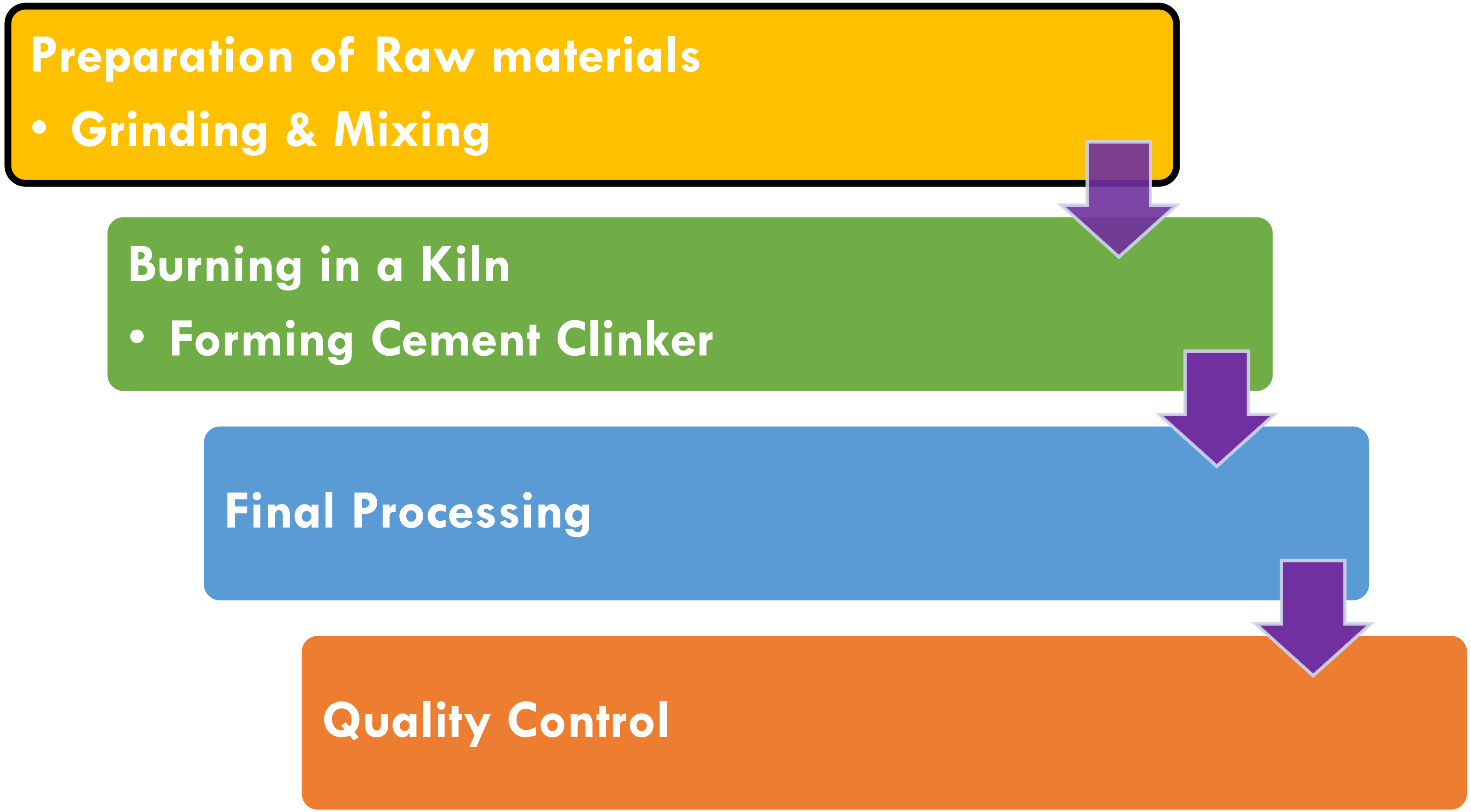
Oxide Formula	Chemical Name	Cement Notation	Mineral Name
$2CaO.SiO_2$	Di-calcium silicate	C_2S	Belite
$3CaO.SiO_2$	Tri-calcium silicate	C_3S	Alite
$3CaO.Al_2O_3$	Tri-calcium aluminate	C_3A	Aluminate
$4CaO.Al_2O_3.Fe_2O_3$	Tetracalcium aluminoferrite	C_4AF	Ferrite
$CaSO_4.2H_2O$	Calcium sulfate dihydrate	$C\bar{S}H_2$	Gypsum
$CaO.H_2O$	Calcium hydroxide	CH	Portlandite
CaO	Calcium oxide	C	Lime

Silicate phases responsible for strength development.

contribute to setting and color.

Controls setting time.

Portland Cement Manufacturing



Preparation of Raw materials
- **Grinding & Mixing**

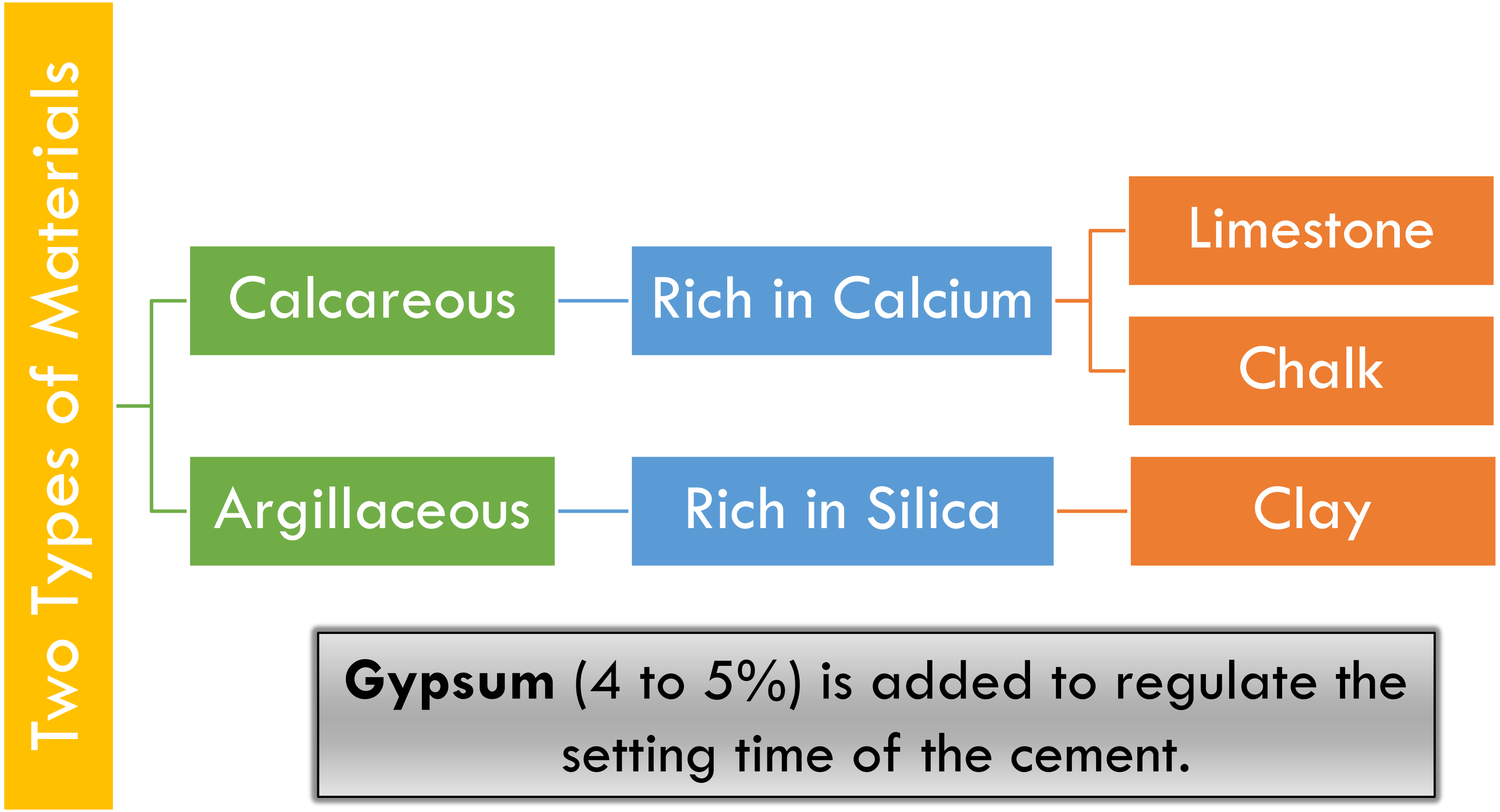
Burning in a Kiln
- **Forming Cement Clinker**

Final Processing

Quality Control

Quality Control refers to the final stage of cement manufacturing, where the produced cement is tested and verified to ensure it meets required standards and specifications.
It involves:
Chemical tests (checking composition like CaO, SiO_2, Al_2O_3).
Physical tests (fineness, setting time, compressive strength).
Process monitoring (temperature, clinker quality, uniform mixing).

Raw Materials



Two Types of Materials

Calcareous — Rich in Calcium — Limestone, Chalk

supply the **lime (CaO)** needed for clinker formation.

Argillaceous — Rich in Silica — Clay

Supply the silica (SiO_2), alumina (Al_2O_3), and iron oxides (Fe_2O_3) needed in cement production.

Gypsum (4 to 5%) is added to regulate the setting time of the cement.

Raw Materials

- Limestone (calcium carbonate) is a common source of calcium oxide.
- Iron-bearing aluminosilicates are the most common source of silica.
- Aluminum and iron oxides act as fluxing agents, i.e. lower fusion temperature of part of the raw mix to a practical firing temperature

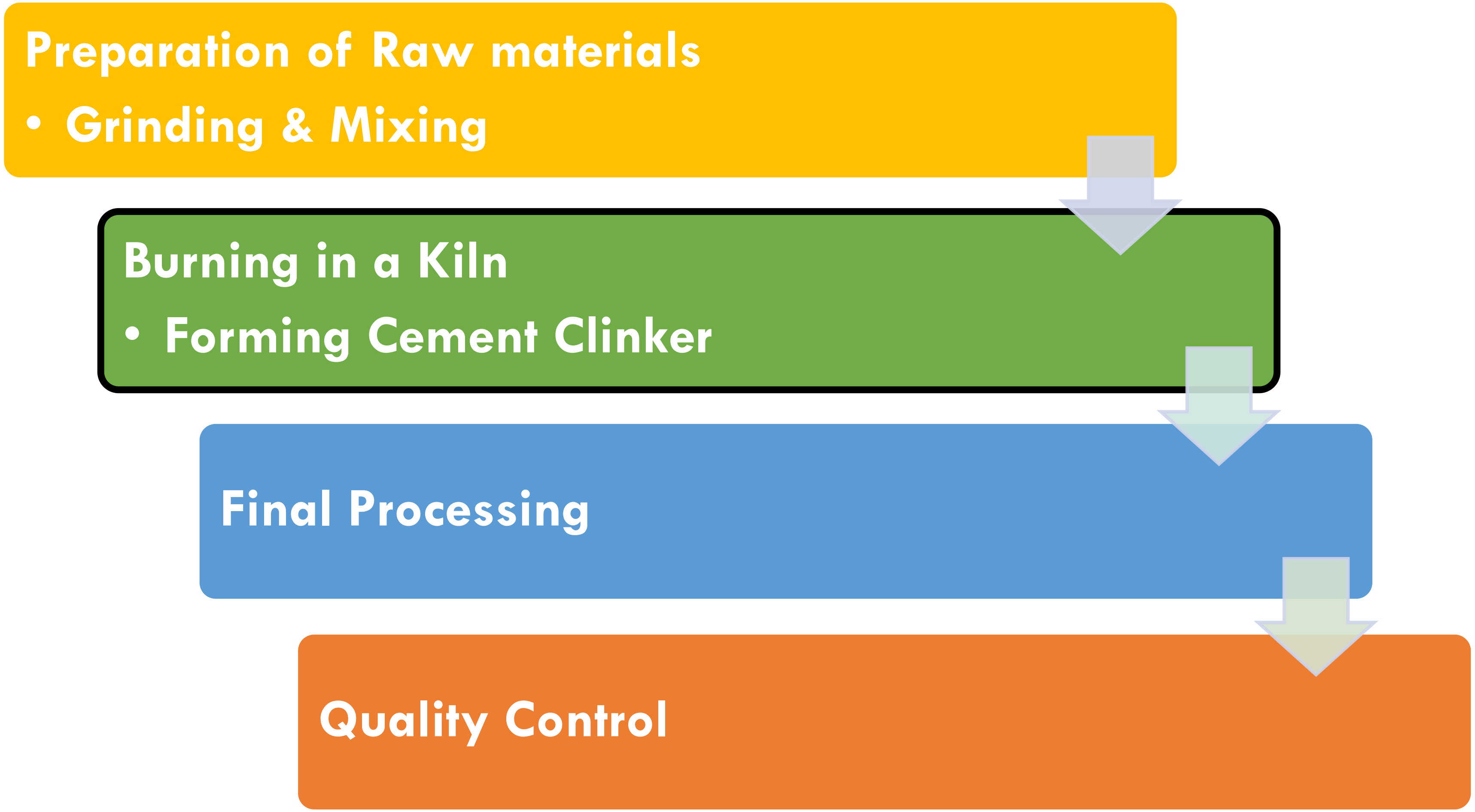
fluxing agents means that **aluminum oxide (Al_2O_3)** and **iron oxide (Fe_2O_3)** help to **reduce the melting (fusion) temperature** of the raw mix in the kiln.

By lowering the required temperature, these oxides make the **formation of clinker minerals easier and more energy-efficient,** ensuring proper reaction and sintering at practical kiln temperatures.

Raw Materials

- Grinding and blending prior to entering the kiln can be performed with the raw ingredients in the form of a slurry (the wet process) or in dry form (the dry process).
- The addition of water facilitates grinding. However, the water must then be removed by evaporation as the first step in the burning process, which requires additional energy.
- The wet process, which was once standard, has now been rendered obsolete by the development of efficient dry grinding equipment, and all modern cement plants use the dry process.
- When it is ready to enter the kiln, the dry raw mix has 85% of the particles less than 90 μm in size.

Portland Cement Manufacturing



Preparation of Raw materials
- Grinding & Mixing

Burning in a Kiln
- Forming Cement Clinker

Final Processing

Quality Control

References :

Shreve’s Book Ch. 10, pp. 171-186

https://www.understanding-cement.com/article-directory.html

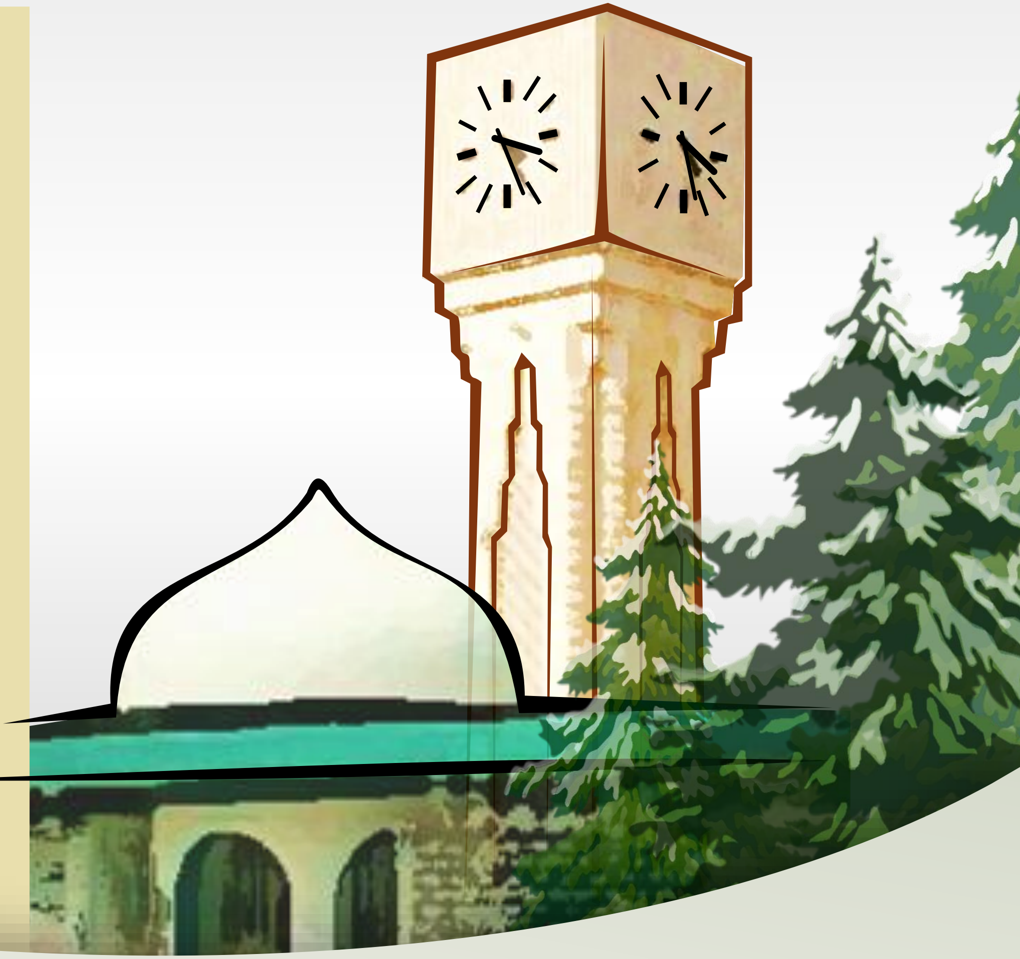
Process (2):
Cement Industry

CHE 0915481

Chemical Process Technology

Fall 2025

Dr. Hatem Alsyouri



The University of Jordan

Chemical Engineering Department

Week 7

Process (2): Cement Industry

Topics	**Lecture 3**	**Raw Materials for Cement Manufacturing** **Clinker Compounds**
	Lecture 4	**Cement Manufacturing**
Learning Outcomes	**LO3.** Describe the main stages of cement manufacturing, including raw materials, additives, clinker formation, and product differentiation between clinker, cement, and concrete, and identify major types of cement and key terminology used in the cement industry. (SO7)	

Lecture 3

Raw Materials for Cement Manufacturing
Clinker Compounds

Raw Materials

- Limestone (calcium carbonate) is a common source of calcium oxide.
- Iron-bearing aluminosilicates are the most common source of silica.
- Aluminum and iron oxides act as fluxing agents, i.e. lower fusion temperature of part of the raw mix to a practical firing temperature

Fluxing agents means that **aluminum oxide (Al_2O_3)** and **iron oxide (Fe_2O_3)** help to **reduce the melting (fusion) temperature** of the raw mix in the kiln.

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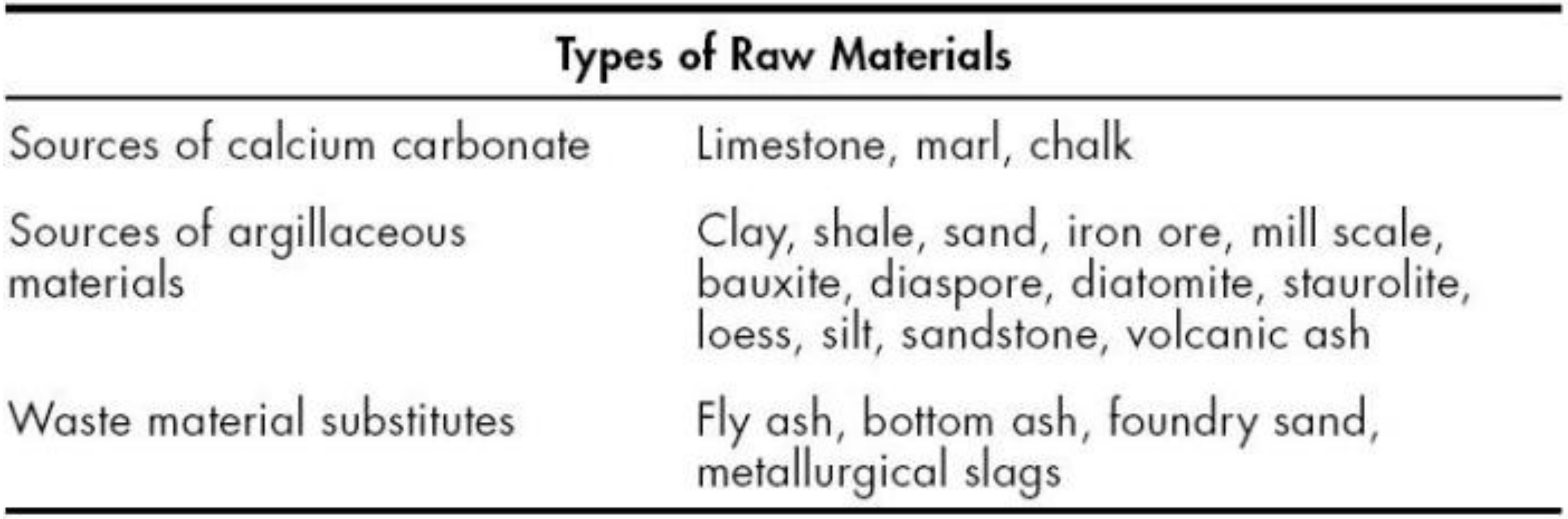
- When it is ready to enter the kiln, the dry raw mix has 85% of the particles less than 90 mm in size.

Raw Materials of Cement

The fundamental chemical compounds to produce cement **clinker** are:

- Lime (CaO)
- Silica (SiO_2)
- Alumina (Al_2O_3)
- Iron Oxide (Fe_2O_3)

Raw materials used in the production of clinker cement



Types of Raw Materials	
Sources of calcium carbonate	Limestone, marl, chalk
Sources of argillaceous materials	Clay, shale, sand, iron ore, mill scale, bauxite, diaspore, diatomite, staurolite, loess, silt, sandstone, volcanic ash
Waste material substitutes	Fly ash, bottom ash, foundry sand, metallurgical slags

FLY ASH: by-product of burning finely grounded coal either for industrial application or in the production of electricity

Sources of Raw Materials

Calcium	Iron	Silica	Alumina	Sulfate
Alkali waste	Blast-furnace flue dust	Calcium silicate	Aluminum-ore refuse	Anhydrite
Aragonite	**Clay**	Cement rock	Bauxite	Calcium sulfate
Calcite	Iron ore	**Clay**	Cement rock	**Gypsum**
Cement-kiln dust	Mill scale	Fly ash	**Clay**	
Cement rock	Ore washings	Fuller's earth	Copper slag	
Chalk	Pyrite cinders	Limestone	**Fly ash**	
Clay	**Shale**	Loess	Fuller's earth	
Fuller's earth		Marl	Granodiorite	
Limestone		Ore washings	Limestone	
Marble		Quartzite	Loess	
Marl		Rice-hull ash	Ore washings	
Seashells		Sand	**Shale**	
Shale		Sandstone	Slag	
Slag		**Shale**	Staurolite	
		Slag		
		Traprock		

Sulfate (often in the form of gypsum) is added during the grinding of the clinker to regulate the setting time of the cement and to improve shrinkage and strength development properties.

Source: PCA, 2003

Limestone (CaCO3)

Origin

- Limestone mainly originates from the accumulated shells and skeletons of plants and animals over millions of years.
- In the cement industry limestone includes calcium carbonate and magnesium carbonate.
- Most high-quality industrial limestone comes from biological sources.

Ideal Cement Raw Mix Composition

The ideal raw mix for Portland cement production contains approximately:

78% $CaCO_3$, 14% SiO_2, 2.5% Al_2O_3, and 1.75% Fe_2O_3.

Memorize the ratio

If the available limestone has lower $CaCO_3$ content or higher levels of alkalis and magnesia, it must be blended with high-grade limestone to achieve the desired composition for proper clinker formation.

Sources of Limestones

Limestone used in cement manufacturing can come from: sedimentary marine deposits, marble (metamorphosed limestone), chalk, marl, coral formations, aragonite deposits, oyster and clam shells, travertine, and tuff.

(Macfadyen, 2006), (Kussmaul, 2003): http://en.wikipedia.org/wiki/Image:Limestoneshale7342.jpg

Argillaceous Minerals

Definition:

Minerals that are rich in clay or clay-forming materials, mainly composed of silica (SiO_2) and alumina (Al_2O_3). They originate from the weathering of rocks and form the clayey part of sediments.

Clay and clay-forming materials are fine-grained natural earth materials composed mainly of hydrated aluminosilicate minerals (such as kaolinite, illite, and montmorillonite). They become plastic when wet and harden when dried or fired, which makes them important raw materials for cement and ceramics.

Sources of Argillaceous mineral:

- Clay and shale for alumina and silica
- Iron ore for iron

Other natural sources of silica and alumina are:
silt, sandstone, volcanic ash, diaspore, diatomite, bauxite

الطمي الحجر الرملي الرماد البركاني

POTENTIAL COMPOUNDS IN CLINKERS

- **Raw materials (limestone, clays, additives)**

High temperature clinker formation reactions in a kiln

$CaO = C$	$MgO = M$	$CO_2 = \overline{C}$
$SiO_2 = S$	$SO_3 = \overline{S}$	$H_2O = H$
$Al_2O_3 = A$	$Na_2O = N$	
$Fe_2O_3 = F$	$K_2O = K$	

$Ca_3SiO_5 = 3CaO.SiO_2 = C_3S$

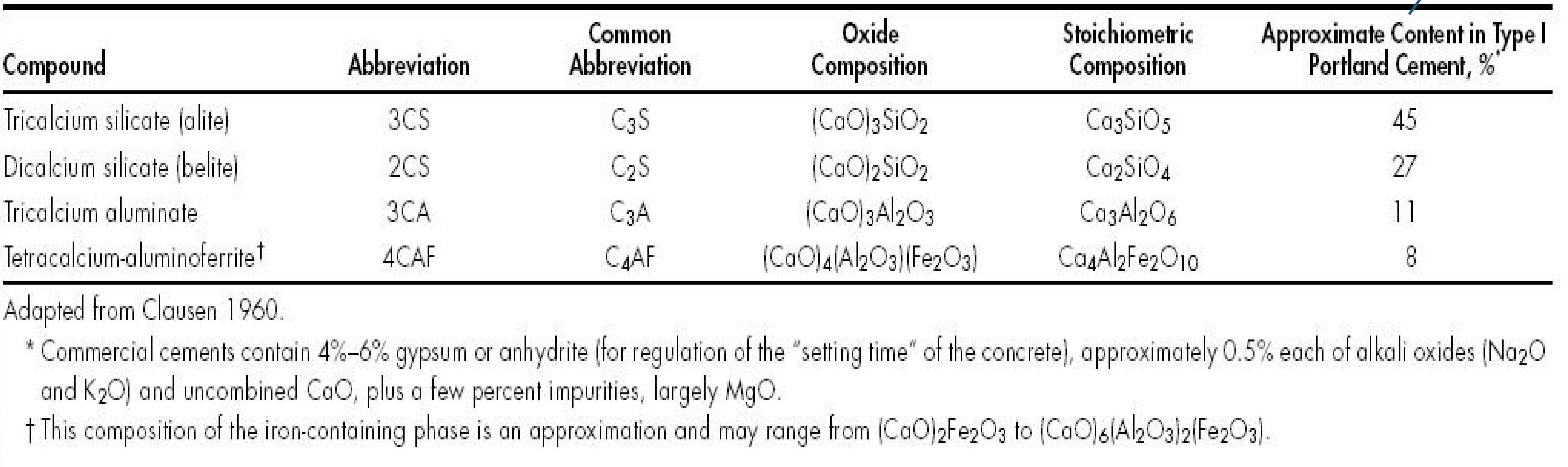
The chief strength-producing constituent of the cement (forms at 1250°C)

- **Clinker components**

$2CaO.SiO_2$	Di-calcium silicate	C_2S
$3CaO.SiO_2$	Tri-calcium silicate	C_3S
$3CaO.Al_2O_3$	Tri-calcium aluminate	C_3A
$4CaO.Al_2O_3.Fe_2O_3$	Tetracalcium aluminoferrite	C_4AF
MgO	Magnesium oxide in free state	M

Clinker compounds in Type-I Portland cement

Values for general knowledge



Compound	Abbreviation	Common Abbreviation	Oxide Composition	Stoichiometric Composition	Approximate Content in Type I Portland Cement, %*
Tricalcium silicate (alite)	3CS	C_3S	$(CaO)_3SiO_2$	Ca_3SiO_5	45
Dicalcium silicate (belite)	2CS	C_2S	$(CaO)_2SiO_2$	Ca_2SiO_4	27
Tricalcium aluminate	3CA	C_3A	$(CaO)_3Al_2O_3$	$Ca_3Al_2O_6$	11
Tetracalcium-aluminoferrite†	4CAF	C_4AF	$(CaO)_4(Al_2O_3)(Fe_2O_3)$	$Ca_4Al_2Fe_2O_{10}$	8

Adapted from Clausen 1960.

* Commercial cements contain 4%–6% gypsum or anhydrite (for regulation of the "setting time" of the concrete), approximately 0.5% each of alkali oxides (Na_2O and K_2O) and uncombined CaO, plus a few percent impurities, largely MgO.

† This composition of the iron-containing phase is an approximation and may range from $(CaO)_2Fe_2O_3$ to $(CaO)_6(Al_2O_3)_2(Fe_2O_3)$.

(Macfadyen, 2006): www.recycleworks.org/images/flyash_concrete.gif

Function of Cement Compounds

Compound	Function
C_3A	Causes initial set; but needs retardation (by gypsum)
C_3S	Provides early strength (first 7–8 days).
C_2S and C_3S	Contribute to long-term strength (up to 1 year).
Fe_2O_3, Al_2O_3, MgO, and Alkalis	Reduce the clinkering temperature.

Reference: Shreve’s Book Ch. 10, Table 10.10

END.

Lecture 4

Cement Manufacturing

Clinker Formation and Compounds

Raw materials

(limestone, clays, additives)

High temperature clinker formation reactions in a kiln

- Water evaporation
- CO_2 evolution
- Reaction between lime & clay

Clinker components

The chief strength-producing constituent of the cement (forms at 1250°C)

$2CaO.SiO_2$	Di-calcium silicate	C_2S
$3CaO.SiO_2$	Tri-calcium silicate	C_3S
$3CaO.Al_2O_3$	Tri-calcium aluminate	C_3A
$4CaO.Al_2O_3.Fe_2O_3$	Tetracalcium aluminoferrite	C_4AF
MgO	Magnesium oxide in free state	M

Main stages of Cement Manufacture

1. **Raw Materials**
   (Limestone, clay/shale, corrective materials)

2. **Preparation of Raw Mix**
   (Crushing, grinding, proportioning, and blending)

3. **Burning / Clinker Formation**
   (Preheating, calcination, sintering, fusion, and clinkering in the kiln)

4. **Final Processing**
   (Clinker cooling, gypsum addition, and final grinding to produce cement)

5. **Quality Control & Testing**
   (Chemical/physical tests for consistency and performance)

Aerial view of a cement plant

Source: PCA, 2003

Preparation of Raw Material

1. **Crushing and pre-homogenization**
   (Break raw materials and create a uniform feed)
2. **Grinding and blending of raw materials**
   (Grind into fine powder and blend to ensure constant composition)
3. **Raw meal storage and final homogenization**
   (Store the powdered mix and achieve uniform chemical properties)
4. **Process routes:**
   1. **Dry process** (most common)
   2. **Wet process** (obsolete)
   3. **Semi-dry / semi-wet process (**rare today, exist in old plants**)**

Wet Process (Mostly obsolete today)

1. Raw materials are crushed, ground, and blended so that ~80% passes a No. 200 sieve (74 µm).
2. Water (30–40%) is added to form a **slurry**, which allows easier mixing and homogenization.
3. The slurry is fed into long rotary kilns (typically **76–153 m** long and **3.6–4.8 m** in diameter).
4. Kiln temperatures reach around **1510°C (2750°F)** to form clinker.
5. Fuels: natural gas, petroleum, or coal.
   High fuel consumption due to water evaporation makes this process uneconomical.

The wet process is largely obsolete in modern cement manufacturing.

Dry Process (Modern Standard)

1. Raw materials are crushed, dried (if needed), ground, and blended so that ~80% passes a No. 200 sieve (74 µm).
2. The raw meal is fed to the **preheater tower and precalciner**, then to the rotary kiln **in a dry, powdered state**.
3. This method requires **much less fuel** because no water needs to be evaporated.
4. The dry process is more **energy-efficient**, environmentally friendly, and is the **dominant method used today**.
5. The process is dustier compared to wet process that is more efficient than grinding.

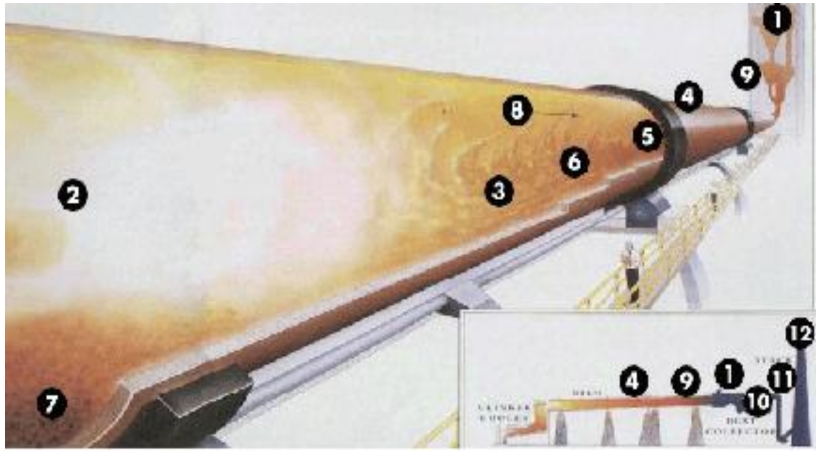
Cement Rotary Kiln

- A cement rotary kiln is a long, rotating, slightly inclined cylinder (up to 200 m long and ~6 m in diameter). It rotates slowly: about 1–2 revolutions per minute.

How it Works

- Raw meal enters at the cool (upper) end of the kiln.
- As the cylinder rotates and the material moves downward, it passes through increasing temperature zones.
- At the lower end, near the burner flame, the highest temperatures cause the formation of cement clinker nodules. The hot clinker then exits the kiln and is cooled before further processing.

Kiln Images


1
9
4
8
5
6
2
3
7
12
STACK
4
9
1
11
10
KILN
CLINKER
COOLER
DUST
COLLECTOR

Four Processes take place in the kiln

1. **Evaporation 240 to 450 °C**

2. **Calcination 600 to 1100 °C**
   - Clay decomposes (600 °C)
   - Limestone decomposes (700 °C) → CO_2 driven off
   - Formation of initial compounds (1000 °C)
   - Initial formation of C2S (1200 °C), formation of calcium aluminates and Ferrites
   - Formation of melt (flux compounds melt) (1350 °C)

3. **Clinkering – charge temperature is 1400 to 1600 °C**
   - Formation of C3S

4. **Cooling**
   - Rate of cooling significantly affects the reactivity of the final cement

Definition of the Burning Processes

- **Sintering** (become a coherent mass with no melting):

Raw materials react in the solid state and stick together **without melting**.
This is the first stage as the material heats up.

- **Fusion** (complete melting)

Higher temperatures cause **melting**, allowing reactions to proceed faster. *This occurs after sintering as the temperature rises further.*

- **Clinkering** – only about ¼ of the charge is in the liquid state

Final high-temperature stage where **about 25% of the mix becomes liquid** and the key clinker minerals (especially alite) are formed.
This is the last phase at the highest kiln temperatures.

All three steps occur sequentially inside the rotary kiln, mainly within the clinkering (burning) zone.

Key Reactions in Dry & Wet Processes

1. Calcination of Limestone (Decomposition)

When limestone is heated in the kiln, water from the raw material is driven off and limestone is decomposed into lime and Carbon Dioxide.

$$CaCO_3 \rightarrow CaO + CO_2$$

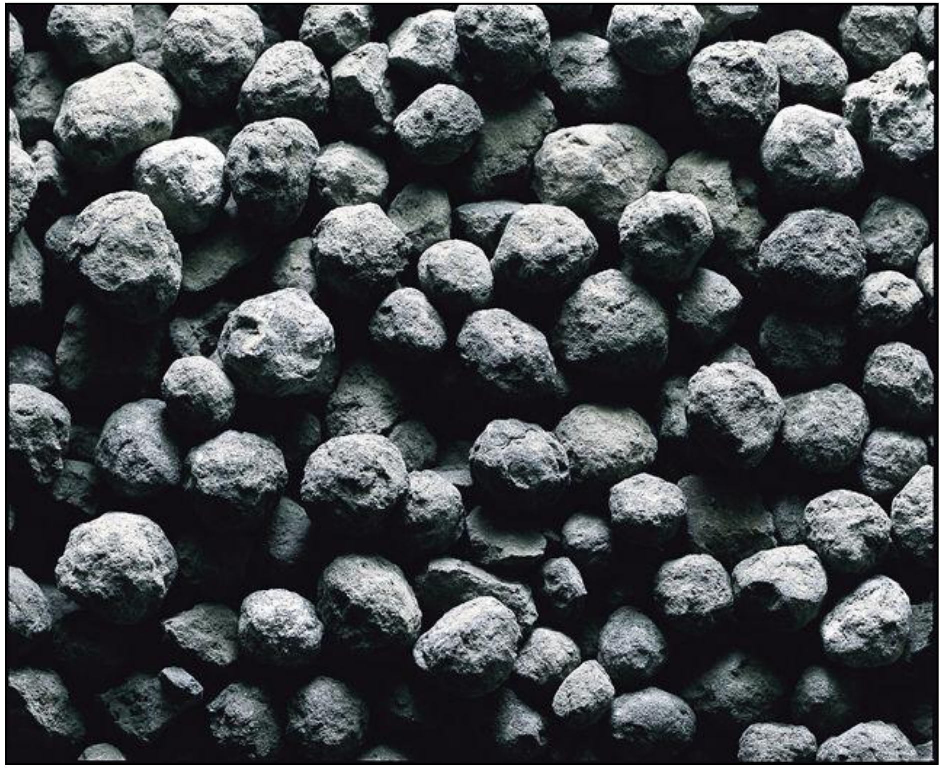
2. Formation of Calcium Aluminates and Silicates (Solid-State Reactions)

In the burning zone (portion of the kiln), silica and alumina from the clay undergo a solid state chemical reaction with lime to produce calcium aluminate.

$$CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3 \ (C_3A)$$
$$2CaO + SiO_2 \rightarrow 2CaO \cdot SiO_2 \ (C_2S)$$
$$3CaO + SiO_2 \rightarrow 3CaO \cdot SiO_2 \ (C_3S)$$

What happens inside the kiln

- ✓ The rotation and shape of kiln allow the blend to flow down the kiln, submitting it to gradually increasing temperature.
- ✓ As the material moves through hotter regions in the kiln, calcium silicates are formed
- ✓ These products, that are black or greenish black in color are in the form of small pellets, called cement clinkers
- ✓ Cement clinkers are hard, irregular and ball shaped particles about 18mm in diameter.



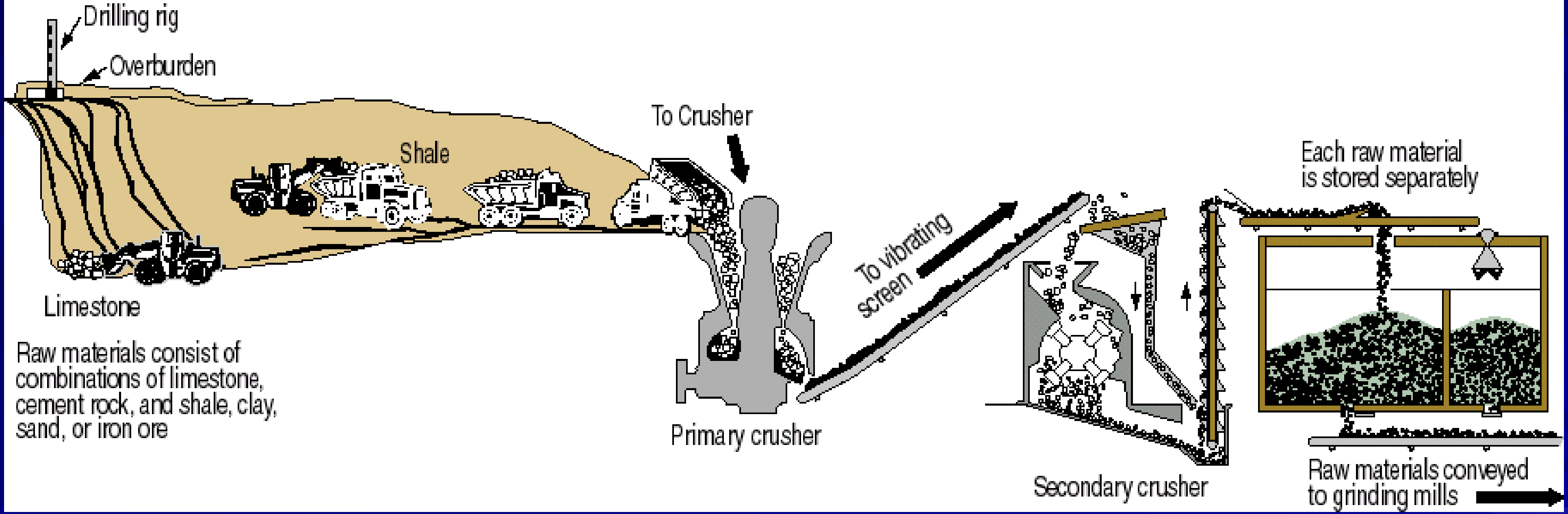
Cement Clinkers

What happens after clinkering

- ✓ The cement clinkers are cooled to about 51°C (150°F) and stored in clinker silos.
- ✓ When needed, clinker are mixed with 2-5% gypsum to retard the setting time of cement when it is mixed with water.
- ✓ The mixture is then ground to a fine powder, and the finished cement is stored in cement silos or bagged.
- ✓ Cement bags should be stored on pallets (ألواح تحميل) in a dry place.

CEMENT SILO

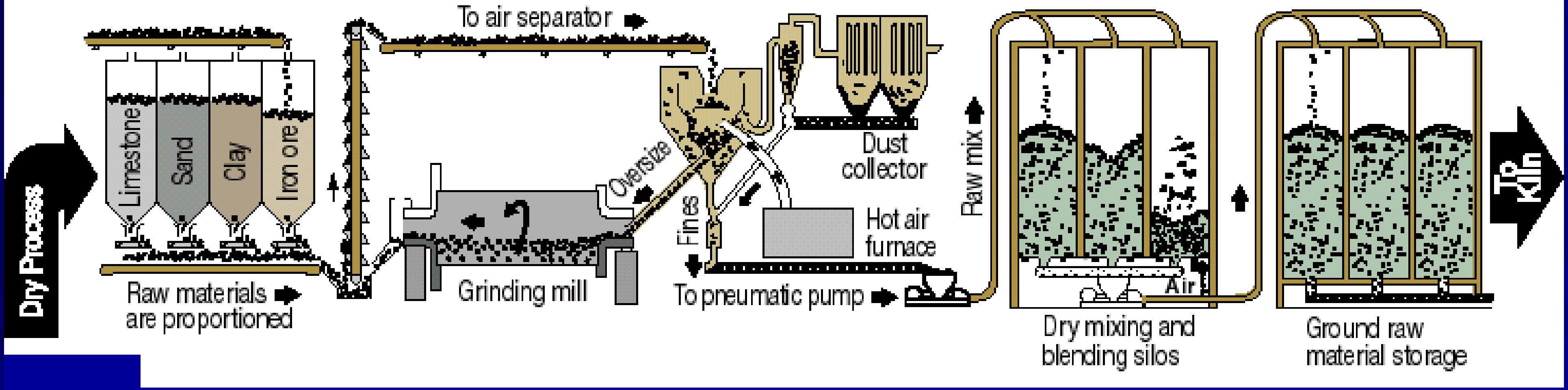
Traditional Manufacture of Portland Cement



1. Stone is first reduced to 125 mm (5 in.) size, then to 20 mm (3/4 in.), and stored.

Source: PCA, 2003

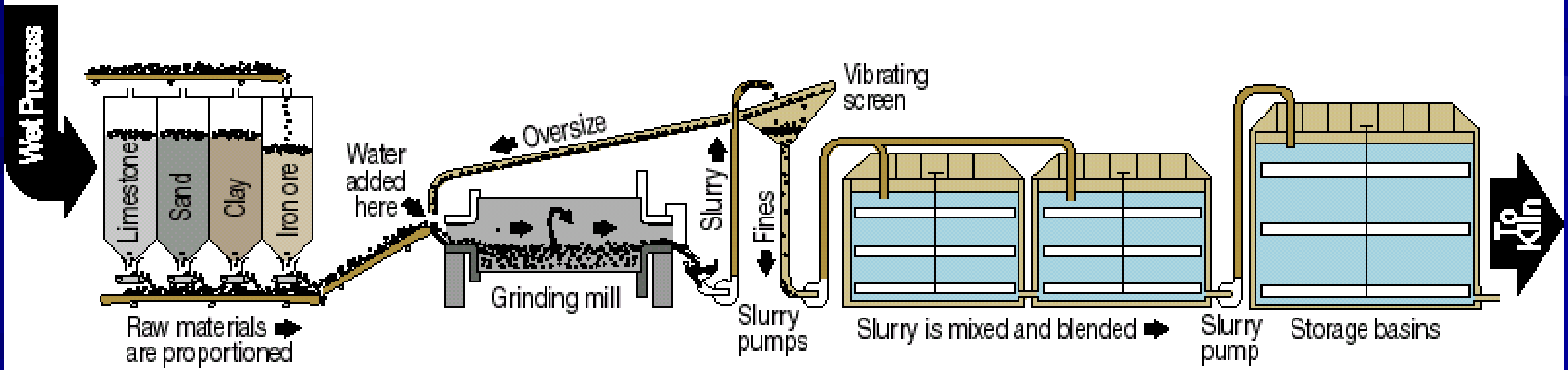
2. Raw materials are ground to powder and blended.

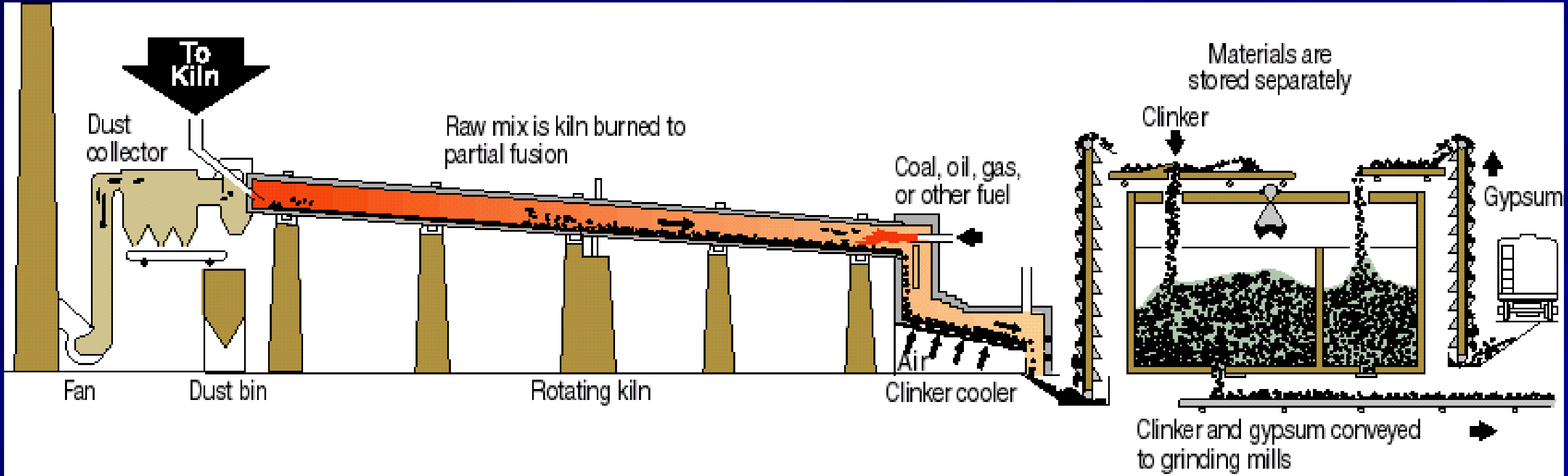


or

Source: PCA, 2003

2. Raw materials are ground, mixed with water to form slurry, and blended.





3. Burning changes raw mix chemically into cement clinker.

Source: PCA, 2003

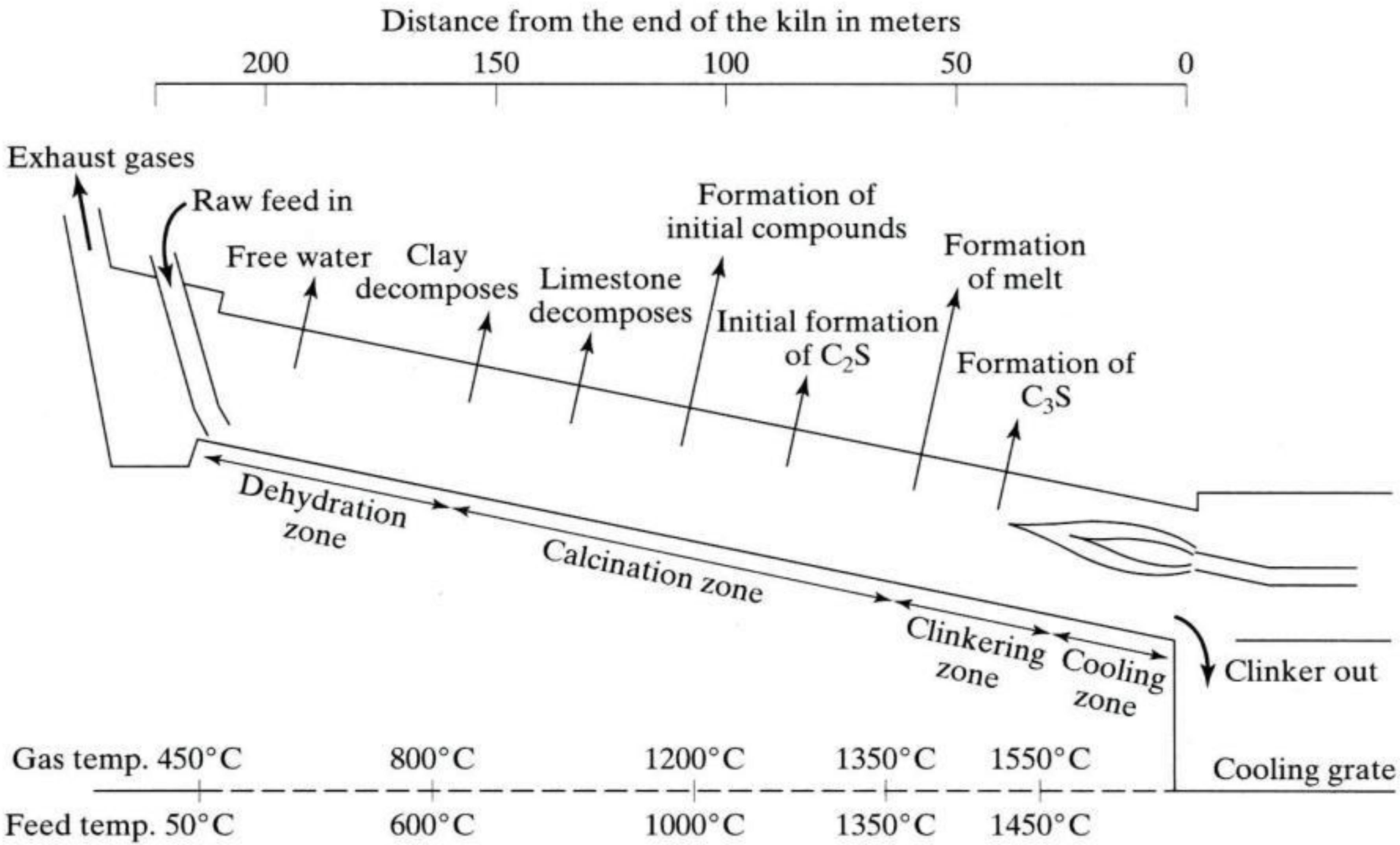


FIGURE 3.2

Schematic outline of conditions and reactions in a typical dry-process rotary kiln. When suspension preheaters are used, dehydration and initial calcination takes place outside the kiln in the preheater tower.

Source: Mindess, Young, and Darwin, 2004

END.

Shreve’s Book, Chapter 9 (pp. 149 – 155)
and other References are used in this topic

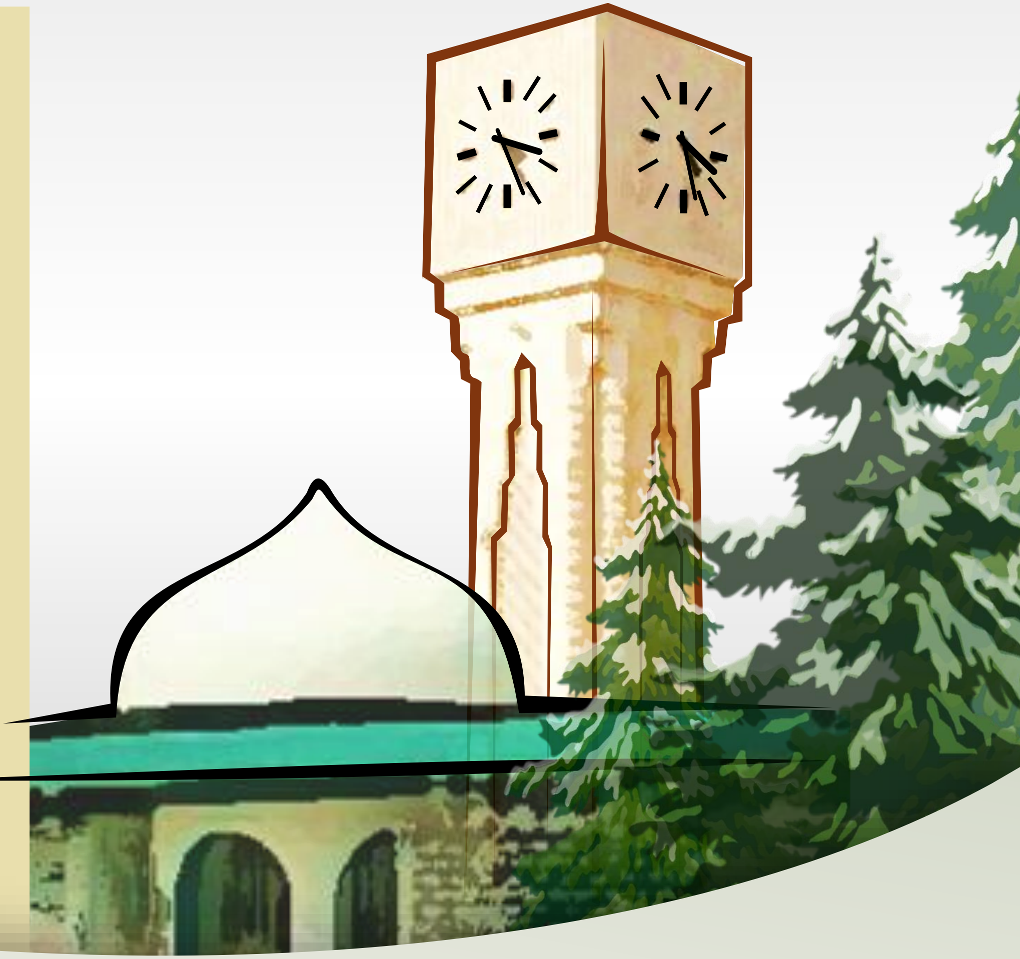
Process (3):
Ceramics Industry

CHE 0915481

Chemical Process Technology

Fall 2025

Dr. Hatem Alsyouri



The University of Jordan
Chemical Engineering Department

Lecture 1

I. Introduction to Ceramics
II. Introduction to Raw Materials & Their Functions

I. Introduction to Ceramics

What are Ceramic Materials

- ❑ Ceramics are inorganic, non-metallic materials formed by shaping raw minerals and hardening them through firing.
- ❑ They include traditional ceramics (bricks, tiles, porcelain) and advanced ceramics (alumina, zirconia, filters, sensors).
- ❑ Ceramics are known for being hard, strong, heat-resistant, and chemically stable.
- ❑ The unique properties of ceramics are due to strong ionic and covalent bonds that leads directly to:
  - High Melting Points (High lattice energy).
  - High Hardness and Strength (Rigid structure).
  - Chemical Stability/Inertness (Requires high energy to break bonds).
  - Electrical and Thermal Insulation (Lack of free electrons).


Schamotte
Fireclay
0-10%
Kaolin
Kaolin

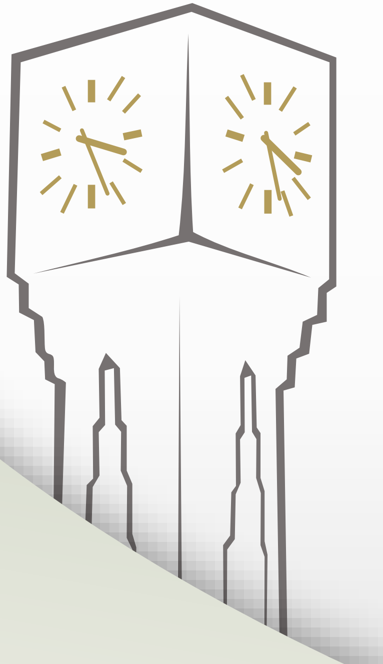

GLOBAL CERAMICS

Examples of Ceramic Products

- ☐ **Whitewares** (pottery, porcelain, stoneware, etc.)
- ☐ **Structural Clay Products** (Building brick, sewer pipes, etc.)
- ☐ **Refractories** (Firebricks, silicon carbide refractories, etc.)
- ☐ **Glasses**
- ☐ **Enamels and enameled metals** الطلاء بالمينا والمعادن المطلية بالمينا
- ☐ **Ceramic composites**
- ☐ **Abrasives**

Importance of Ceramics in Daily Life

- ☐ **Used in construction** (tiles, bricks, pipes), household products (dishes, sanitary ware), and industrial equipment (refractories, filters).
- ☐ **Essential in technology** (insulators, capacitors, coatings) and healthcare (dental ceramics, implants).
- ☐ **Their unique properties (**high temperature resistance, durability, corrosion resistance, and electrical insulation) make them vital across many industries.



II. Introduction to Raw Materials & Their Functions

What are Ceramic Raw Materials?

- ☐ Ceramic raw materials are naturally occurring minerals or synthetic powders used to create ceramic bodies with specific properties.
- ☐ Traditional ceramics mainly rely on natural minerals such as clays, silica, and feldspar, while advanced ceramics use engineered powders such as alumina and zirconia.

Functions and Selection Criteria of Raw Materials

1. Plasticity & Workability
Provided mainly by clays
Enables shaping, extrusion, molding

2. Structural Strength in the Green Body
Clay and quartz contribute to rigidity before firing

3. Control of Drying & Firing Shrinkage
Quartz reduces shrinkage
Ball clay increases shrinkage

4. Vitrification Behavior
Feldspar melts → forms glassy phase
Governs porosity, density, mechanical strength

5. Thermal & Mechanical Properties
Refractories (Al_2O_3, MgO) improve heat resistance
Silica improves thermal shock behavior

6. Color & Opacity
Fe_2O_3 → brown/red
TiO_2, ZrO_2 → opacity
CuO, CoO → decorative colors

Definitions

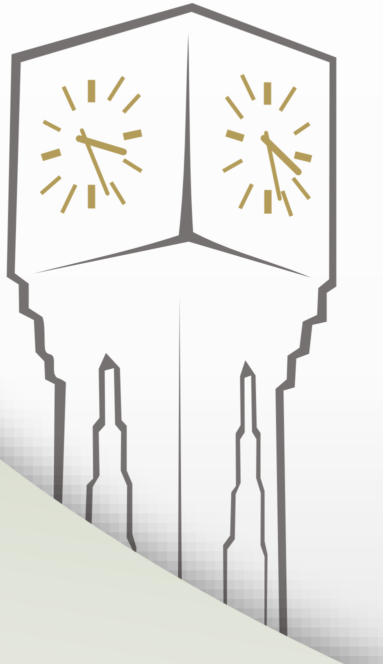
Plasticity: The ability of the clay-water mixture to undergo permanent deformation without cracking. It's an issue of **rheology**.

Green Body: The unfired, shaped ceramic article held together by capillary forces and binders, possessing sufficient green strength for handling before firing.

Vitrification: The formation of a non-crystalline (glassy) phase that fills the pores of the ceramic body during firing, leading to densification and strength increase.

Lecture 2

III. Classification and Types of Raw Materials



III. Classification and Types of Raw Materials

Major Classes of Raw Materials

1. Plastic (Clay-Based) Materials

Used for shaping and workability

Examples: Kaolinite, Ball clay, Bentonite / Montmorillonite, Illite

2. Non-Plastic (Inert) Materials

Control shrinkage, strength, and thermal stability

Examples: Quartz (silica), Alumina, Magnesia, Talc

3. Fluxes (Melting Aids)

Lower melting and vitrification temperature

Examples: Feldspar (potash, soda), Lead oxide, Borates, Sodium carbonate, Dolomite

4. Additives (Functional Agents)

Modify color, opacity, porosity, plasticity.

Examples

- Colorants: (Fe_2O_3, CoO, CuO),
- Opacifiers: TiO_2, ZrO_2, SnO_2
- Binders: lignin, PVA
- Deflocculants: sodium silicate مُشتِّتات / مخفِّفات اللزوجة
- Strengtheners: MgO, alumina

Raw materials are chosen to balance:

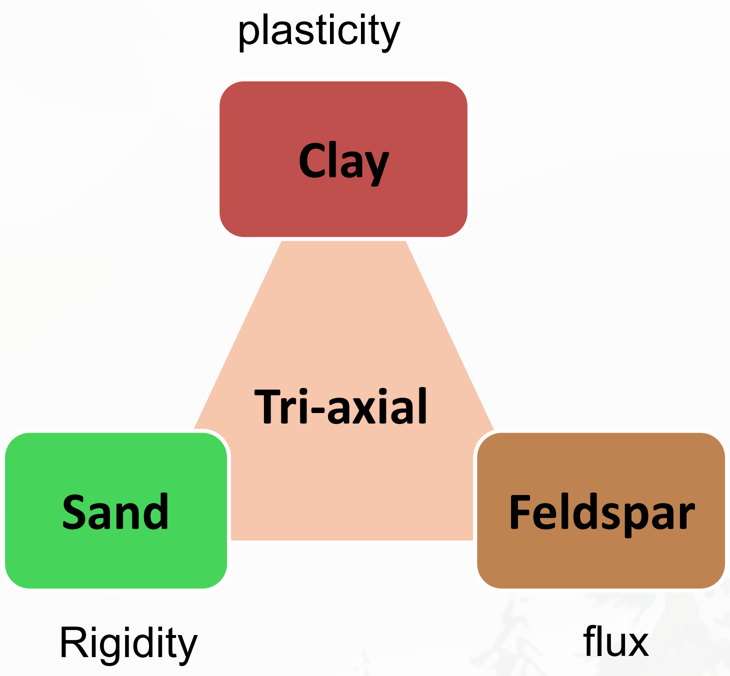
Plasticity → shaping,
Strength → structure,
Melting → vitrification,
Final performance → color, porosity, durability.

Tri-Axial Body Composition and Blending

Tri-Axial Ceramic Body Composition

Ceramic bodies are commonly formulated from three key components:

- **Clay (≈ 50%)**
  Provides plasticity, green strength, and workability.
- **Feldspar (≈ 25%)**
  Acts as a flux; promotes vitrification and reduces firing temperature.
- **Quartz/Silica (≈ 25%)**
  Controls shrinkage, improves rigidity, and stabilizes thermal behavior.



plasticity

Clay

Tri-axial

Sand

Feldspar

Rigidity

flux

Importance of Proper Blending

- Ensures uniform distribution of particle types and sizes
- Prevents defects such as cracking, warping, or uneven firing
- Controls plasticity and drying behavior of the body
- Supports consistent sintering and predictable shrinkage
- Helps achieve stable color and final product quality

Definition

Tri-Axial Ceramic Body: A traditional ceramic composition standardized by three main components: Clay (for plasticity), Flux (for vitrification/melting), and Filler (for strength/shrinkage control).

Key Components: Mineralogy and Properties

Clay

- Impure hydrated aluminum-silicates originating from feldspar mineral by weathering of igneous rocks
- There are many clay minerals, which contains mixtures of kaolinite, montmorillonite (bentonite), and illite.
- Clays are plastics and moldable when sufficiently pulverized and wet
- Clays are rigid when dry, vitreous when fired at suitable temperature

Feldspar

- A common mineral composed of silica alumina.
- There are 3 major types of feldspars: Potash feldspar, soda feldspar, and lime feldspar.
- Feldspar is an important fluxing constituent in ceramics

Sand

- Also called flint, a natural material composed of granular minerals
- It is composed mainly of silica (in the form of quartz)

Kaolinite Chemical Formula and Structure

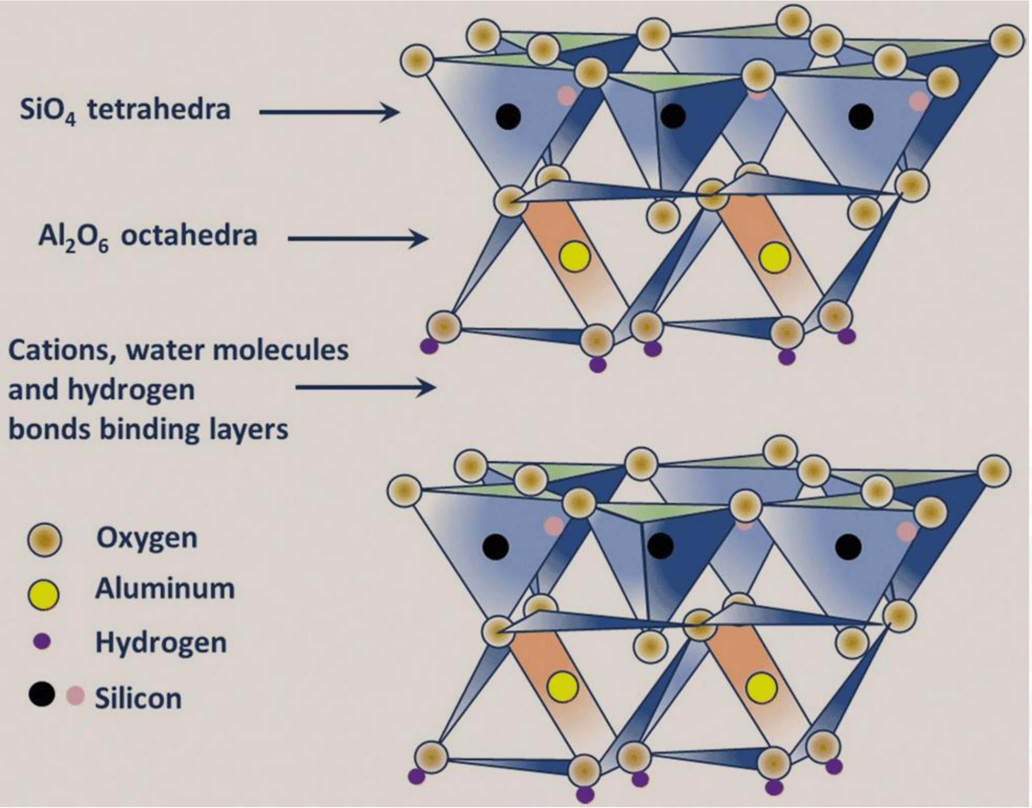
Mineral: Kaolinite (main Clay mineral)

Chemical Formula:
$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ **or** $Al_2(Si_2O_5)(OH)_4$

Key Structural Feature
Kaolinite consists of alternating sheets
1:1 Layered Silicate

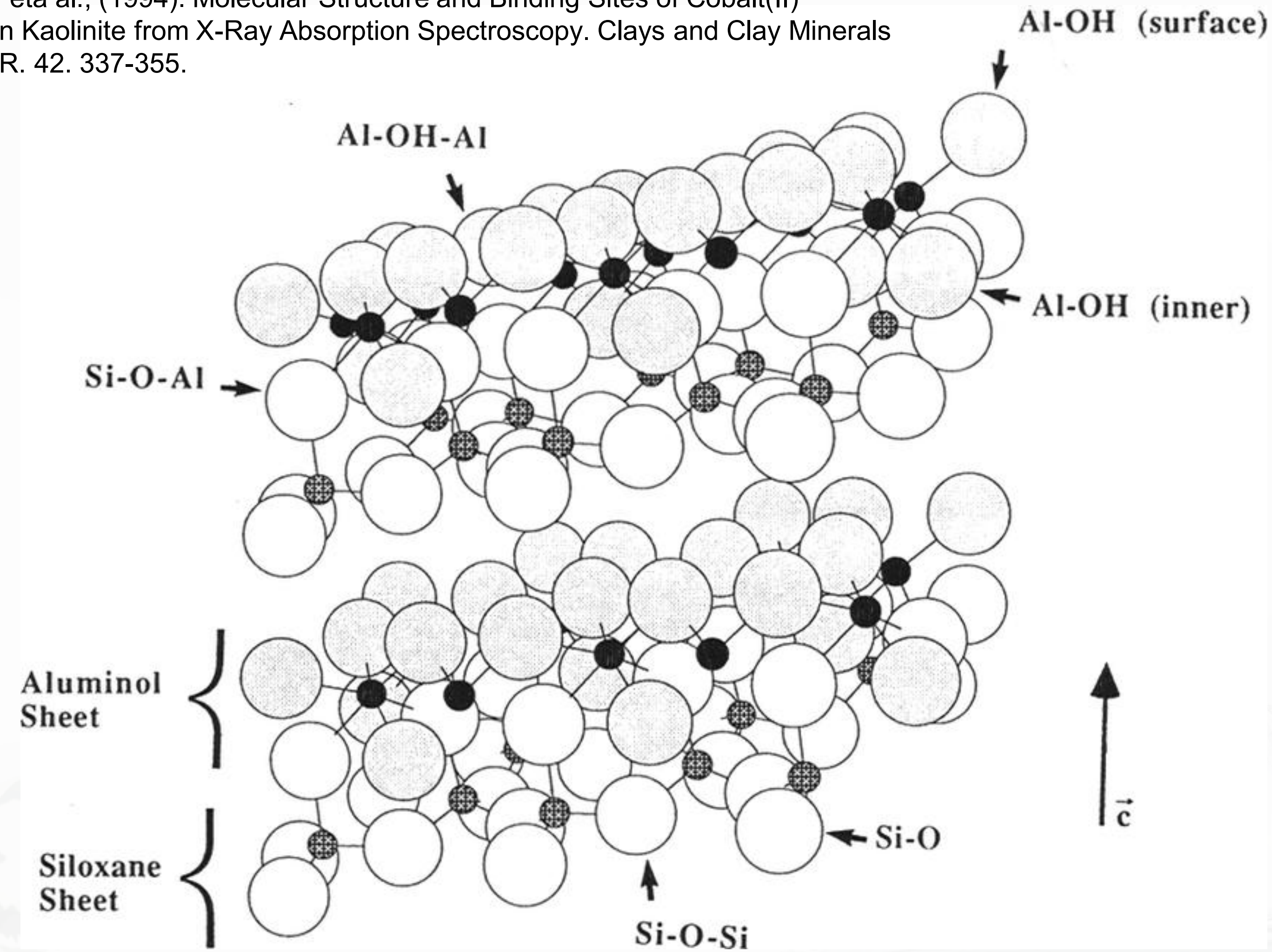
- One tetrahedral SiO_4 layer
- One octahedral $Al(OH)_6$ layer

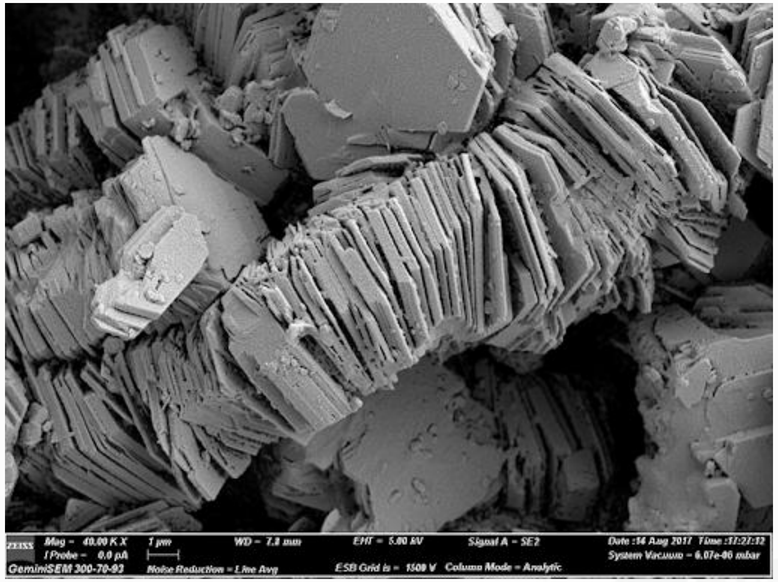
Engineering Relevance: This sheet structure allows the layers to slide past one another when wetted, which is the primary source of the clay's essential plasticity..



Two layers of Kaolinite with **Si^{4+} tetrahedra** and **Al^{3+} octahedra**. Each are bonded to oxygen atoms (orange) and hydroxyl groups allow for hydrogen bonding between the layers.

Reference: O'Day, P. eta al., (1994). Molecular Structure and Binding Sites of Cobalt(II) Surface Complexes on Kaolinite from X-Ray Absorption Spectroscopy. Clays and Clay Minerals - CLAYS CLAY MINER. 42. 337-355.

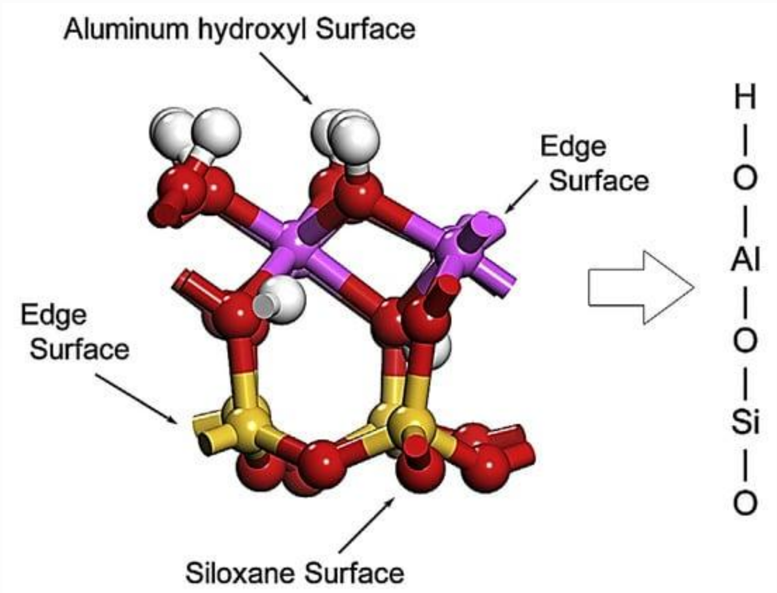




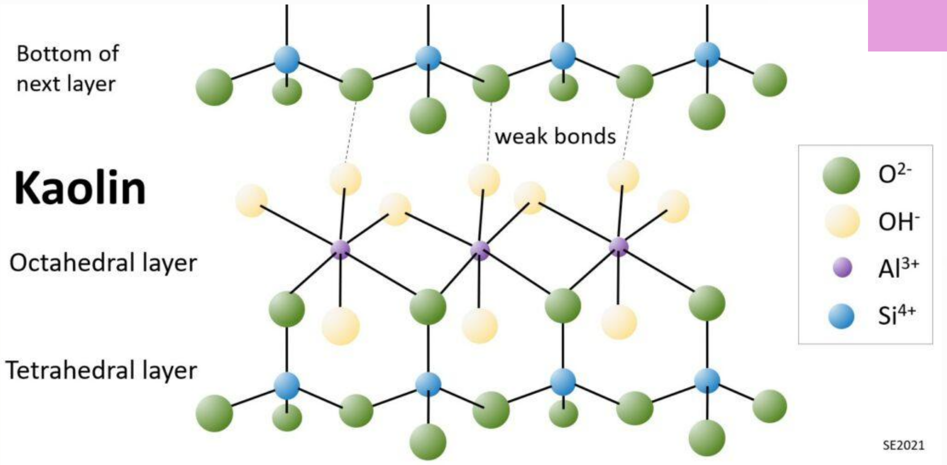
Scanning Electron Micrograph Showing Plates of the Clay Mineral Kaolin

Kaolinite crystal structure showing the aluminol and siloxane sheets forming 1:1 layers, and surface oxygen atoms exposed on faces that may act as reactive surface sorption sites. Atoms: Al = solid; Si = hatched; O = open; OH = shaded.

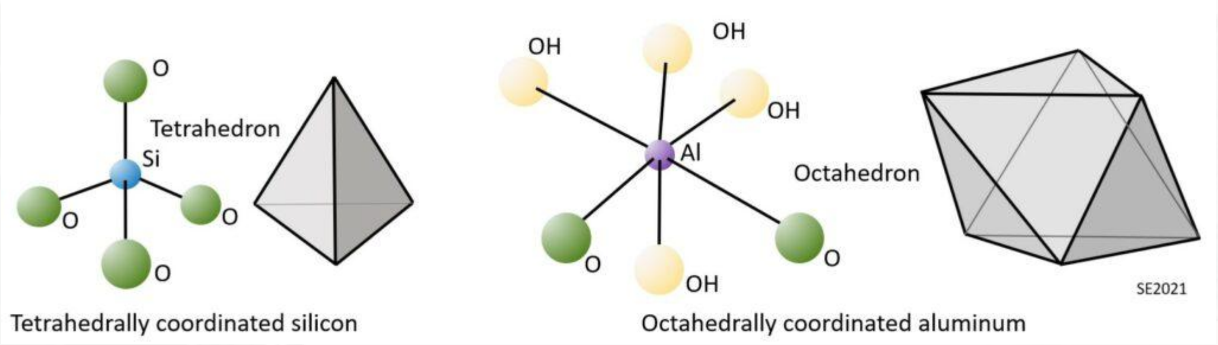
Self Reading



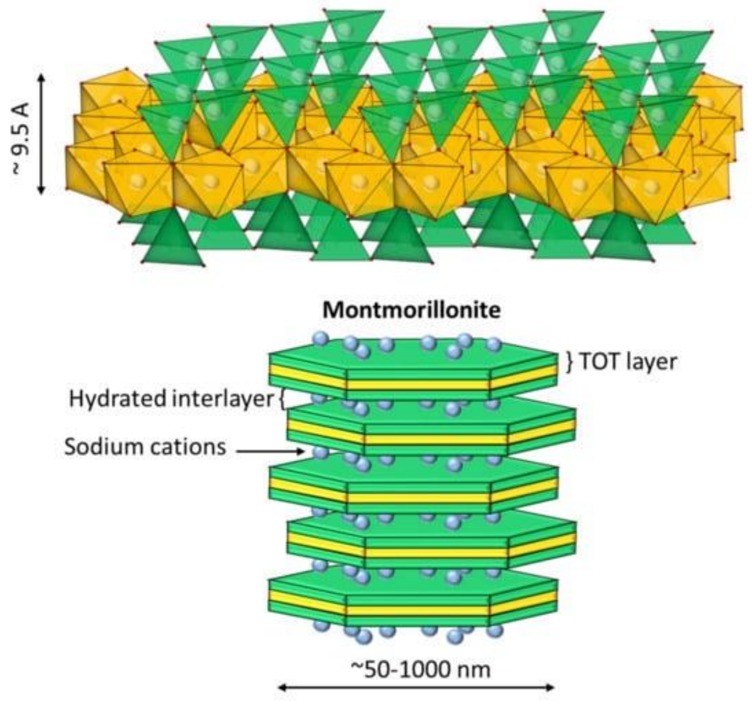
Structure of kaolinite primitive cell (white, hydrogen; red oxygen; pink, aluminum; yellow, silicon).



Representation of the Tetrahedral-Octahedral Layer Structure of the 1:1 Clay Mineral Kaolin. The layers are held together with weak van der Waals bonds.

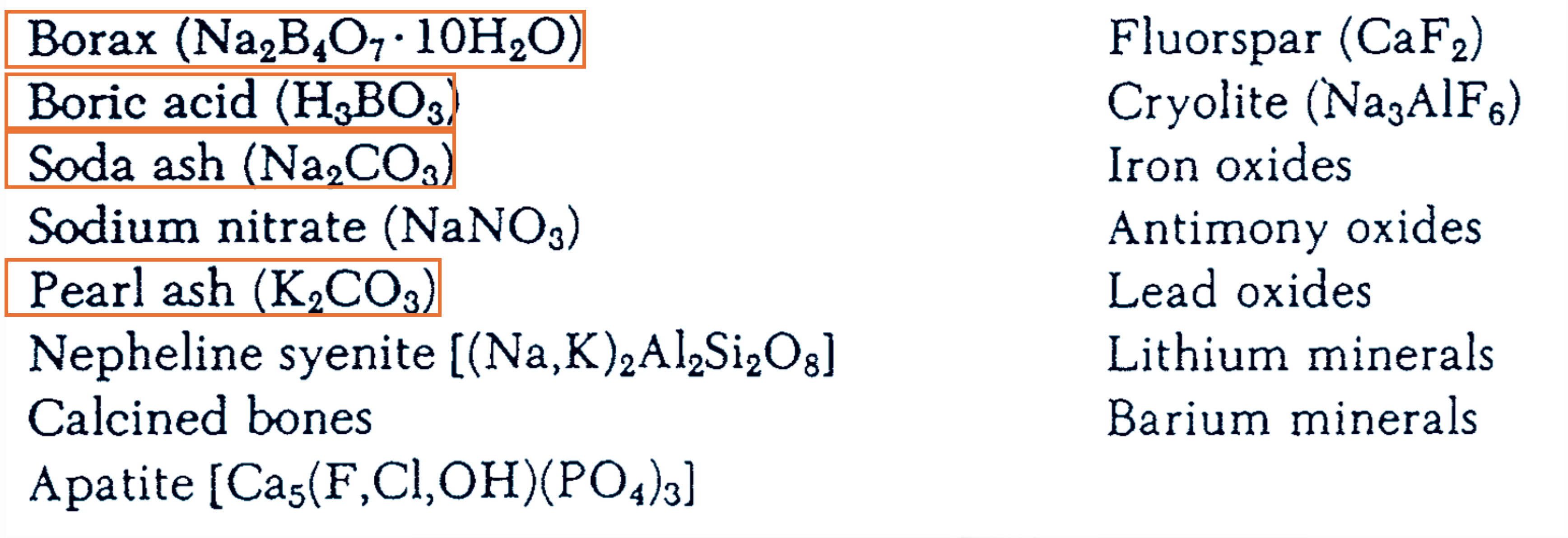


Representations of the Silica Tetrahedra and Aluminum Octahedra That Combine to Form Clay Minerals



Structure of Na-montmorillonite. The green sheet indicates a tetrahedral silica layer (T), the yellow sheet indicates an octahedral alumina layer (O), and the blue spheres represent sodium cations.

Examples of Specialized Fluxing Agents

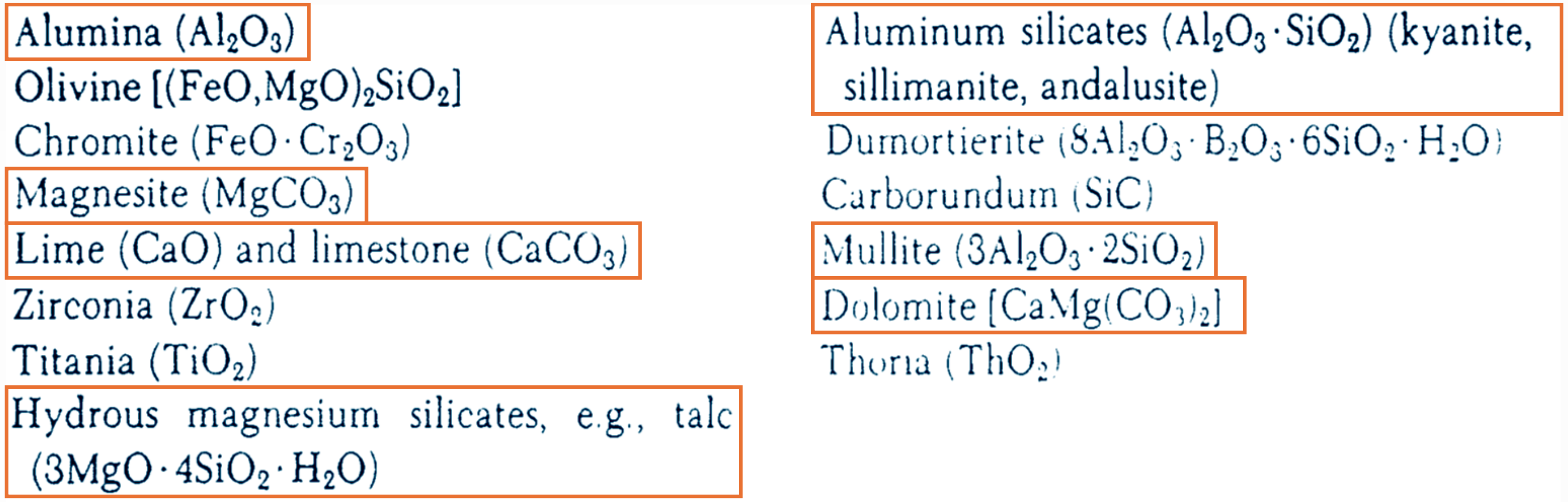


- Borax ($Na_2B_4O_7 \cdot 10H_2O$)
- Boric acid (H_3BO_3)
- Soda ash (Na_2CO_3)
- Sodium nitrate ($NaNO_3$)
- Pearl ash (K_2CO_3)
- Nepheline syenite [$(Na,K)_2Al_2Si_2O_8$]
- Calcined bones
- Apatite [$Ca_5(F,Cl,OH)(PO_4)_3$]
- Fluorspar (CaF_2)
- Cryolite (Na_3AlF_6)
- Iron oxides
- Antimony oxides
- Lead oxides
- Lithium minerals
- Barium minerals

Key Fluxing Minerals in Ceramics

Mineral Class	Common Example	Chemical Formula	Role in Ceramics
Potassium Feldspar	Microcline / Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	Primary source of K_2O flux
Sodium Feldspar	Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	Primary source of Na_2O flux
Calcite	Limestone	$CaCO_3$	Source of CaO flux

Examples of Specialized Refractory Agents



- Alumina (Al_2O_3)
- Olivine [$(FeO,MgO)_2SiO_2$]
- Chromite ($FeO \cdot Cr_2O_3$)
- Magnesite ($MgCO_3$)
- Lime (CaO) and limestone ($CaCO_3$)
- Zirconia (ZrO_2)
- Titania (TiO_2)
- Hydrous magnesium silicates, e.g., talc ($3MgO \cdot 4SiO_2 \cdot H_2O$)
- Aluminum silicates ($Al_2O_3 \cdot SiO_2$) (kyanite, sillimanite, andalusite)
- Dumortierite ($8Al_2O_3 \cdot B_2O_3 \cdot 6SiO_2 \cdot H_2O$)
- Carborundum (SiC)
- Mullite ($3Al_2O_3 \cdot 2SiO_2$)
- Dolomite [$CaMg(CO_3)_2$]
- Thoria (ThO_2)

Refractory Property:
The material's capacity to withstand high temperatures (> 1500°C) without softening, deformation, melting, or failure under load (mechanical stress) or chemical attack.

The melting point of Al2O3 (~2050°C) as a reference.

END.

Shreve’s Book, Chapter 9 (pp. 149 – 155)
and other References are used in this topic

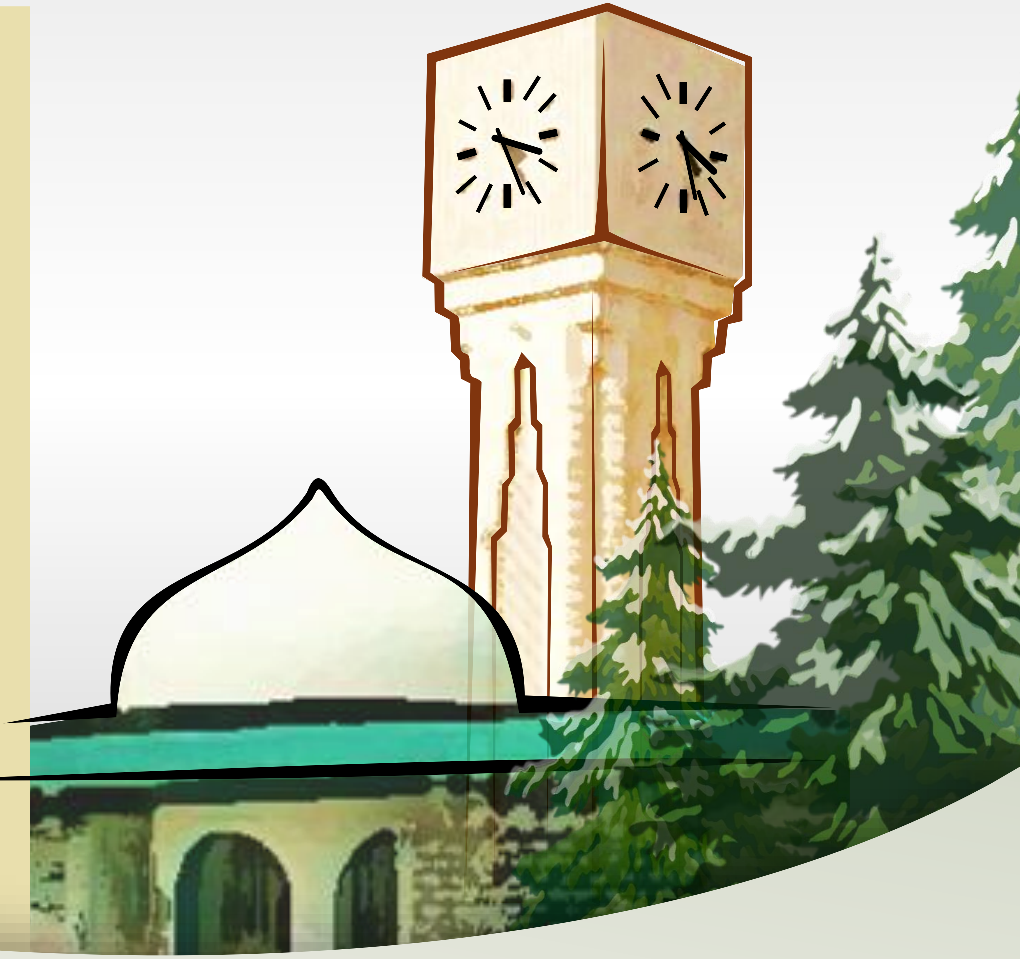
Process (3):
Ceramics Industry

CHE 0915481

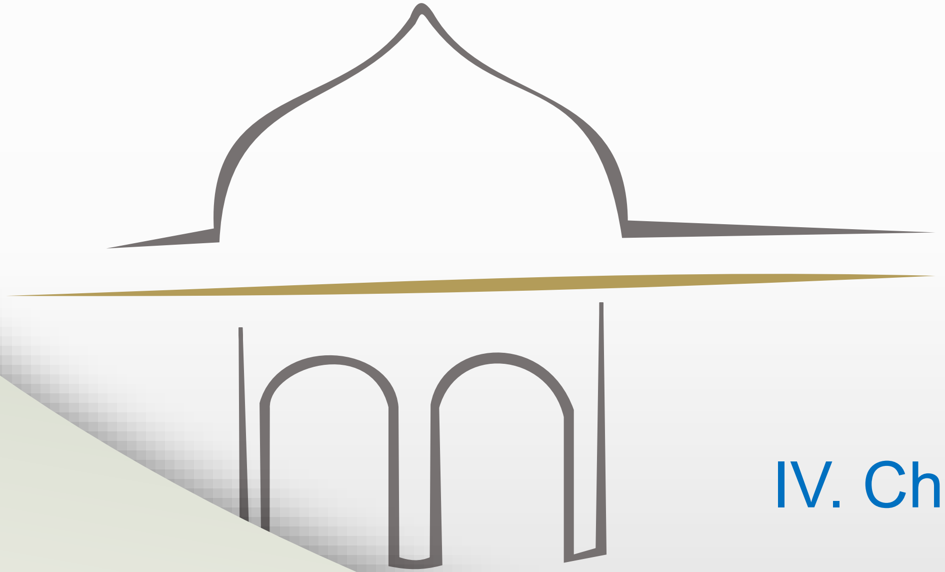
Chemical Process Technology

Fall 2025

Dr. Hatem Alsyouri



The University of Jordan
Chemical Engineering Department



Lecture 3

IV. Chemistry, Mineralogy, and Thermal Behavior

IV. Chemistry, Mineralogy, and Thermal Behavior

Chemical Basis: Key Oxide Components

Ceramic raw materials are mainly composed of oxides. Their proportions control plasticity, vitrification, sintering, and final product strength.

Key Point
The balance between SiO_2, Al_2O_3, and flux oxides determines firing behavior, vitrification level, porosity, and final strength.

1. Alumina (Al_2O_3)

- Increases **strength, toughness, and refractoriness**
- Essential in forming mullite during firing
- Higher Al_2O_3 → higher firing temperature
- Source: clays, bauxite, kaolin

2. Silica (SiO_2)

- Major structural oxide in ceramics
- Controls **refractoriness**, hardness, and thermal expansion
- Too much → high shrinkage & risk of cracking
- Source: quartz, sand

Chemical Basis: Key Oxide Components

3. Flux Oxides (K_2O, Na_2O, CaO, MgO)

Fluxes lower the melting point and promote vitrification.

K_2O / Na_2O (alkali fluxes):

- Found in feldspar
- Strong glass formers → enhance vitrification and densification
- Too much may increase thermal expansion

CaO:

- Provides stable glass structures
- Improves chemical durability
- Source: limestone, feldspar

MgO:

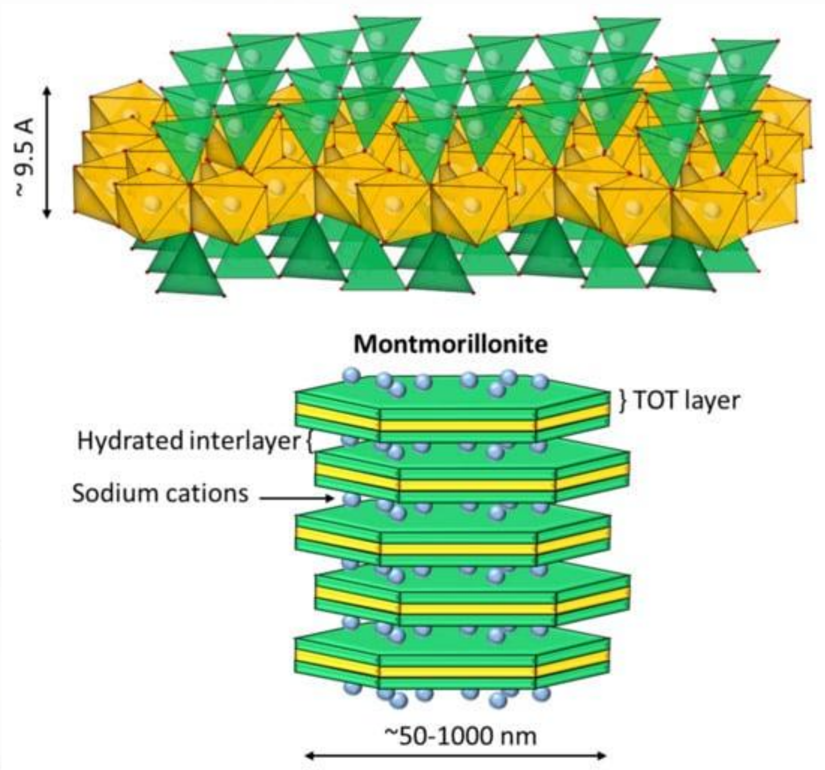
- Helps control thermal expansion
- Contributes to crystal formation in some ceramics
- Source: dolomite, talc

Fluxing Mechanism: Network Modifiers

Fluxing Definition: Fluxes (K_2O, Na_2O, CaO) are critical because they act as network modifiers in the SiO2 glass structure.

Mechanism: SiO_2 forms a strong, continuous tetrahedral network. When alkali or alkaline earth oxides are introduced:

1. The metal ion (Na+) enters an interstitial position.
2. The oxygen from the flux (e.g., Na_2O) breaks a strong Si-O-Si bridge, creating a non-bridging oxygen atom.
3. This disrupts the rigid network structure, dramatically reducing the internal friction and, therefore, the melt's viscosity.



Result: The lower viscosity allows the glassy phase to flow and fill pores at lower temperatures, effectively lowering the vitrification temperature and promoting densification.

Chemical Conversion during Firing

- Ceramic processing consist of these general steps:

Mixing → Shaping → Firing (700 – 2000°C)

- Such temperatures cause a number of reactions which are the bases of chemical conversion:

1. **Dehydration:** Chemical water smoking at 150 – 650°C
2. **Calcination;** e.g., of $CaCO_3$ at 600 – 900°C
3. **Oxidation** of ferrous and organic matter at 350 – 900°C
4. **Silicate formation** at 900°C and higher (phase change according to phase diagram)

Reactions of Clay (Kaolinite) Heating

Definition of Amorphous and Crystalline (next slide)

- Driving off water of hydration
  - occurs at 600 – 650 °C and absorbs much heat
  - leaves an amorphous mixture of alumina and silica

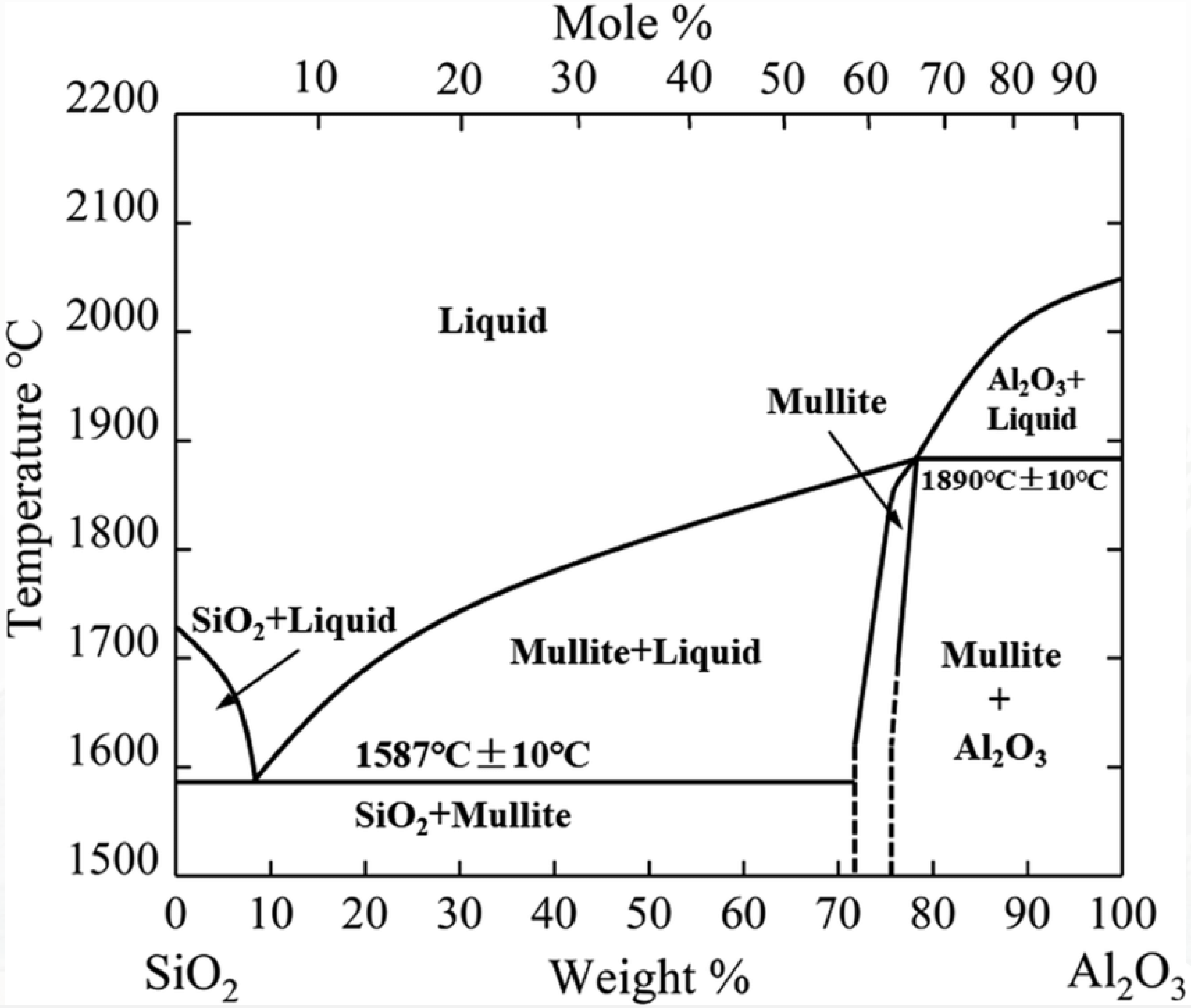
$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 + 2SiO_2 + 2H_2O$$

- Amorphous alumina changes sharply at 940 °C to crystalline form, **γ-alumina**, with the evolution of considerable heat.
- At about 1000 °C, alumina and silica combine to form **mullite** ($3Al_2O_3 \cdot 2SiO_2$)
- At higher temperature, remaining silica is converted to crystalline **cristobalite**.
- Overall reaction:

$$\underbrace{3(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)}_{\textit{Kaolinite}} \rightarrow \underbrace{3Al_2O_3 \cdot 2SiO_2}_{\textit{Mullite}} + \underbrace{4SiO_2}_{\textit{Cristobalite}} + 6H_2O$$

Al_2O_3/SiO_2 System Phase Diagram

- **Mullite Formation**: The diagram shows the stability of Mullite ($3Al_2O_3 \cdot 2SiO_2$), the primary crystalline phase that gives the ceramic its high-temperature strength and low thermal expansion.
- **Glassy Phase** nucleation: The eutectic point (at ~1595 °C) is the minimum temperature at which a liquid (glassy) phase can form, even if the pure components melt much higher.
- **Vitrification Mechanism**: The liquid phase acts as a cementing matrix binding the Mullite grains. This liquid enables Vitrification (densification), eliminating porosity.
- **Role of Fluxes**: Ceramic fluxes (K_2O, Na_2O) are added to drastically lower the eutectic temperature (introducing a ternary eutectic), ensuring the glassy phase forms at practical, industrial firing temperatures (~1000 °C – 1200 °C).

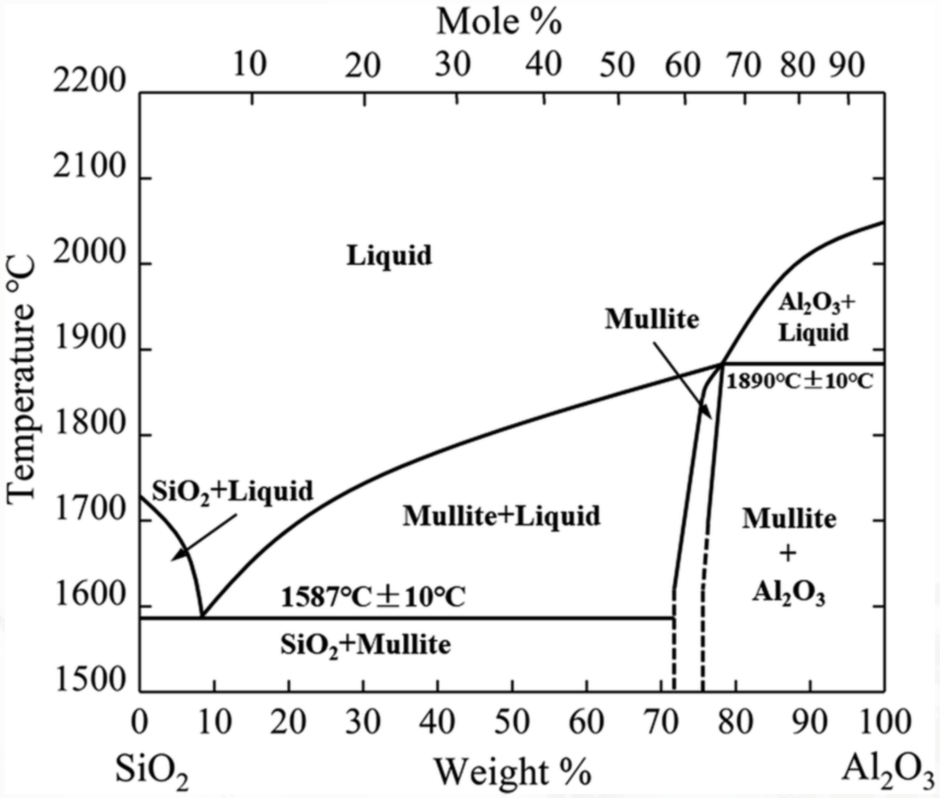


Reference: Wu, D. et al. (2020). In situ synthesis of melt-grown mullite ceramics using directed laser deposition. Journal of Materials Science. 55. 10.1007/s10853-020-04938-3.

Self Reading

Description of the Diagram

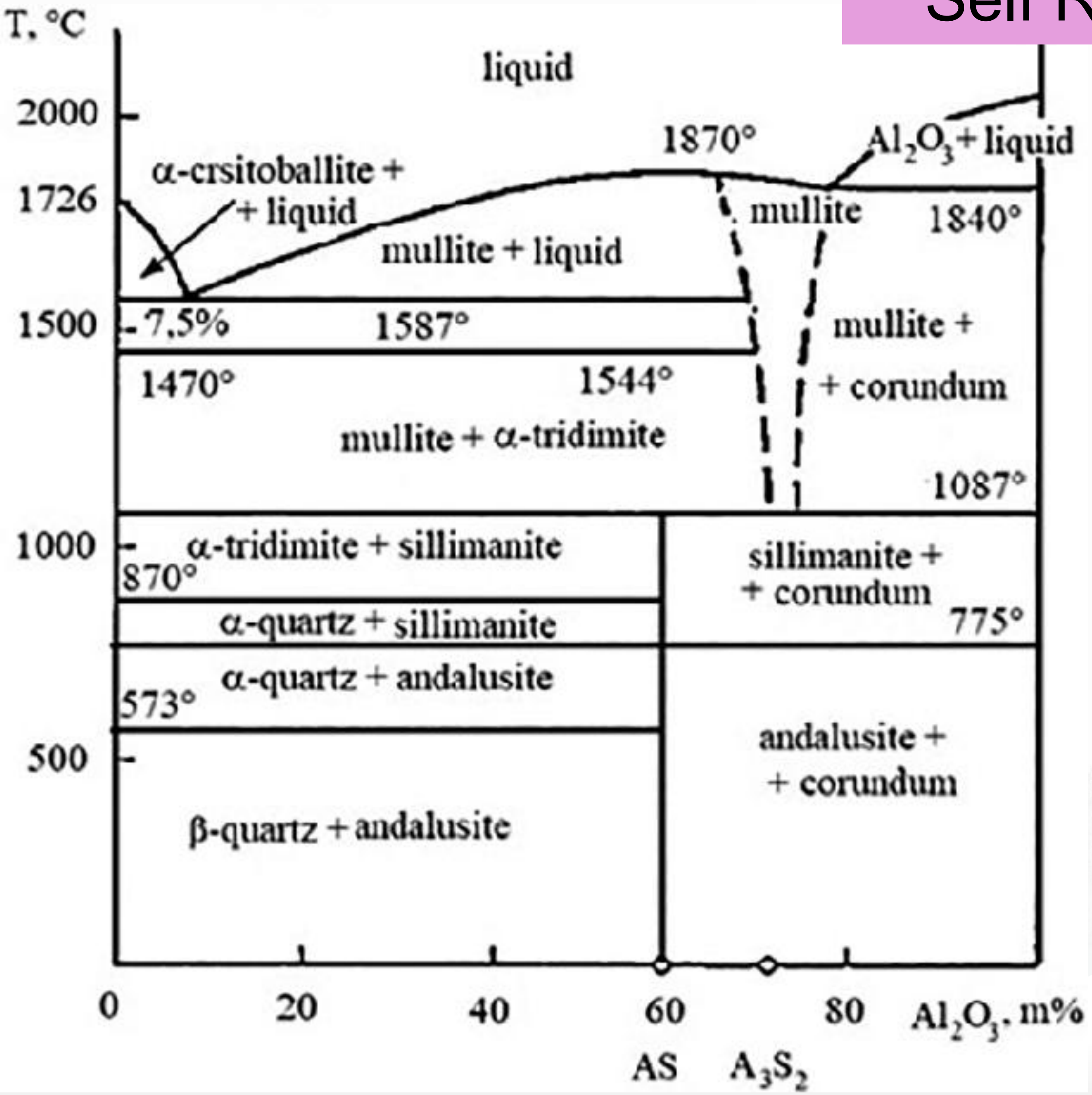
Region	Phases Present	Description
I. Liquid Region	Liquid (L)	Occurs at the highest temperatures, where all the Al_2O_3 and SiO_2 have dissolved into a homogeneous liquid (melt).
II. Liquid + Solid SiO_2	Liquid (L) + Silica (SiO_2) / Cristobalite	As the temperature drops below the liquidus line, SiO_2-rich compositions begin to precipitate solid Silica (or Cristobalite) crystals from the melt.
III. Liquid + Solid Mullite	Liquid (L) + Mullite ($3Al_2O_3{\cdot}2SiO_2$)	This is the key liquid–solid region. As Al_2O_3-rich compositions cool, Mullite crystals precipitate from the liquid. This remaining liquid becomes the precursor to the final glassy matrix.
IV. Solid Mullite + Solid SiO_2	Mullite ($3Al_2O_3{\cdot}2SiO_2$) + Silica (SiO_2)	Stable low-temperature region for compositions left of the Mullite point. Contains two crystalline solids.
V. Solid Mullite + Solid Al_2O_3	Mullite ($3Al_2O_3{\cdot}2SiO_2$) + Alumina (Al_2O_3) / Corundum	Stable phase field for high-alumina compositions (right of Mullite). Contains Mullite with excess Alumina, typical for refractory ceramics.



Self Reading

More detailed SiO2-Al2O3 phase diagram in literature

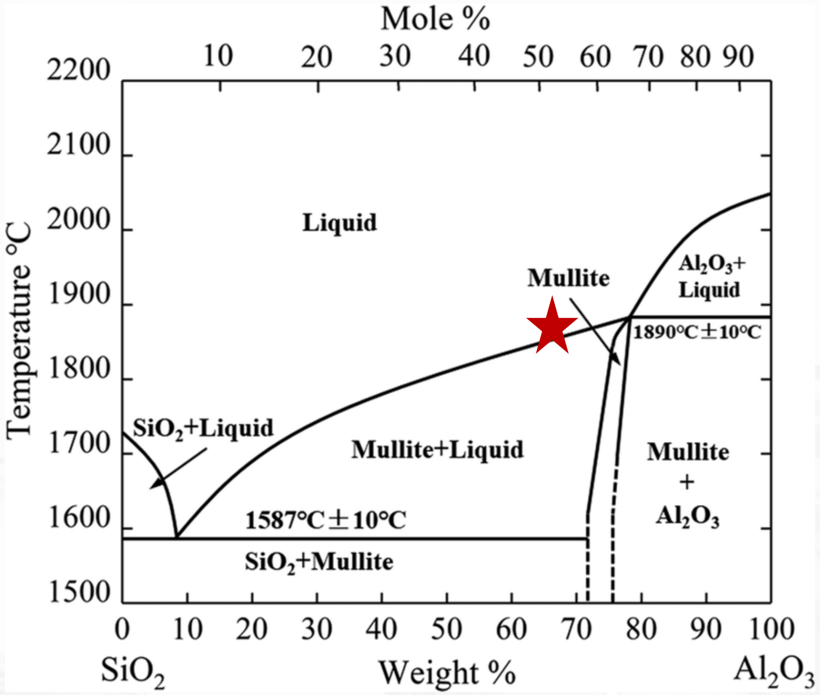
Reference:
Kurovics, E., et al. (2019). *Preparation of particle-reinforced mullite composite ceramic materials using kaolin and IG-017 bio-origin additives.* Építőanyag – Journal of Silicate Based and Composite Materials, 71(4), 114–119. https://doi.org/10.14382/epitoanyag-jsbcm.2019.20



Preferred Region for Ceramic Production (Al_2O_3–SiO_2 System)

Preferred Region for Ceramic Production (Al_2O_3–SiO_2 System)

- Preferred composition range lies in **Region III (Liquid + Mullite)**, typically near **~25% Al_2O_3**.
- Used for **traditional ceramics**: whiteware, porcelain, and stoneware.
- Goal: Form **fine Mullite crystals** surrounded by a **continuous glassy matrix**.



Why Region III?

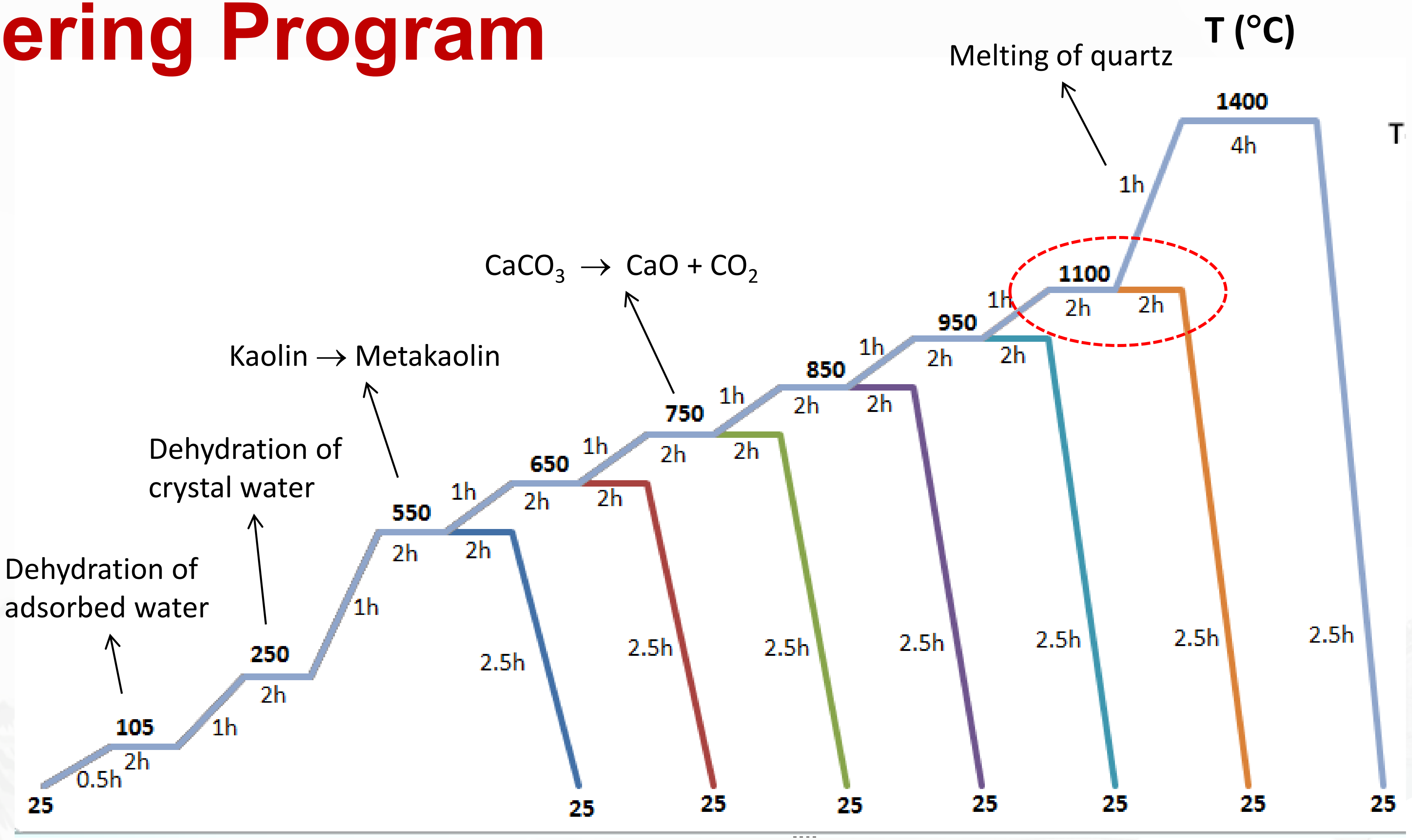
- **Mullite Formation:**
  - Provides **high strength**, **chemical resistance**, and **low thermal expansion**.
- **Vitrification & Densification:**
  - Liquid phase at firing temperatures enables:
    - Wetting of solid particles
    - Pore filling and reduction
    - Capillary-driven densification
  - Results in a **strong, dense, low-porosity** ceramic body.

Role of Fluxes in Real Ceramics

- Real ceramic bodies include **fluxes (K_2O, Na_2O)**.
- Fluxes **lower the eutectic temperature** to practical firing levels (**1000–1200°C**).
- Ensure formation of the **liquid phase** needed for vitrification at economical temperatures.

Self Reading

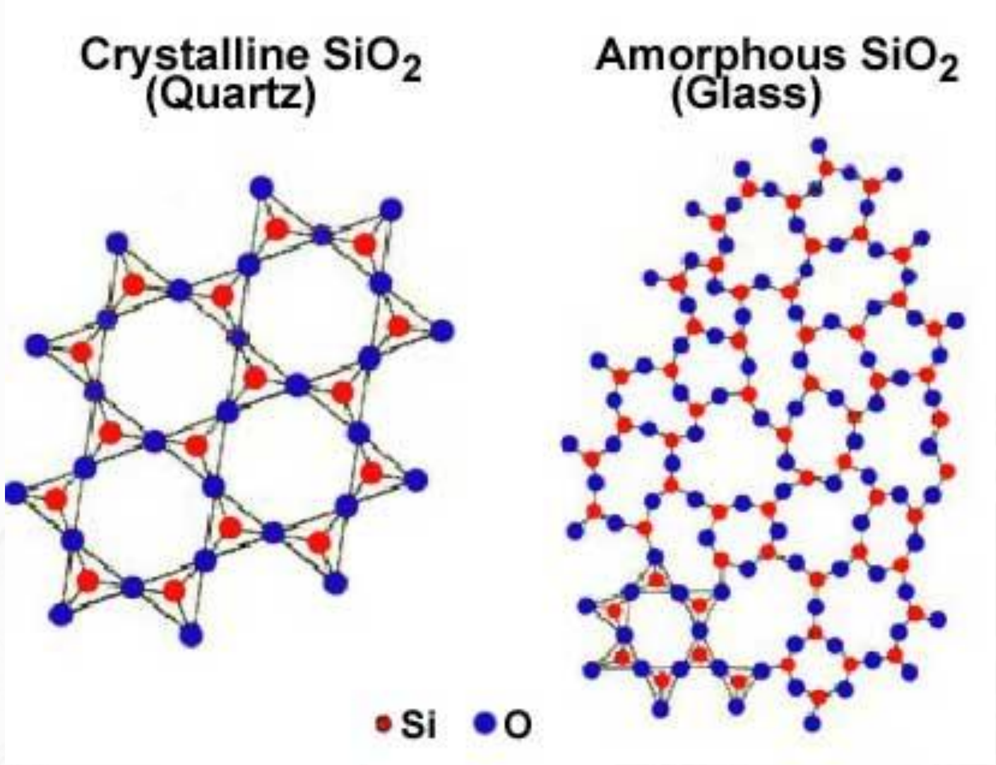
Sintering Program



Definition of Amorphous and Crystalline Solids

Amorphous Phase
A solid material that lacks long-range, ordered structure; its atoms or molecules are randomly arranged, similar to a liquid (e.g., glass, metakaolin).

Crystalline Phase
A solid material characterized by a highly ordered, repeating three-dimensional arrangement of atoms, ions, or molecules (a crystal lattice). This structure provides high stability and definitive properties (e.g., Mullite, quartz, γ-alumina).



Relevance:
In the heating of kaolinite (clay), the initial product, **Metakaolin (Al2O3.2SiO2)**, is **amorphous**. It has lost its chemically bound water but has not yet rearranged its atoms. At higher temperatures, this material undergoes a thermodynamically driven process to form the stable, **crystalline** phase known as **Mullite (3Al2O3.2SiO2)**, which provides the ceramic's final high-temperature strength.

Thermal Weight Loss (Dehydroxylation Mass Balance)

- Calculate the theoretical **mass loss** percentage (Dehydroxylation: removal of chemically bound water) of pure kaolinite (13.9%).
- The first reaction in the heating sequence is Dehydroxylation at 450 - 650°C.

$$\boldsymbol{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O\ (kaolinite) \xrightarrow{heat} Al_2O_3 \cdot 2SiO_2 (metakaolin) + 2H_2O}$$

- **Engineering Relevance:** This is a crucial step for mass balance and predicting the shrinkage and internal stress that occurs during the firing process.
- **Percentage shrinkage (per 1 mole of kaolinite used)**
  - Molar mass (kaolinite) = 258.16 g/mol → 1 mole kaoline = 258.16 g
  - Molar Mass (water) = 18.02 g/mol
  - Per 1 mole kaolinite → 2 moles water released → mass of water = 2×18.02 = 36.04 g
  - Shrinkage (or mass loss percentage) = (mass of water released / Mass of kaolinite used)×100%

    = (36.04 / 258.6) x100% = **13.96%**

Vitrification: : Glass Formation in Ceramics

- All ceramics undergo certain amount of vitrification (glass formation) during heating.
- Vitrification means progressive reduction in porosity
- Degree of vitrification depends upon:
  - Relative amounts of refractory and fluxing oxides
  - Temperature
  - Time of heating
- Vitreous phase imparts desirable properties to ceramic body:
  - Act as a bond
  - Impart translucency in chinaware
  - etc.

شبه شفافية

Definition

Sintering:
The thermal densification process where fine particles are heated to below their melting point, causing them to bond into a single, cohesive solid. The driving forcer of this process is **the reduction of total surface area** (surface energy), which eliminates pores and increases the ceramic body's density and strength.

Classification by Degree of Vitrification

The degree of vitrification provides the basis of a useful classification of ceramic products as follows:

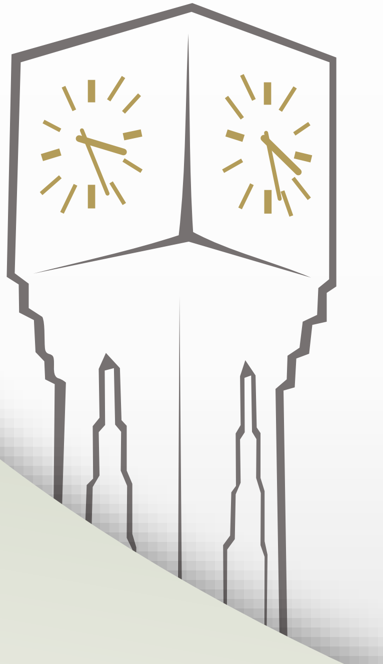
1. **Whitewares:** varying amounts of fluxes, heat at moderately high temperatures, varying vitrification.
2. **Heavy-clay products:** abundant fluxes, heat at low temperatures, little vitrification.
3. **Refractories:** few fluxes, heat at high temperatures, little vitrification.
4. **Enamels:** very abundant fluxes, heat at moderate temperatures, complete vitrification.
5. **Glass:** moderate fluxes, heat at high temperatures, complete vitrification.

Role of Fluxes in the Final Glassy Phase

- Actual ceramic body contains more ingredients than clay, thus there will be other chemical species beside mullite and cristobalite in the final product.
- Various silicates and aluminates of Ca, Mg, and alkali metals may present.
- The alkali portion of feldspar and most of the fluxing agents become part of the glassy (vitreous) phase of the ceramic body.

Lecture 4

V. Raw Material Preparation Before Processing



V. Raw Material Conditioning Before Processing

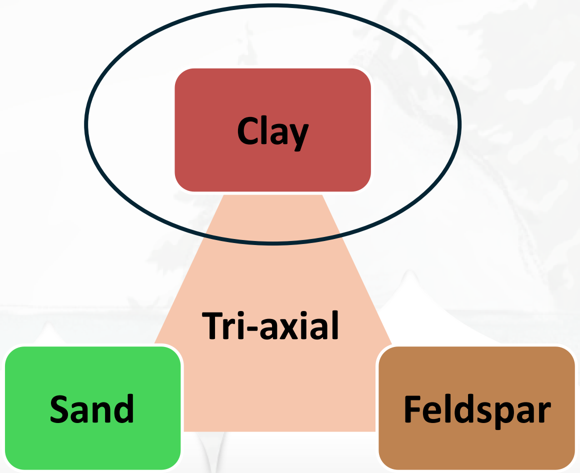
Clay beneficiation

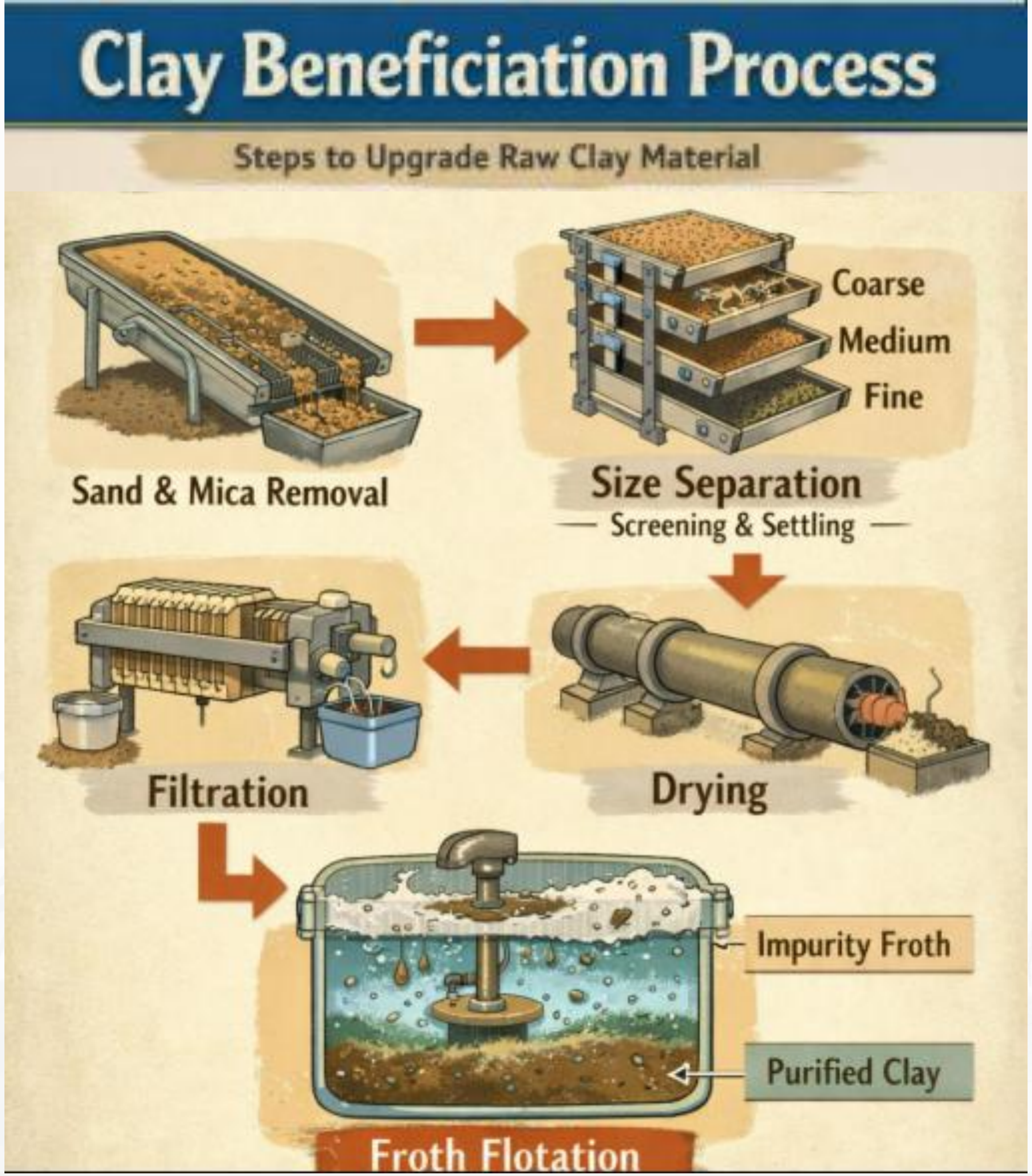
Water content & slurry preparation

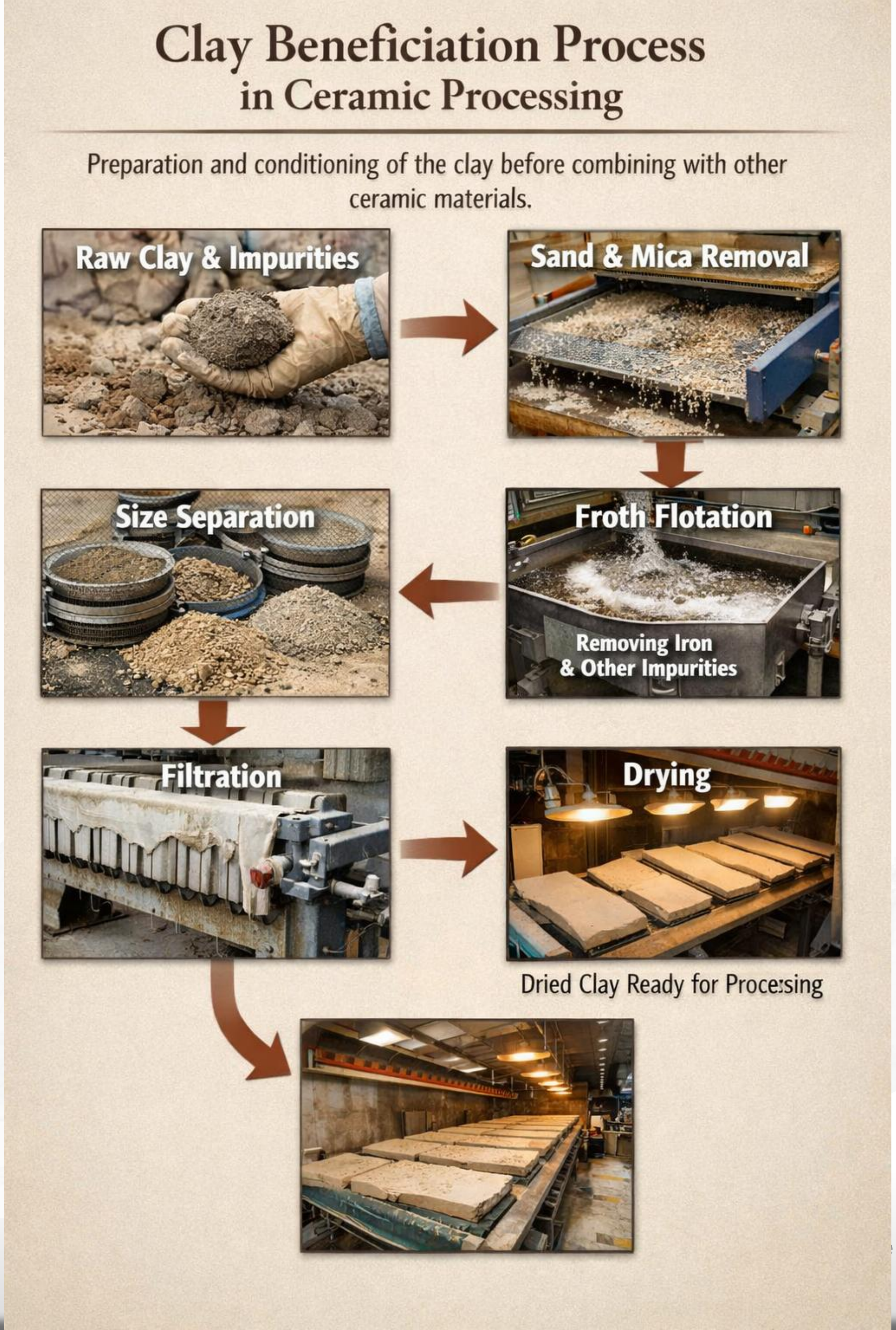
Rheology control

Clay Beneficiation

- Note: The focus here is on preparation and conditioning of the clay component, before it is combined with other ceramic raw materials.
- Clays vary so much in their physical properties, and in the impurities present (feldspar, quartz, oxides of iron, etc.)
- Therefore, it is frequently necessary to upgrade the clay by **beneficiation process**, which includes:
  1) Sand and mica removal
  2) Size separation by screening or selective settling
  3) Filtration
  4) Drying
  5) Froth flotation






Clay Beneficiation Process in Ceramic Processing

Preparation and conditioning of the clay before combining with other ceramic materials.

Clay Beneficiation

1. **Sand and mica removal**: Removal of coarse, non-plastic impurities such as sand and mica that reduce clay plasticity and cause defects. Typically achieved by washing, gravity separation, or screening based on size and density differences.
2. **Size separation**: Classification of particles to obtain a uniform and fine clay fraction, improving forming behavior and sintering. This is done using sieves for coarse particles or sedimentation in water for fine particles.
3. **Filtration:** Dewatering of the clay slurry to remove excess water and produce a workable solid or semi-solid clay body. This is commonly done using filter presses or vacuum filtration.
4. **Drying:** Controlled removal of remaining moisture to produce dry clay powder suitable for storage and subsequent ceramic processing, without altering the clay’s chemical composition.
5. **Froth flotation:** An optional beneficiation technique used mainly for high-purity clays (e.g., kaolin) to selectively remove finely dispersed impurities such as iron oxides, titanium minerals, feldspar, or quartz that cannot be separated by size or density alone. Impurities are made hydrophobic by chemical reagents and removed with air bubbles, while the clay remains in suspension.

Water, Slurry, and Rheology Control.

Water is essential in ceramics for plastic forming and for producing slip (slurry) in casting and glazing.

1. Moisture Content

Controls **plasticity**, **moldability**, and **green strength**

- Too much water → high drying shrinkage & cracking
- Too little water → poor workability

Typical moisture:

- Plastic forming: **15–25%**
- Slip casting: **30–40% water in slurry**

2. Deflocculants

Chemicals added to reduce viscosity (without adding extra water) and allow higher solid loading.

Examples: **sodium silicate, sodium carbonate**

Functions:

- Disperse particles through electrostatic repulsion.
- Reduce slurry viscosity (improve flowability, reduce drying shrinkage and cracking)
- Allow more solids for faster casting (Leads to **denser, stronger green bodies** and better surface quality)

Proper moisture, controlled viscosity, and effective deflocculation are essential for stable forming, reduced defects, and high-quality ceramic products.

Water, Slurry, and Rheology Control.

3. Rheology Control

Rheology = flow behavior of clay-water mixtures.

Control methods:

- Adjusting **water content**
- Adding **deflocculants** (thin the slurry)
- Adding **binders** (increase cohesion)
- Monitoring **viscosity** to ensure consistent casting or forming

Good rheology ensures:

- Smooth casting
- Uniform particle distribution
- Reduced defects (pinholes, lamination, segregation)

Definition

Shear-Thinning:
A non-Newtonian fluid behavior where the **viscosity decreases under increasing shear stress**, allowing ceramic slurries to flow easily during processing but stiffen at rest.

Shreve's Book, Chapter 9 (pp. 149 – 155)
and other References are used in this topic

CERAMICS INDUSTRY

LECTURES 5 AND 6
PROCESSING OF TRADITIONAL CERAMICS

Dr. Hatem Alsyouri

Lecture 5

I. Ceramics Particulate Processing
II. Raw Materials Preparation

I. Ceramics Particulate Processing

Types of Ceramics and Their Processing

- Ceramic materials are divided into three categories:
  1. Traditional ceramics – particulate processing
  2. New ceramics – particulate processing
  3. Glasses – solidification processing

- The particulate processes for **traditional** as well as certain **composite materials** are covered in this slide set

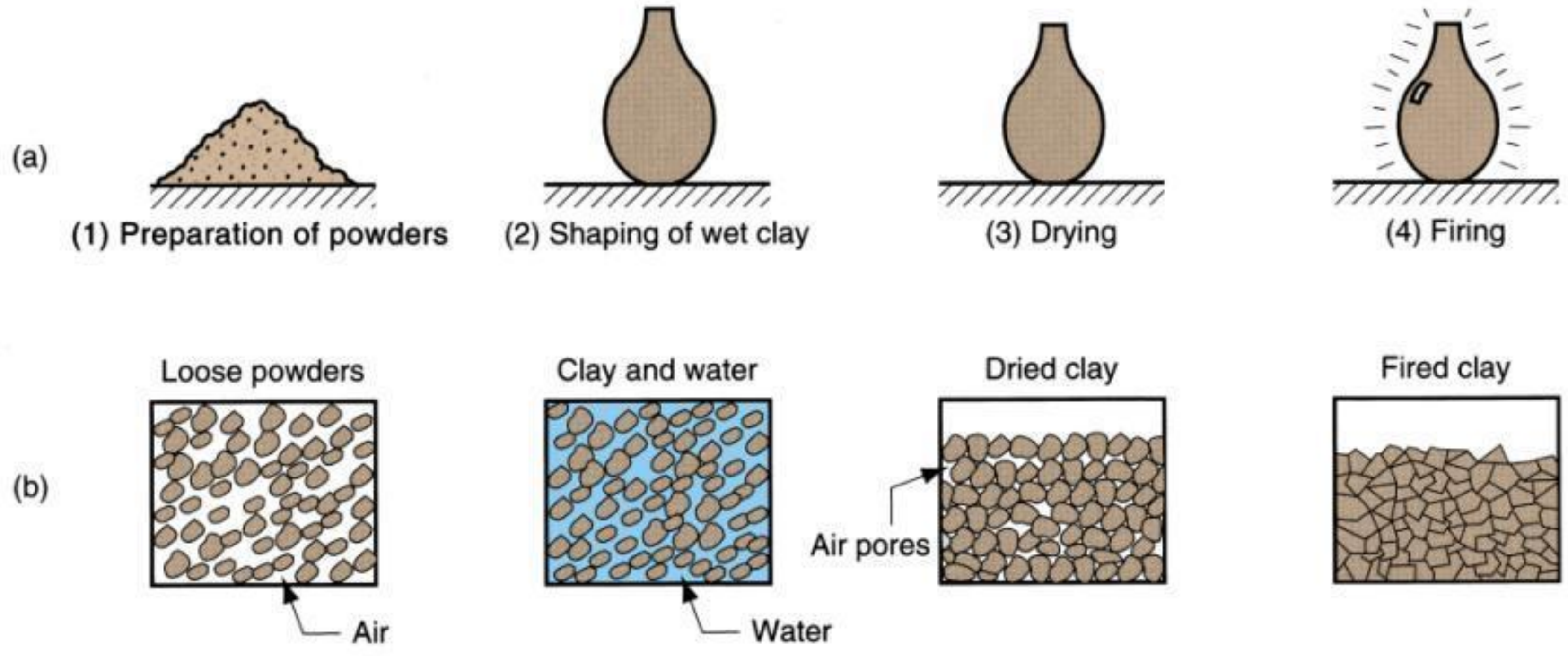
Ceramics Particulate Processing

- **Traditional ceramics** are made from minerals occurring in nature
  - Products include pottery, porcelain, bricks, and cement
- **New ceramics** are made from synthetically produced raw materials
  - Products include cutting tools, artificial bones, nuclear fuels, and substrates for electronic circuits
- The starting material for all of these items is powder

Ceramics Particulate Processing

- For **traditional ceramics**, the powders are usually mixed with water to temporarily bind the particles together and achieve the proper consistency for shaping
- For **new ceramics**, substances other than water are used as binders during shaping
- After shaping, the green parts are fired (sintered):
  - To effect a solid state reaction which bonds the material into a hard solid mass

Traditional Ceramics Processing



(a) shows the work part during the sequence

(b) shows the condition of the powders

II. Raw Materials Preparation

Raw Material Preparation for Traditional Ceramics

- Shaping processes for traditional ceramics require the starting material to be a plastic paste.
  - This paste is comprised of fine ceramic powders mixed with water.
- The raw ceramic material usually occurs in nature as rocky lumps, and reduction to powder (**comminution**) is the purpose of the preparation step in ceramics processing.

الطحن و التكسير

Comminution

الطحن والتكسير و تفتيت المواد الصلبة

- Reducing particle size in ceramics processing by use of mechanical energy in various forms such as impact, compression, and attrition

المواد الهشّة

- Comminution techniques are most effective on brittle materials such as cement, metallic ores, and brittle metals
- Two general types of comminution operations:
  1. Crushing
  2. Grinding

Comminution

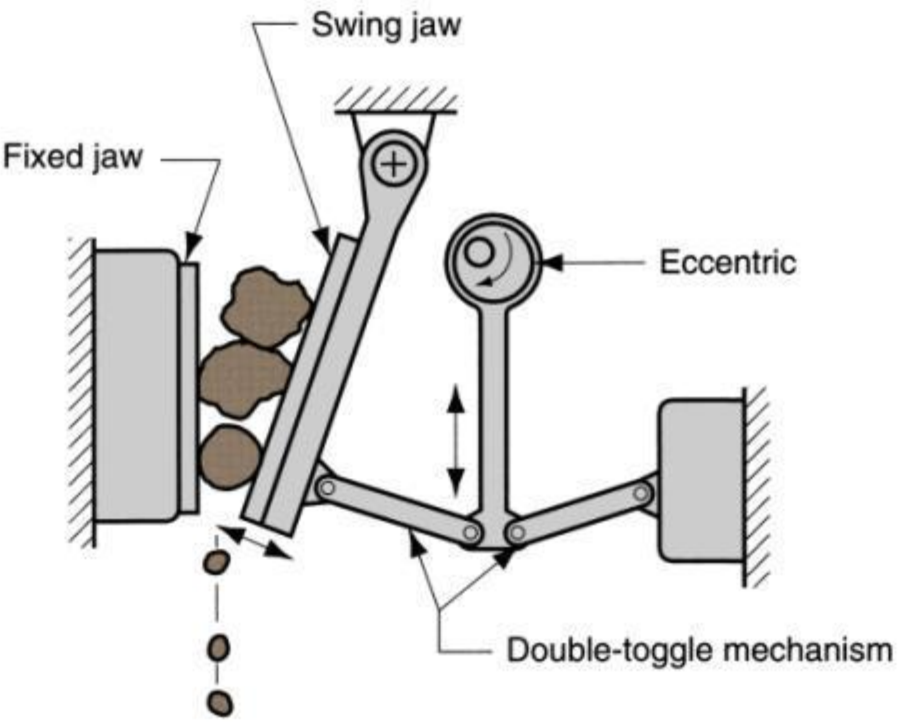
Crushing

- Reduction of large lumps from the mine to smaller sizes for subsequent further reduction
- Several stages may be required (e.g. primary crushing, secondary crushing), the reduction ratio in each stage being in the range 3 to 6
- Crushing of minerals is accomplished by compression against rigid surfaces or by impact against surfaces in a rigid constrained motion
- Examples of crushing include:
  - Jaw Crusher
  - Roll Crusher

Crushing

Jaw Crusher

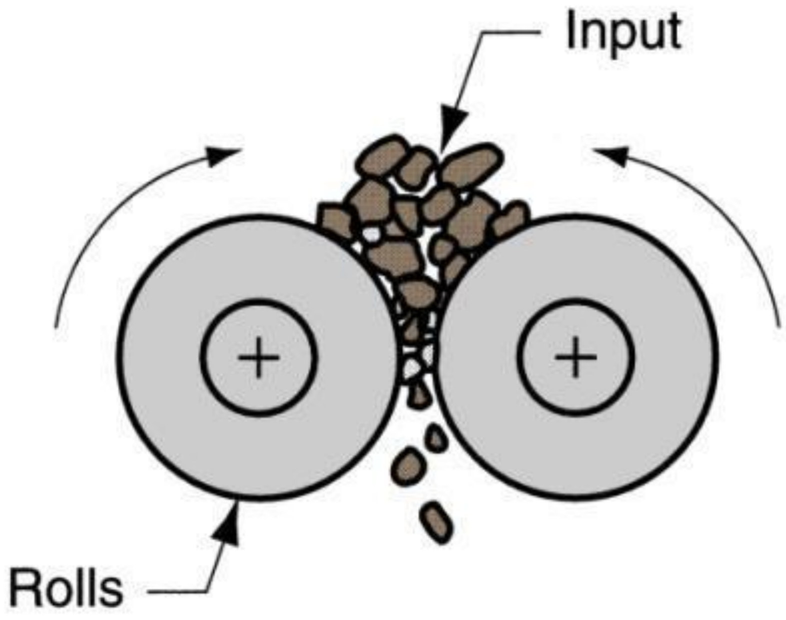
- Large jaw toggles back and forth to crush lumps against a hard, rigid surface



Crushing

Roll Crusher

- Ceramic lumps are squeezed between rotating rolls



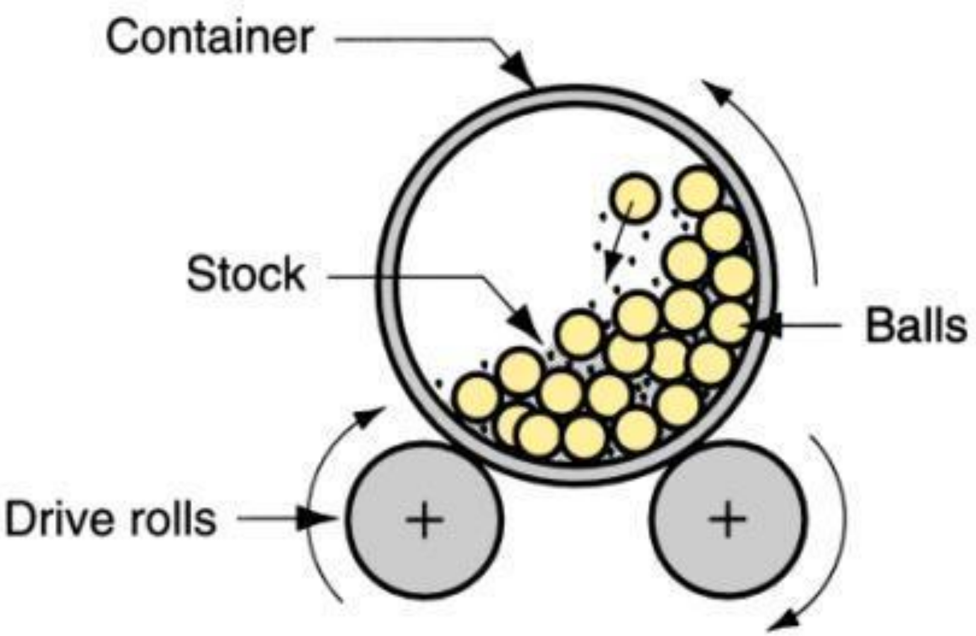
Grinding

- In the context of comminution, grinding refers to the operation of reducing the small pieces after crushing to a fine powder
- Accomplished by abrasion, impact, and compaction by hard media such as balls or rolls
- Examples of grinding include:
    - Ball mill
    - Roller mill
    - Impact grinding

Grinding

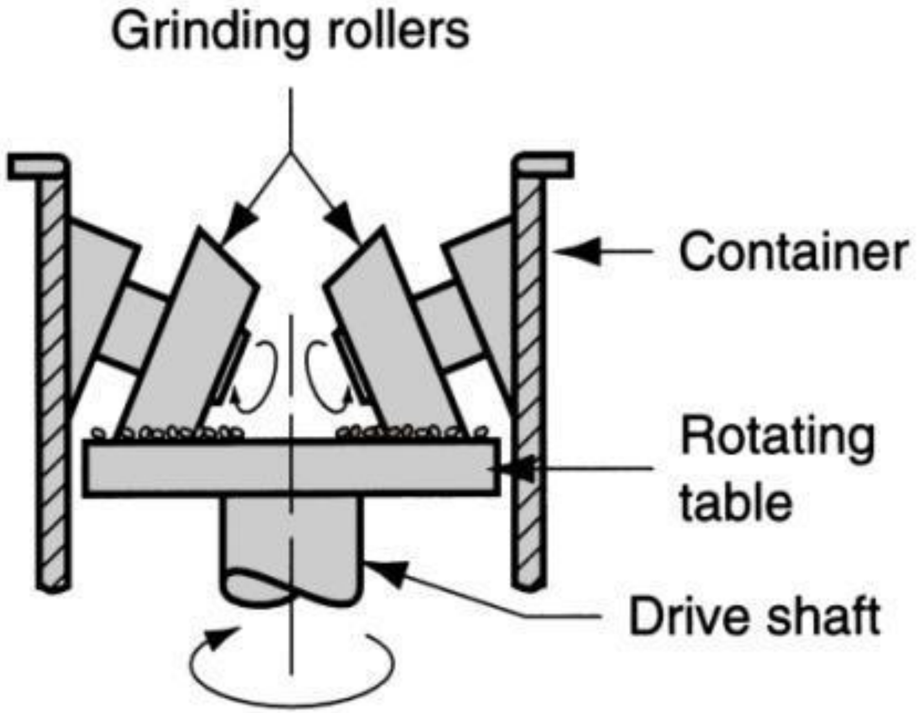
Ball Mill

- Hard spheres mixed with stock are rotated inside a large cylindrical container
- Mixture is carried up the container wall as it rotates, and then pulled back down by gravity for grinding action



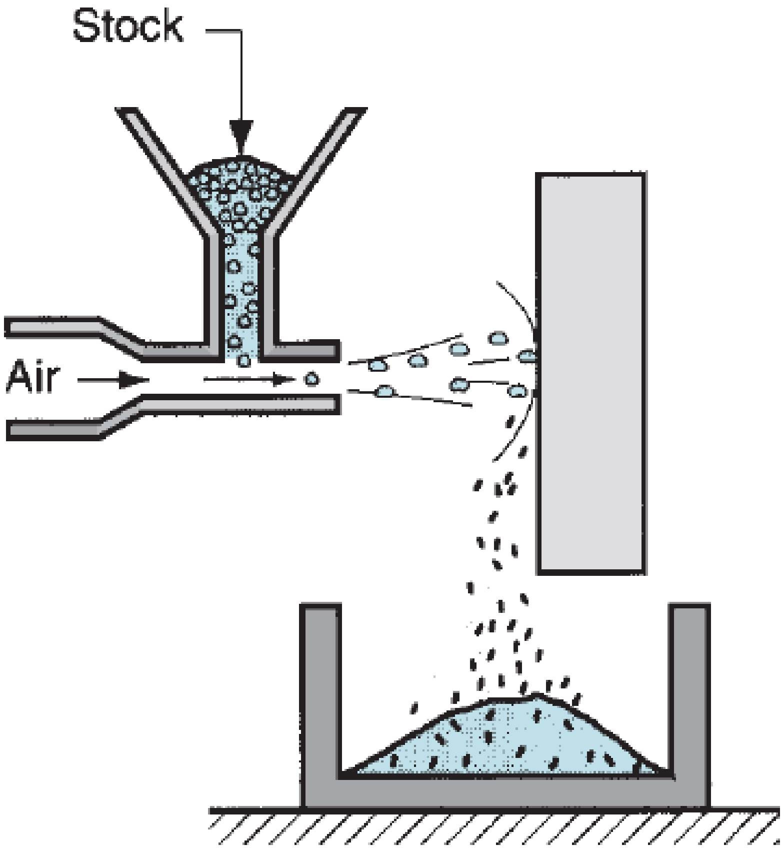
Roller Mill

- ☐ Stock is compressed against a flat horizontal grinding table by rollers riding over the table surface



Impact Grinding

- ☐ less frequently used
- ☐ particles of stock are thrown against a hard flat surface, either in a high velocity air stream or a high-speed slurry.



Lecture 6

III. Shaping Processes
IV. Drying & Glazing

IV. Shaping Processes

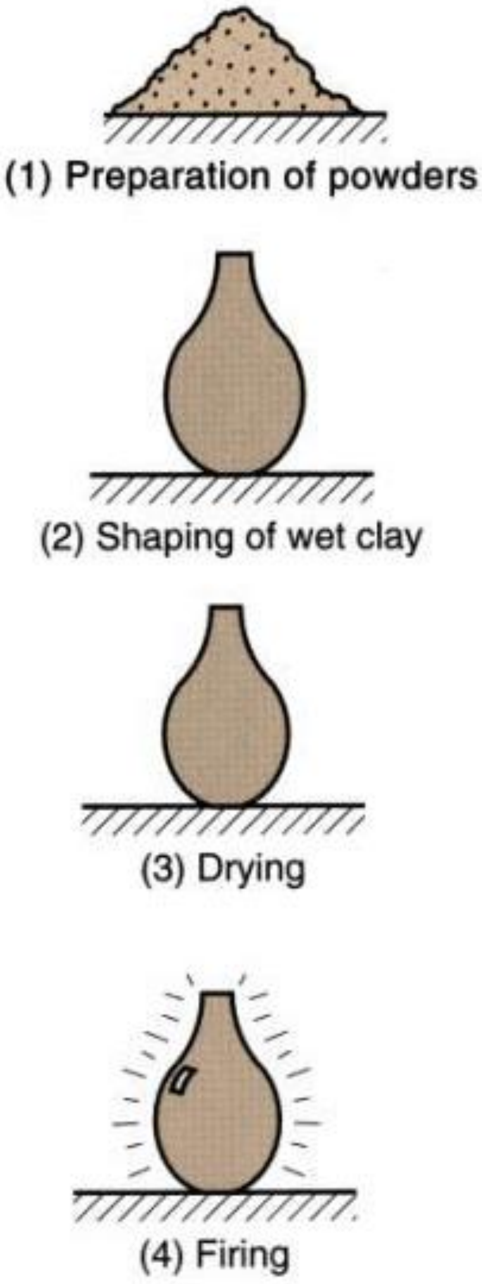
Ingredients of Ceramic Paste for Shaping

1. *Clay* (hydrous aluminum silicates) - usually the main ingredient because of ideal forming characteristics when mixed with water
2. *Water* – creates clay-water mixture with suitable plasticity for shaping
3. Non-plastic raw materials, such as *alumina* and *silica* - reduce shrinkage in drying and firing but also reduce plasticity of the mixture during forming
4. Other ingredients, such as *fluxes* that melt (vitrify) during firing and promote sintering, and *wetting agents* to improve mixing of ingredients

Shaping Processes

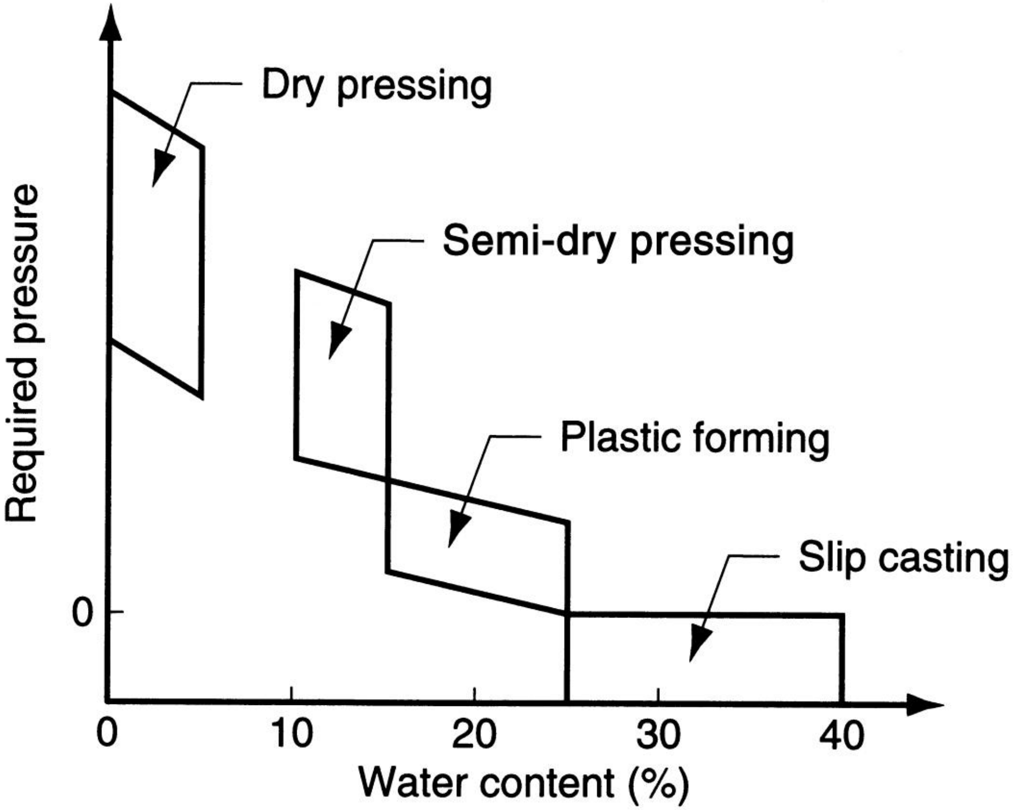
الصب

- **Slip casting**
  - The clay-water mixture is a slurry
- **Plastic forming methods**
  - The clay is plastic
- **Semi-dry pressing**
  - The clay is moist but has low plasticity
- **Dry pressing**
  - The clay is basically dry (less than 5% water) and has no plasticity



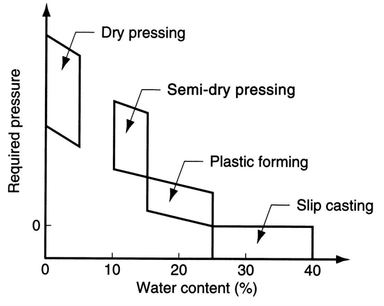
Categories of Shaping Processes

Four categories of shaping processes used for traditional ceramics, compared to ***water content*** and ***pressure required*** to form the clay.



Shaping Processes

Slip Casting السبك بالمعلّق



- A suspension of ceramic powders in water, called a *slip*, is poured into a porous plaster mold so that water from the mix is absorbed into the plaster to form a firm layer of clay at the mold surface

قالب جبسي مسامي

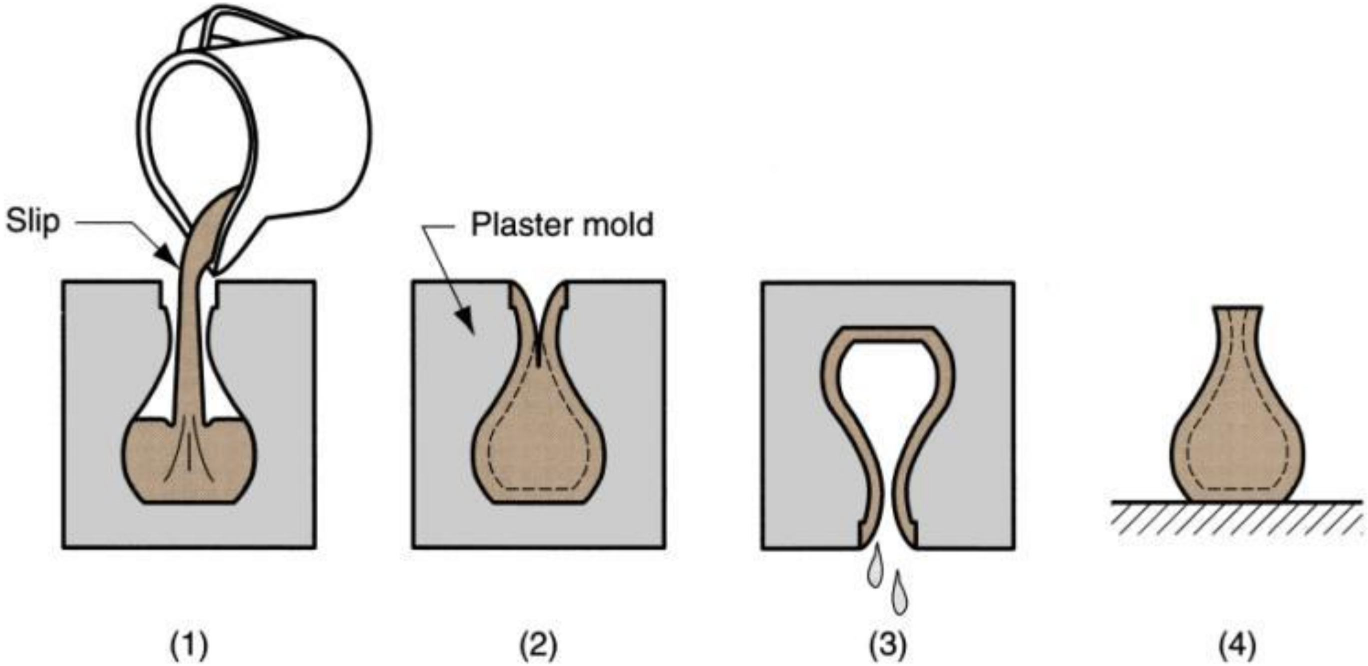
- The slip composition is 25% to 40% water
- Two principal variations:
  - ***Drain casting*** - the mold is inverted to drain excess slip after a semi-solid layer has been formed, thus producing a hollow product
  - ***Solid casting*** - to produce solid products, adequate time is allowed for entire body to become firm

السبك بالتفريغ (منتج مجوف)

السبك الصلب (منتج غير مجوف)

Slip Casting

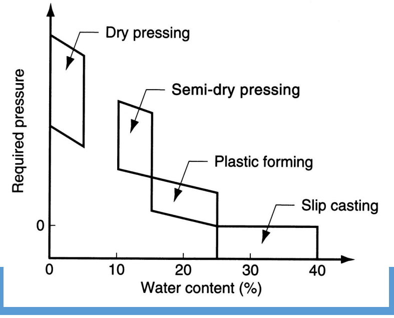
Drain Casting



(1) Slip is poured into mold cavity, (2) water is absorbed into plaster mold to form a firm layer, (3) excess slip is poured out, and (4) part is removed from mold and trimmed.

Shaping Processes

Plastic Forming



- The starting mixture must have a plastic consistency, with 15% to 25% water
- Variety of manual and mechanized methods
  - **Manual methods** use clay with more water because it is more easily formed
    - More water means greater shrinkage in drying
  - **Mechanized methods** generally use a mixture with less water so starting clay is stiffer

Plastic Forming Methods

1. Hand modeling (manual method)
2. Jiggering (mechanized method) التشكيل بالدولاب
   - For mass production of simple round objects (cups, saucers, and plates)
3. Plastic pressing (mechanized method) الكبس اللدن
   - For production of complex shapes (art-ware and laboratory-ware)
4. Extrusion (mechanized method) البثق

Plastic Forming Methods

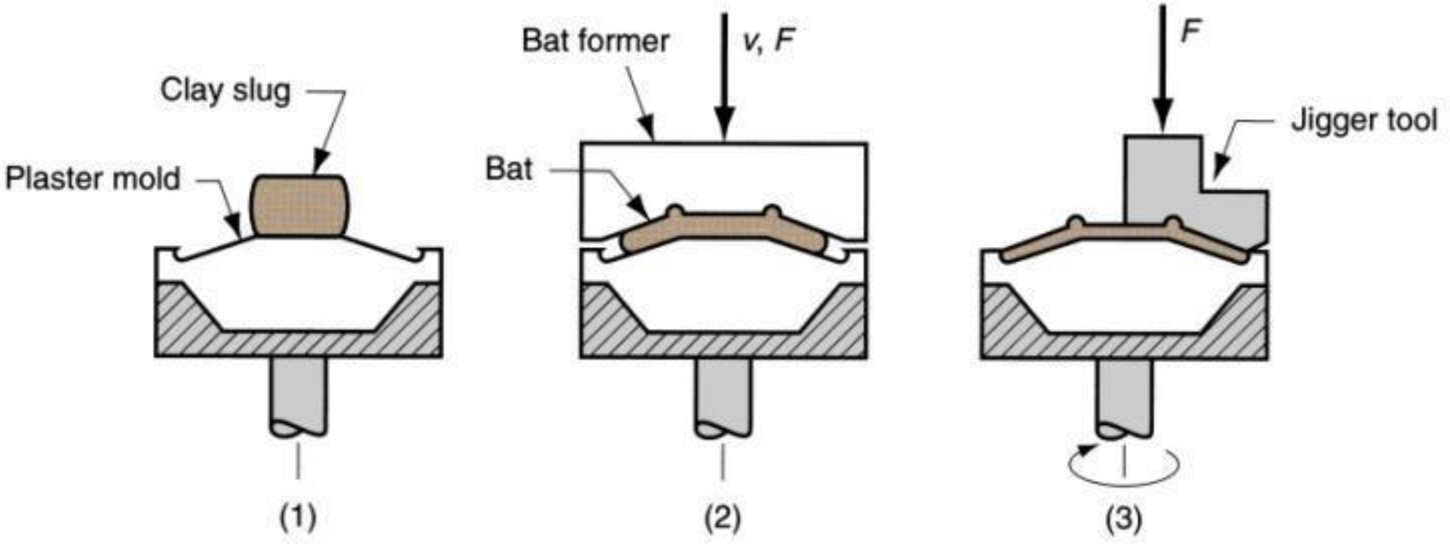
Hand Modeling

- Creation of the ceramic product by manipulating the mass of plastic clay into the desired geometry
- ***Hand molding*** - similar only a mold is used to define portions of the part geometry
- ***Hand throwing*** on a potter's wheel is another refinement of handcraft methods
  - *Potter's wheel*: a round table that rotates on a vertical spindle, powered either by motor or foot-operated treadle
  - Products of circular cross-section can be formed by throwing and shaping the clay, sometimes using a mold to provide the internal shape

Plastic Forming Methods

Jiggering

- Similar to potter's wheel methods, but hand throwing is replaced by mechanized techniques



(1) wet clay slug is placed on a convex mold; (2) batting; and (3) a jigger tool imparts the final product shape

Plastic Forming Methods

Plastic Pressing

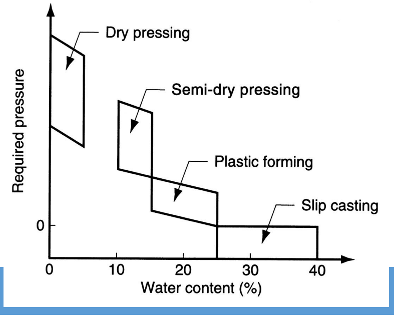
- Forming process in which a plastic clay slug is pressed between upper and lower molds contained in metal rings
- Molds are made of porous material such as gypsum, so when a vacuum is drawn on the backs of the mold halves, moisture is removed from the clay
- The mold sections are then opened, using positive air pressure to prevent sticking of the part in the mold
- **Advantages:** higher production rate than jiggering and is not limited to radially symmetric parts

Plastic Forming Methods

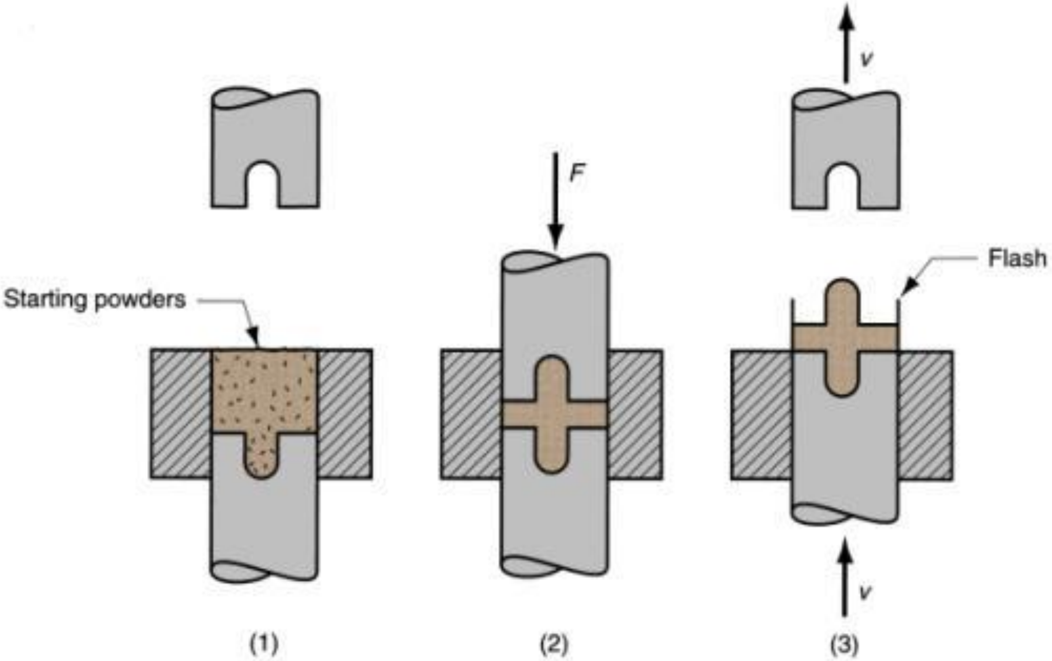
Extrusion

- Compression of clay through a die orifice to produce long sections of uniform cross-section, which are then cut to required piece length
- Equipment utilizes a screw-type action to assist in mixing the clay and pushing it through die opening
- **Products:** hollow bricks, shaped tiles, drain pipes, tubes, and insulators
- Also used to make the starting clay slugs for other ceramics processing methods such as jiggering and plastic pressing

Semi-Dry Pressing



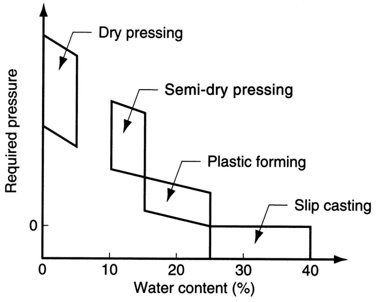
- Uses high pressure to overcome the clay’s low plasticity and force it into a die cavity



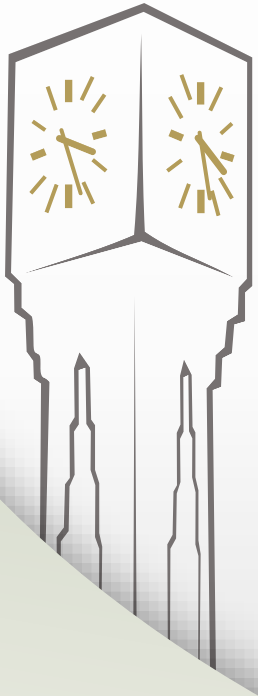
(1) depositing moist powder into die cavity, (2) pressing, and (3) opening the die sections and ejection

Shaping Processes

Dry Pressing

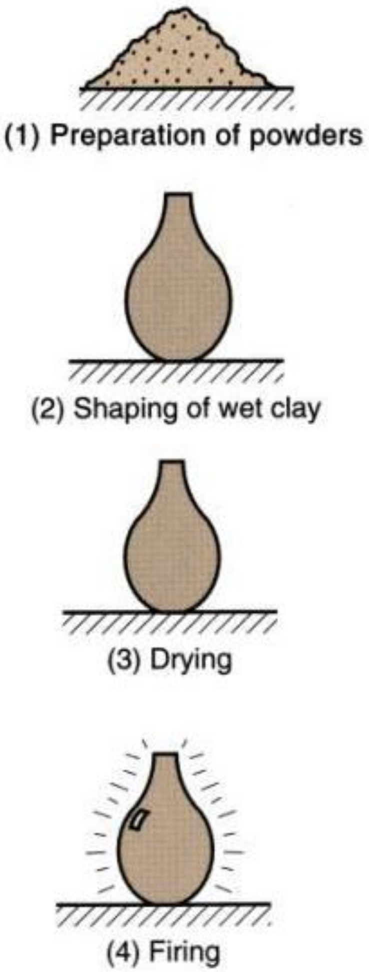


- Process sequence is similar to semi-dry pressing - the main distinction is that the water content of the starting mix is typically below 5%
- Dies must be made of hardened tool steel or cemented carbide to reduce wear since dry clay is very abrasive
- No drying shrinkage occurs, so drying time is eliminated and good dimensional accuracy is achieved in the final product
- Typical products: bathroom tile, electrical insulators, refractory brick, and other simple geometries



III. Drying & Glazing

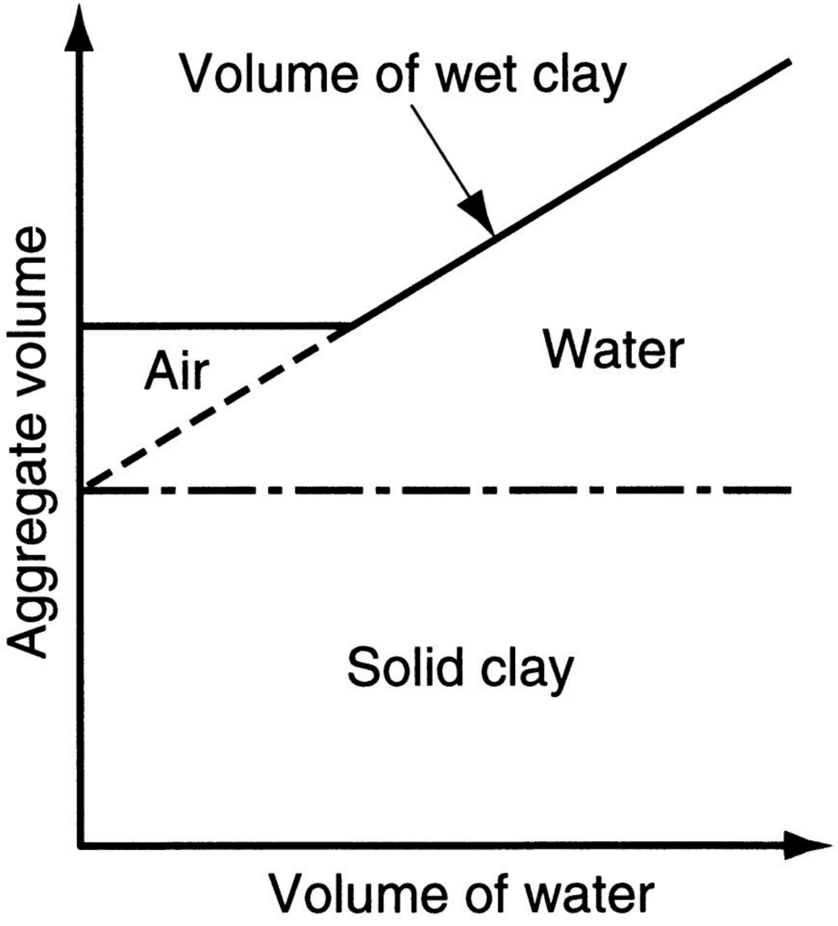
Drying



- ☐ Water plays an important role in most of the ***traditional ceramics shaping processes***.
- ☐ Thereafter, it has no purpose and must be removed from the clay piece before firing.
- ☐ Shrinkage is a problem during drying because water contributes volume to the piece, and the volume is reduced when it is removed.

Clay Volume vs. Water Content

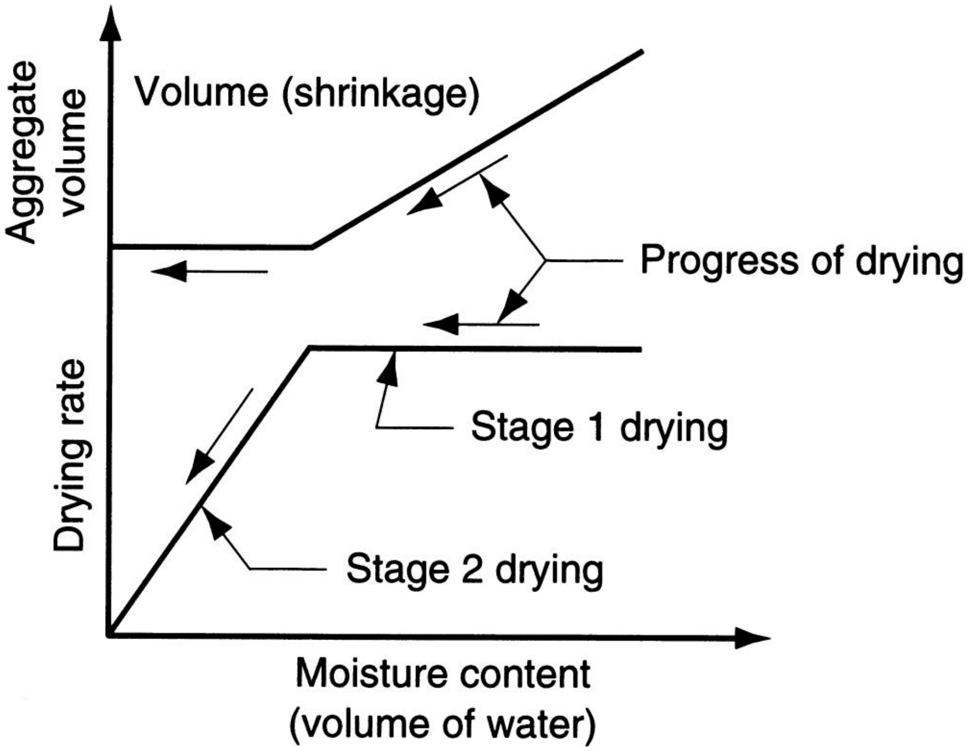
- Relationship shown here is typical; it varies for different clay compositions



Drying

The drying process occurs in two stages:

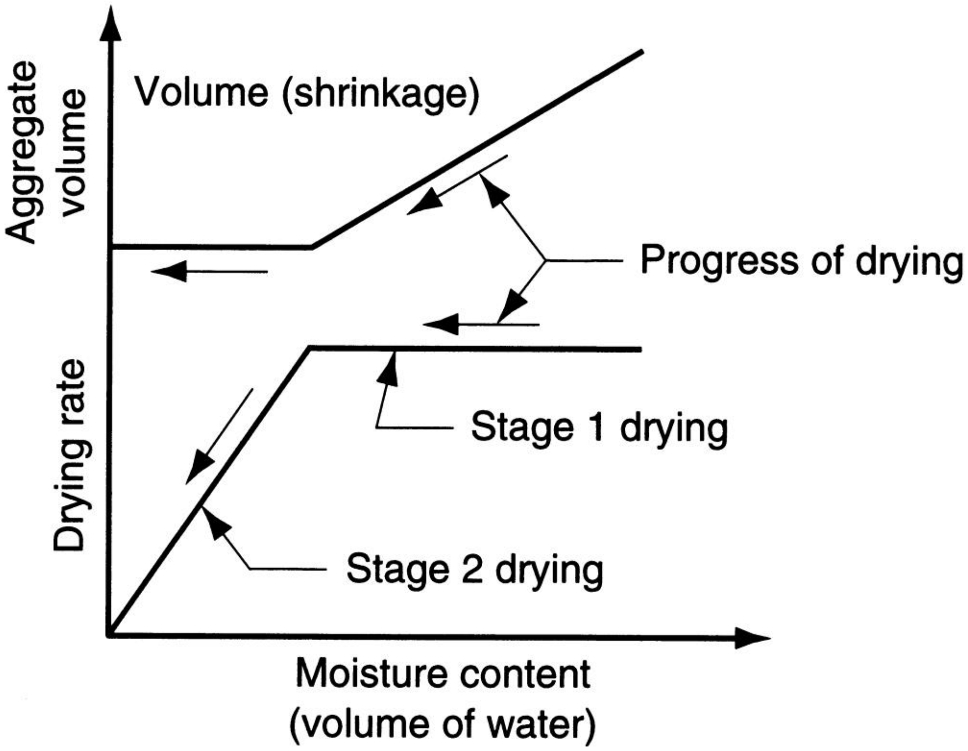
- ***Stage 1*** - drying rate is rapid and constant as water evaporates from the surface into the surrounding air and water from the interior migrates by capillary action to the surface to replace it
  - This is when shrinkage occurs, with the risk of warping and cracking



Drying

- ***Stage 2*** - the moment content has been reduced to where the ceramic grains are in contact
  - Little or no further shrinkage occurs

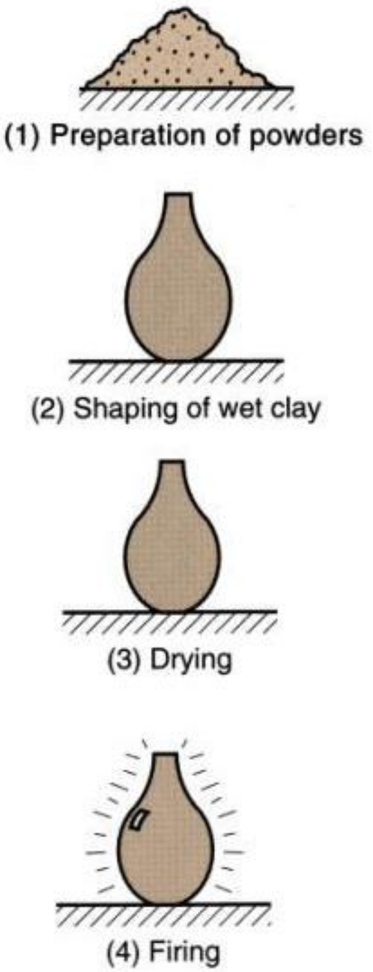
- ***Note:*** Drying rate in stage 2 is depicted here as a straight line; the function is sometimes concave or convex



Drying

- In production, drying is usually accomplished in drying chambers in which **temperature and humidity are controlled** to achieve the proper **drying schedule**.
- Care must be taken so that water is not removed too rapidly, lest large moisture gradients be set up in the piece, making it more prone to crack.
- Heating is usually conducted by a combination of convection and radiation, using infrared sources.
- Typical drying times range between a **quarter of an hour for thin sections** to **several days for very thick sections**.

Firing of Traditional Ceramics



- Heat treatment process that ***sinters*** the ceramic material
  - Performed in a furnace called a ***kiln***
  - Bonds are developed between the ceramic grains, and this is accompanied by densification and reduction of porosity
  - Additional shrinkage occurs in the polycrystalline material in addition to that which has already occurred in drying
  - In the firing of traditional ceramics, a glassy phase forms among the crystals which acts as a binder

Glazing

- Application of a ceramic surface coating to make the piece more impervious to water and enhance its appearance

- The usual processing sequence with glazed ware is:
  1. Fire the piece once before glazing to harden the body of the piece
  2. Apply the glaze
  3. Fire the piece a second time to harden the glaze (1050 to 1300°C)

Glazing

To avid defects such as “crazing” and “shivering”:

- The glaze must be bonded to the ware.
- The glaze coefficient of expansion must be sufficiently close to that of the ware.

The glaze may be put on by

- dipping
- spraying
- pouring
- brushing

Shreve's Book, Chapter 9 (pp. 149 – 155)
and other References are used in this topic

CERAMICS INDUSTRY

LECTURE 7

CERAMIC PRODUCTS

Dr. Hatem Alsyouri

Lecture 7

Main Ceramic Products
1. Whitewares
2. Structural-Clay Products

Major Types of Ceramics

Ceramics

- A wide range group of materials whose main ingredients are clays, sand, and feldspar

Major types of Ceramics

1. White wares
2. Structural clay products
3. Refractories
4. Vitreous enamels
5. Glasses

(1) White wares

- White ware is a generic term for ceramic products which are usually white and of fine texture.
- They are based on selected grades of clay bonded together with varying amounts of fluxes and heated to a moderately high temperature in a kiln (1200 to 1500 °C).

White Wares

- Different amounts and kinds of fluxes are used, leading to variation in the degree of vitrification among white wares.
- White Ware Classes:
  1. Earthenware الفخار (semivitreous dinnerware)
  2. Chinaware أواني الخزف
  3. Porcelain
  4. Sanitary ware الأدوات الصحية
  5. Stoneware
  6. Whiteware Tiles بلاط السيراميك الأبيض

Understanding Material Differences

Self-Reading

The categories of ceramic whitewares look similar at a glance, however, their internal structures differ significantly due to how they are manufactured.

A common question arises: why is a porcelain teacup light and translucent, while a stoneware mug is heavy and opaque? The answer lies not just in the clay used, but in what happens inside the kiln during the firing process.

The Role of Firing and Vitrification:

- A key technical process here is **Vitrification**. It is defined as the formation of a glassy phase during firing that fills internal pores, making the ceramic dense, strong, and non-porous.

- **Earthenware** is a low-firing, porous material that is usually glazed. It is specifically defined as **non-translucent** (or **opaque)** dinnerware with a soft glaze.
- **Stoneware** is a medium–high firing, dense, and vitrified ware positioned between earthenware and porcelain. It is similar to porcelain in strength but uses less refined clay and is fired slightly lower.
- **Porcelain** undergoes the highest firing to become fully vitrified and white.

Light passes through directly with perfect clarity, such as a clear glass vase or high-purity fused silica.

Light passes through but is scattered into a soft glow, like the delicate appearance of Fine Bone China or frosted glass.

Light is completely blocked or reflected, as seen in dense ceramic products like terracotta pots or stoneware mugs.

White Wares Classes

الفخار

1) Earthenware (semivitreous dinnerware)

- Porous and non-translucent dinnerware with a soft glaze

2) Chinaware

- Vitrified translucent ware with a medium glaze
- Resists abrasion to a degree
- Used for nontechnical purposes

White Wares Classes

3) Porcelain

- Vitrified translucent ware with a hard glaze.
- Resists abrasion to the maximum degree.
- Includes chemical, insulating, and dental porcelain.

4) Sanitary ware

- Formerly made from clay and was porous
- Vitreous composition is presently used

White Wares Classes

5) Stoneware

- One of the oldest ceramic wares
- May be regarded as crude porcelain fabricated from raw material of a poorer grade

6) Whiteware Tiles

- **Floor tiles**
  - Resistant to abrasion and impervious to stain penetration
  - May be glazed or unglazed
- **Wall tiles**
  - Hard, permanent surface
  - Variety of colors and textures

Self-Reading

White Wares

High Voltage Porcelain Insulator

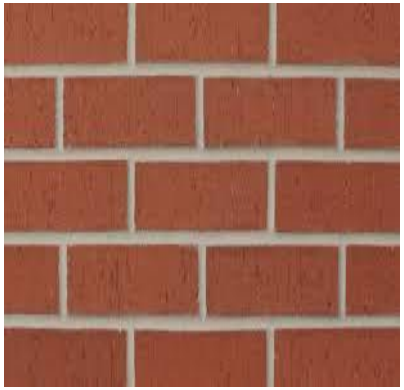
- Porcelain ceramic components used in power transmission systems to electrically isolate conductors at high voltages.
- They are **highly vitrified, dense, and low-porosity** to provide excellent electrical insulation, mechanical strength, and resistance to weathering and contamination.

Low Voltage Porcelain Insulator

- Porcelain ceramic insulators used in low-voltage electrical applications (e.g., building wiring and equipment supports).
- They require good dielectric strength and moderate vitrification, but are less demanding in size, strength, and insulation performance than high-voltage insulators.

(2) Structural-Clay Products





- Low cost, but very durable products, such as:
  a) Building Brick
  b) Face Brick
  c) Terra-cotta
  d) Sewer Pipe
  e) Drain Tile

Structural-Clay Products

- Structural-clay products are frequently manufactured from the cheapest common clays with or without glazing.
- The clay used generally carry sufficient impurities to provide the needed fluxes for binding.
- When the clay is glazed, as in sewer pipe or drain tile, this may be done by throwing salt (salt glaze) upon the kiln fire.
    - The volatilized salt reacts to form the fusible coating or glaze

Structural-Clay Products

- Face Bricks

- Sewer pipe

- Building Bricks

Structural-Clay Products

- Terra-Cotta

- Drain Tile

Lecture 8

3. Refractories
4. Vitreous Enamels

(3) Refractories

Definition

- Refractories are termed acid, basic, neutral, and super-refractories.
- Refractories are used to withstand the effect of thermal, chemical and physical effects in furnace procedures.
- Refractories are sold in the form of:
  - firebricks
  - silica, magnesite, chromite and magnesite-chromite brick
  - silicon carbide and zirconia refractories
  - aluminum silicate and alumina products.
- The fluxes required to bind the particles of the refractories together are kept at a minimum to reduce vitrification.

Self-Reading

Chemical Properties

- Commercial refractories are divided into acid, basic and neutral groups
  - Silica bricks are acid
  - Magnesite bricks are strongly basic
  - Fire-clay bricks are generally placed in the neutral group
- It is usually not advisable to employ an acid bricks in contact with an alkaline product or vice versa.
- Both of chemical reactions and physical properties should be considered as criterion of acceptable behavior.

Porosity

- Porosity is directly related to many other physical properties of brick, including resistance to chemical attack.
- The higher the porosity of brick, the more easily it is penetrated by molten fluxes and gases.
- For a given class of brick, those with the lowest porosity have the greatest strength, thermal conductivity, and heat capacity.

Spalling التقشّر الحراري

- It is a fracture that happens to a refractory brick due to uneven heat stresses or compression caused by heat.
- Bricks usually expand when heated.
- Bricks that undergo the greatest expansion at the least uniform rate are the most susceptible to spalling when rapidly heated or cooled.

Varieties of Refractories

- Fire-Clay Brick
- Silica Brick
- High-Alumina Refractories
- Basic Refractories
- Magnesia Refractories
- Insulating Brick
- Silicon Carbide
- Electrocast or Corhart Refractories
- Pure Oxide Refractories
- Refractories from Crystalline Alumina or Aluminum Silicate

Varieties of Refractories

- About 95% of refractories manufactured are non basic, with silica (acid) and fire-clay (neutral) brick predominant.
- Refractories rarely fail due to heat only, they usually fail by the chemical action at the operating temperature.
- Steel industries are the largest consumers of refractories for the linings of blast furnaces, stoves, open hearths and other furnaces.
- Other industries: glass furnaces, brass and copper furnaces, continuous ceramic and metallurgical kilns and boiler.

(4) Vitreous Enamel

Vitreous Enamel

- **Porcelain or vitreous enamel** is a ceramic mixture containing a large proportion of fluxes applied cold and fused to the metal at moderate red heat, where complete vitrification takes place.
- The enamel is used in the old ancients as a coat to gold, silver and copper.
- Enamel has come to commercial use because
  - it provides a product of great durability and wide application
  - it is easy to clean
  - it is corrosion resistance

Vitreous Enamel Uses

- Plumbing fixtures

- Cooking utensils

- Industrial equipment

- Glass-enameled steel for chemical use

Raw Materials

- Characteristics of raw materials:
  - High purity
  - Fineness
  - Suitable mineral composition
  - Proper grain shape
- May be divided into six different groups:

Refractories

Fluxes

Opacifiers

Color

Floating agents

Electrolytes

Application of the Enamel

- Sheet-iron coats are generally applied by:
  1. Dipping or Slushing
  2. Draining
  3. Spraying
  4. Powder process

  - Slushing differs from draining in that the enamel slip is thicker and must be shaken from the ware.
- After coating, the enamel is air dried and colors are brushed and stenciled on.
- The enamel is usually applied in two coats for premium ware.

Preparation of Metal Parts

- The success of enameling depends on the uniformity of the metal base to which the enamel is fused and on obtaining a parallelism between the coefficients of expansion of the enamel and the metal.
- In cast-iron enameling industry casting are frequently made in the same factory in which they are enameled.
- Sheet-metal enameler usually purchases sheets to meet a definite specification.
- Before the liquid enamel (suspension in water) is applied to the metal, the surface must be thoroughly cleaned of all foreign matter.
- Sheet metal is cleaned by pickling in dilute hydrochloric or sulfuric acid at 60c after the iron has been annealed.

Application of the Enamel

- In the powder process the steel is coated by electrostatic spraying.
- This process is evolving to a two-coat, one-fire system, consisting of a thin powder base coat and a powder cover coat.
- Both coats are cured at once in a single fire.
- This produces a quality product at much lower cost than the conventional process.

Firing

- All enamels must be fired on the ware to melt them into a smooth, continues, glass layer.
- The requirements for successful firing of a good enamel are:
  1. Proper firing temperature (730 to 800 °C)
  2. Time (1 to 15 minute)
  3. Proper support of the ware
  4. Uniform heating and cooling of the ware
  5. An atmosphere free of dust

Surface Coatings

Chemical Process Technology

Fall 2025

Dr. Hatem Alsyouri

Lecture 1

Classification of Coating
Paint Constituents

Introduction

aesthetic appearance = المظهر الجمالي

- Surface coatings include paints, varnishes, and lacquers.
- Surface coatings are used: a) to protect from weather, and b) to increase aesthetic appearance of products.

القار (الزفت)

- Historical religious texts describe the use of pitch (tar) as a waterproof coating in the Ark of Noah.
- Ancient inhabitants recorded their history on walls using colored paints.
- Crude (or early) paints consisted of colored natural clays dispersed in water.

شمع العسل

- Natural resin (e.g., beeswax) were discovered and used as film-forming ingredients.
- Surface coatings represent a large industry with significant annual sales

Classification of Coatings

Architectural (or decorative) Coatings

- Used to coat buildings and furniture.
- Applied to wood, gypsum wallboards, plaster-coated surfaces, etc.

الأسطح المطلية بالجص

Industrial Coatings

- Used on materials during manufacturing
- Applied to metals, textiles, rubber, paper, plastics, & wood.

Gypsum (الجبس) is a raw material, and
Plaster (الجص) is a material produced from gypsum and used to coat walls and ceilings.

Historical Classification of Coatings

Paints الدهانات

- Opaque solid coating applied as thin layer.
- Film forms by polymerization (depending on binder type).

Varnishes الورنيش

- Clear coatings

Enamels المينا

- Pigmented coatings that form hard, glossy films

Lacquers

- Films form by solvent evaporation

Printing Inks حبر الطباعة

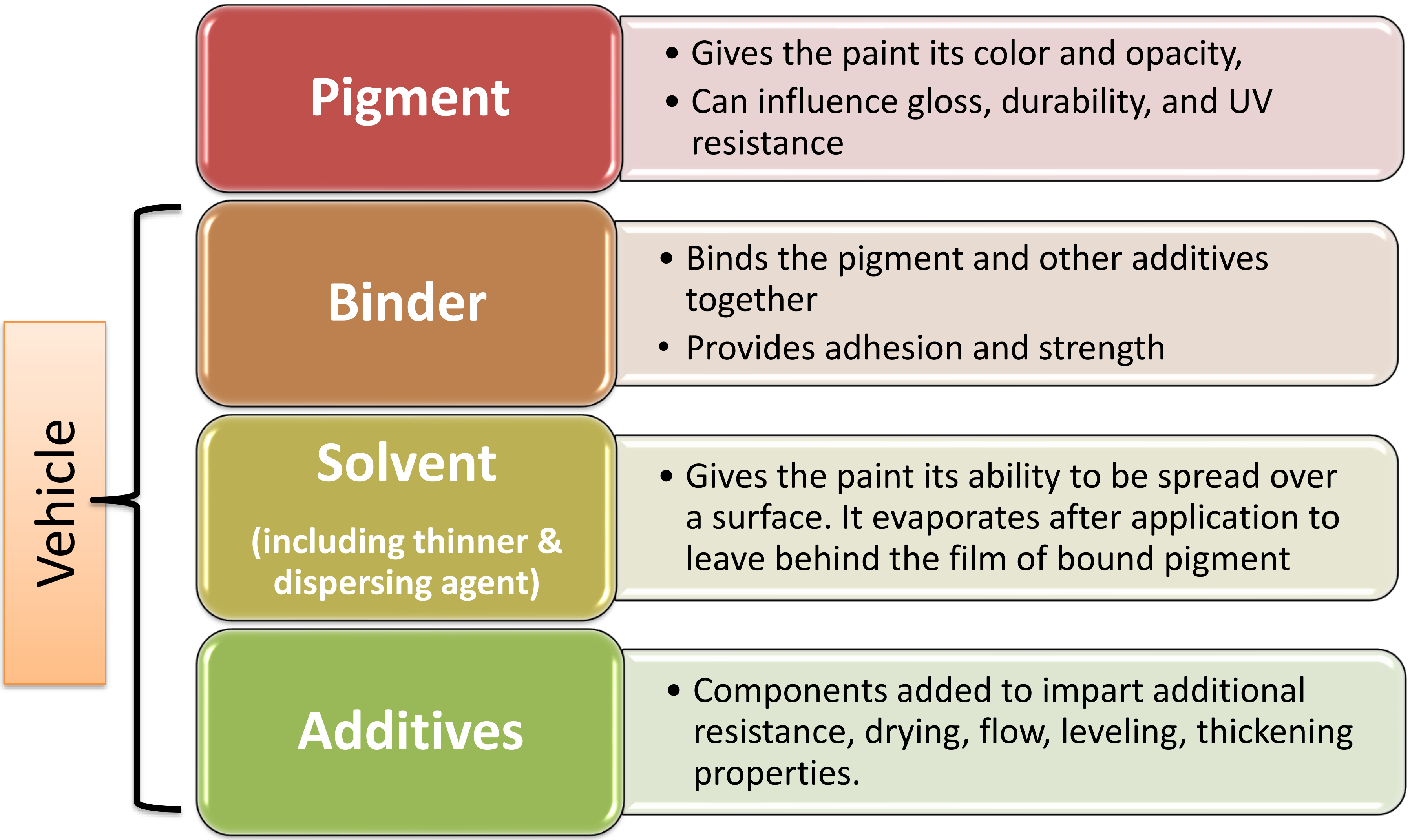
Low-viscosity pigmented coatings for text and images.

Polishes مادة تلميع

Coatings used to enhance surface appearance and gloss.

However, the introduction of plastic resins into this industry has changed this classification

Paint Constituents



Pigment

- Gives the paint its color and opacity,
- Can influence gloss, durability, and UV resistance

Binder

- Binds the pigment and other additives together
- Provides adhesion and strength

Solvent

(including thinner & dispersing agent)

- Gives the paint its ability to be spread over a surface. It evaporates after application to leave behind the film of bound pigment

Additives

- Components added to impart additional resistance, drying, flow, leveling, thickening properties.

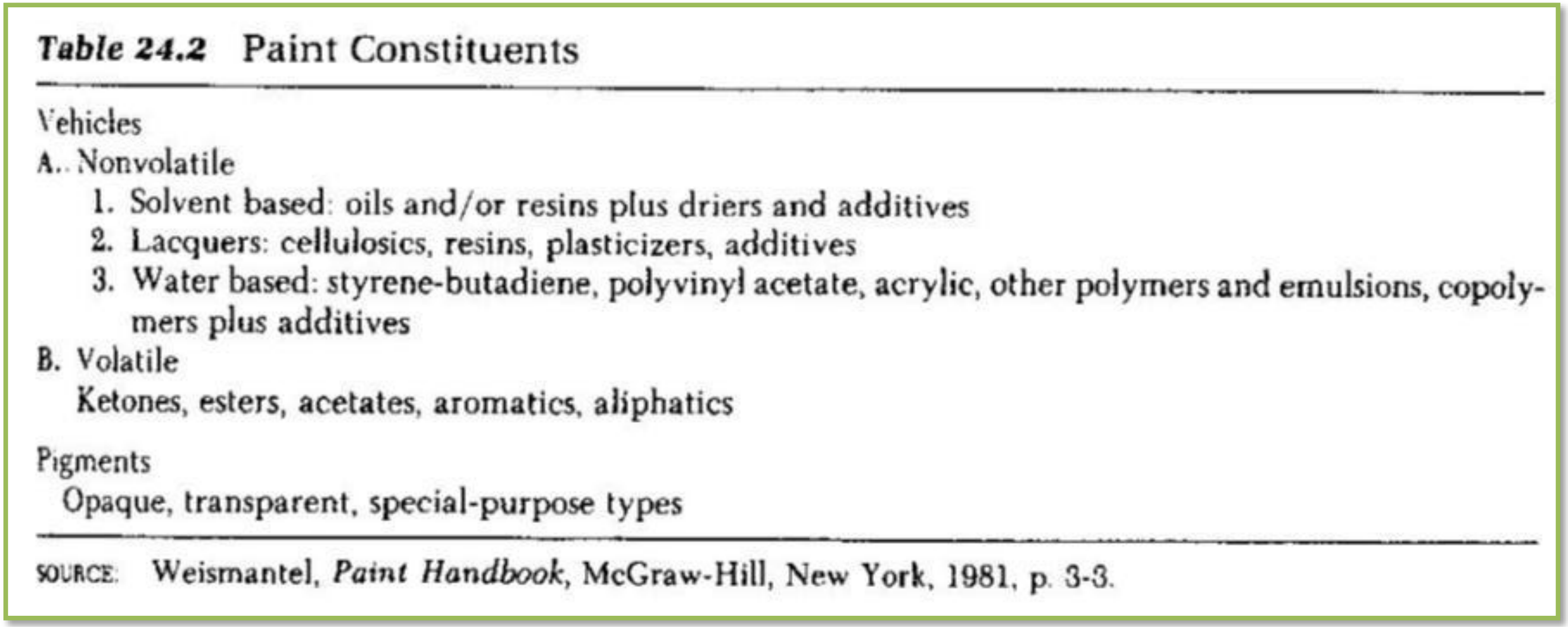


Table 24.2 Paint Constituents

Vehicles

A. Nonvolatile

1. Solvent based: oils and/or resins plus driers and additives
2. Lacquers: cellulosics, resins, plasticizers, additives
3. Water based: styrene-butadiene, polyvinyl acetate, acrylic, other polymers and emulsions, copolymers plus additives

B. Volatile

Ketones, esters, acetates, aromatics, aliphatics

Pigments

Opaque, transparent, special-purpose types

SOURCE: Weismantel, *Paint Handbook*, McGraw-Hill, New York, 1981, p. 3-3.

(1) Binder

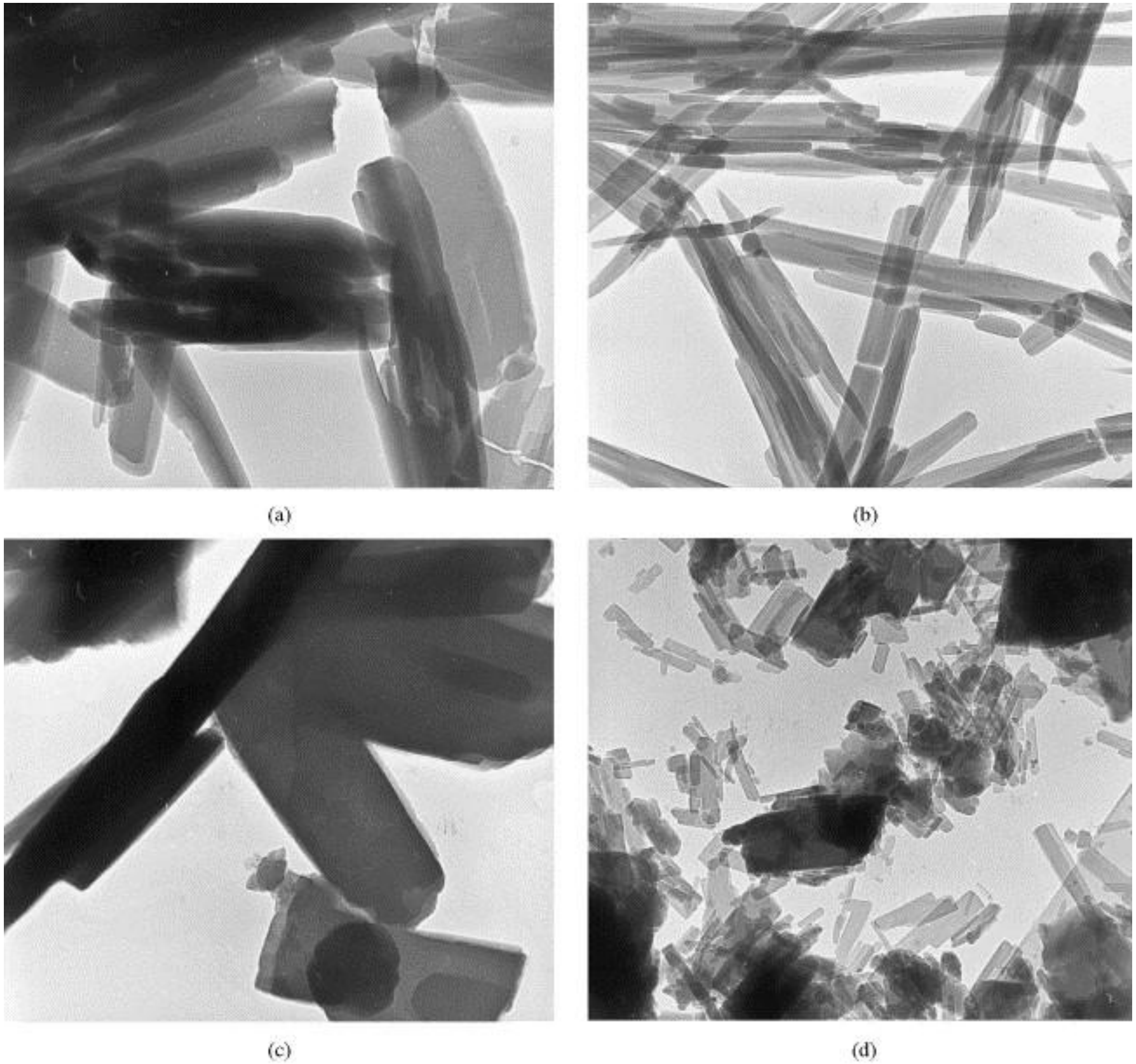
- The **binder** (film former) is the paint component that forms a continuous solid film after drying.
- It provides desired chemical and physical properties and determines the durability, adhesion, and flexibility of the paint
- **Common Binder types**

Acrylic	Alkyd	Cellulose	Chlorinated rubber
Emulsion	Epoxy	Natural oils	Phenolic
Polyurethane	Silicone	Styrene	Vinyl

- A paint type is usually identified by its binder, e.g., alkyd paint.

(2) Pigments

- Pigments are dry colorants, usually insoluble solid powders.
- Pigments are not only used for adding color to the coating, they are also used to improve the strength and adhesion of the paint, protect against corrosion, reduce gloss and modify application properties.
- The optimum pigment particle size is typically **0.2–0.4 µm**, which is close to half the wavelength of visible light, providing maximum light scattering and opacity. (below this scattering is low).
- Pigments occur in different shapes, such as **rod-like** (reinforcement, gloss reduction) and **plate-like** particles (form layers that prevent water and gas penetration).
- Pigments may be **natural or synthetic**, and **organic or inorganic**.



Scanning Electron Microscopy (SEM) images show pigment particles with different shapes and sizes, such as rod-like and plate-like structures.

Particle morphology affects opacity, gloss, strength, and barrier properties of the coating.

Plate-like pigments enhance water resistance by forming layered structures, while rod particles improve strength and reduce gloss.

Chisholm et al., Effects of fluorination on the properties of organic pigments
Dyes and Pigments, 1999, 42 (2), pp. 159–172

Types of Pigments

Opaque pigments	• Providing color and opacity • Examples: carbon (black), TiO2 (white)
Anti-corrosive pigments	• Improve corrosion protection • Example: Zinc chromate
Metallic pigments	• Provide metallic properties and appearance. • Can offer corrosion protection by means of cathodic protection (examples: zinc, aluminum)
Extender pigments	• Increase viscosity and reduce gloss • Improve adhesion. • They are also cheap (Kaolin, china clay, talc).
Lamellar pigments	• Increase resistant to water penetration • Increase the tensile strength of the coating (mica, glass & iron flakes)

Property		Pigment Preference	Reasons
السطوع والوضوح **Brilliance and clarity**	Ability of a pigment to produce bright and clean colors.	Organic	The most attractive, cleanest colors can only be obtained with organic pigments.
White & black paints	Ability of a pigment to produce pure white or deep black coloration.	Inorganic	The purest white pigment is titanium dioxide and the most jet black is carbon black. There are no organic black and whites.
عدم النزف **Non-bleeding**	Resistance of a pigment to dissolving or migrating into surrounding materials or solvents.	Inorganic	Inorganic compounds have negligible solubilities in organic solvents. Some organics are very insoluble.
الثبات الضوئي **Light fastness**	Resistance of a pigment to fading or color change when exposed to light, especially UV light.	Inorganic	The valency bonds in inorganic compounds are generally more stable to UV light than those in organic compounds.
الثبات الحراري **Heat stability**	Ability of a pigment to retain its color and structure at elevated temperatures.	Inorganic	Very few organic compounds are stable at or above 300°C. Some decompose or melt at much lower temperatures.
Anti-corrosive action	مقاومة التآكل	Inorganic	All anti-corrosive pigments are inorganic.

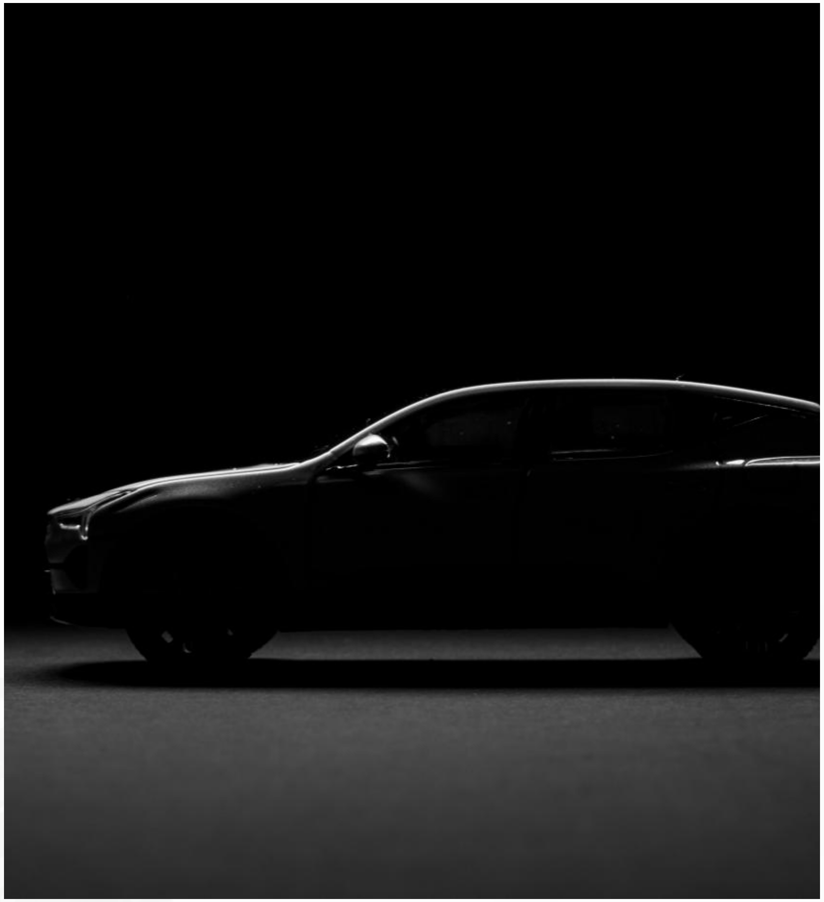
Carbon black (finely divided elemental carbon)

- It absorbs light extremely efficiently and is the standard pigment used to produce deep black colors in paints, inks, coatings, and plastics.

Materials like carbon nanotube (CNT) arrays absorb >99.9% of light (e.g., Vantablack). These are not typical pigments and are rarely used as conventional paints.

Car coated in Vantablack

- A special exhibition version used **Vantablack**, made from vertically aligned **carbon nanotubes**.
- The finish absorbs nearly all visible light, making surfaces appear almost flat and detail-less.



Why you can't buy one

You won't see this car in a local showroom for three main reasons:

1. **Safety:** It is too dangerous for the road. Other drivers cannot judge the car’s distance or speed because their brains cannot perceive its 3D shape.
2. **Durability:** The carbon nanotubes are incredibly fragile. Touching the car with your finger can crush the "forest" of tubes, leaving a permanent shiny spot. A car wash would destroy the finish instantly.
3. **Thermal Issues:** Because it absorbs nearly all light and converts it to heat, the car would become dangerously hot under direct sunlight.

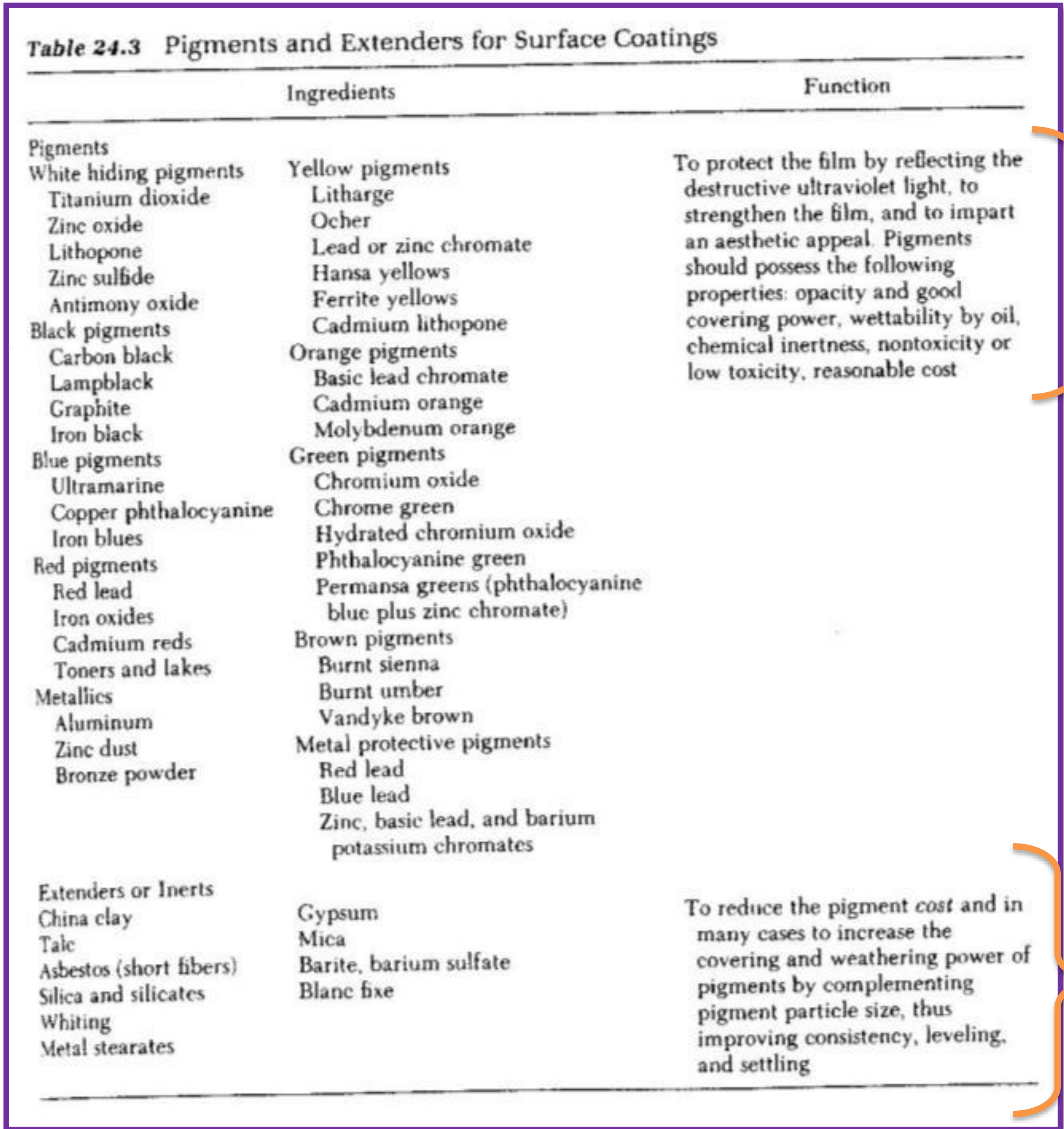


Table 24.3 Pigments and Extenders for Surface Coatings

Ingredients		Function
Pigments White hiding pigments Titanium dioxide Zinc oxide Lithopone Zinc sulfide Antimony oxide Black pigments Carbon black Lampblack Graphite Iron black Blue pigments Ultramarine Copper phthalocyanine Iron blues Red pigments Red lead Iron oxides Cadmium reds Toners and lakes Metallics Aluminum Zinc dust Bronze powder	Yellow pigments Litharge Ocher Lead or zinc chromate Hansa yellows Ferrite yellows Cadmium lithopone Orange pigments Basic lead chromate Cadmium orange Molybdenum orange Green pigments Chromium oxide Chrome green Hydrated chromium oxide Phthalocyanine green Permansa greens (phthalocyanine blue plus zinc chromate) Brown pigments Burnt sienna Burnt umber Vandyke brown Metal protective pigments Red lead Blue lead Zinc, basic lead, and barium potassium chromates	To protect the film by reflecting the destructive ultraviolet light, to strengthen the film, and to impart an aesthetic appeal. Pigments should possess the following properties: opacity and good covering power, wettability by oil, chemical inertness, nontoxicity or low toxicity, reasonable cost
Extenders or Inerts China clay Talc Asbestos (short fibers) Silica and silicates Whiting Metal stearates	Gypsum Mica Barite, barium sulfate Blanc fixe	To reduce the pigment cost and in many cases to increase the covering and weathering power of pigments by complementing pigment particle size, thus improving consistency, leveling, and settling

Memorize this function of pigments

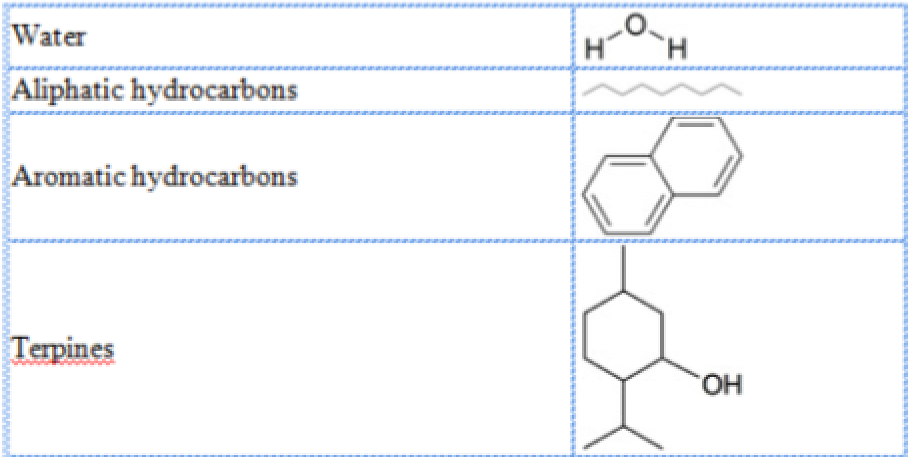
Memorize this function of extenders

Lecture 2

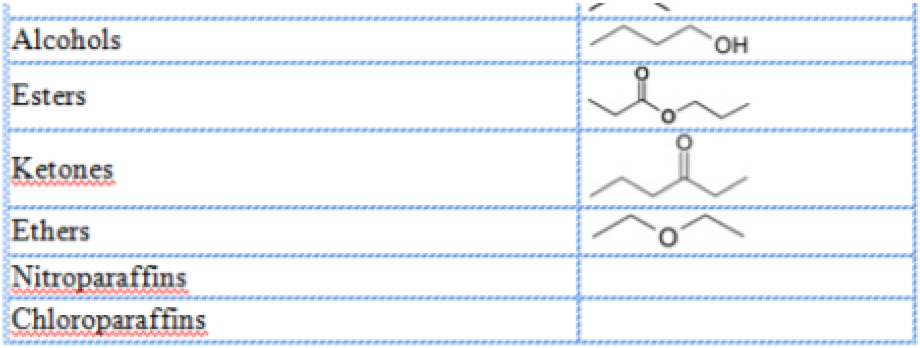
Constituents of Paints (cont’d)
Types of Paints

(3) Solvent

- A solvent gives the paint the ability to be spread over a large surface area.
- The solvent must be volatile to evaporate from the paint surface leaving the paint film.
- Solvents can affect the physical properties of the paint; the drying and gloss, therefore the solvent must be chosen carefully to suit the desired needs
- **Examples of solvents**:



Water	
Aliphatic hydrocarbons	
Aromatic hydrocarbons	
Terpines	



Alcohols	
Esters	
Ketones	
Ethers	
Nitroparaffins	
Chloroparaffins	

Types of Paints

There are many different types of paint. All of which are different chemically and have different physical properties.

1) **Laquers** - General industrial finishing, cars, furniture
2) **Emulsions** - Household and industrial
3) **Oils and varnishes** - Wood and steel primers
4) **Alkyds** - Household
5) **Acrylics** - Domestic
6) **Epoxies** - Anti-corrosive
7) **Polyurathanes** - Floors, boats, corrosion resistant metal finishes, concrete and plastic coating.

1) Laquer Paints

What it is
- Fast-drying paint based on polymer dissolved in solvent

Binder / Base
- Thermoplastic polymers (cellulose, acrylics)

How it dries
- Solvent evaporation (no chemical reaction)

Key properties
- Very fast drying
- High gloss, smooth finish

Typical applications
- Furniture and wood finishing
- Automotive clear coats

🧠 *Memory key:* **“Lacquer = fast dry, glossy, solvent evaporation”**

2) Emulsion (Latex) Paints

What it is
Water-based paint with polymer particles dispersed in water

Binder / Base
Acrylic or vinyl polymer emulsions

How it dries
Water evaporation + particle coalescence

Key properties

- Low odor, environmentally friendly
- Easy cleanup with water

Typical applications

- Interior and exterior walls
- Household and architectural coatings

🧠 *Memory key:* **“Emulsion = water-based, safe, walls”**

3) Oils and Varnishes Paints

What it is
Traditional coatings based on drying oils

Binder / Base
Natural oils (linseed, tung) + resins

How it dries
Oxidation with air (slow drying)

Key properties
- Good penetration into wood
- Warm, decorative finish

Typical applications
- Wood protection
- Furniture and doors

🧠 *Memory key:* **"Oils = wood + slow air drying"**

4) Alkyd Paints

What it is
- Modified oil-based paints with synthetic resins

Binder / Base
- Alkyd resins (oil-modified polyesters)

How it dries
- Oxidation + polymer crosslinking

Key properties
- Better durability than oils
- Smooth, glossy finish

Typical applications
- Metal primers
- Household enamels

🧠 *Memory key:* **“Alkyd = improved oil paint”**

5) Acrylic Paints

What it is
- Synthetic polymer paints with excellent durability

Binder / Base
- Acrylic polymers (water or solvent based)

How it dries
- Water or solvent evaporation

Key properties
- Excellent UV resistance
- Color stability

Typical applications
- Exterior building coatings
- Decorative and domestic paints

🧠 *Memory key:* **“Acrylic = weather & UV resistant”**

6) Epoxy Paints

What it is
- High-performance protective coatings

Binder / Base
- Epoxy resin + hardener

How it cures
- Chemical cross-linking (thermoset)

Key properties
- Excellent chemical and corrosion resistance
- Very strong adhesion

Typical applications
- Industrial floors
- Anti-corrosion coatings for steel

🧠 *Memory key:* **“Epoxy = strong, chemical-resistant”**

7) Polyurethane Paints

What it is
- Tough, flexible, high-performance coatings

Binder / Base
- Polyurethane resins

How it cures
- Chemical reaction (moisture or hardener)

Key properties
- Excellent abrasion resistance
- High gloss and durability

Typical applications
- Floors and marine coatings
- Automotive and protective finishes

🧠 *Memory key:* **“PU = tough, flexible, premium”**

Quick Comparison

Paint	Key Feature
Lacquer	Fastest drying
Emulsion	Water-based & safe
Oil	Traditional wood finish
Alkyd	Improved oil durability
Acrylic	UV & weather resistant
Epoxy	Chemical & corrosion resistance
Polyurethane	Tough & abrasion resistant

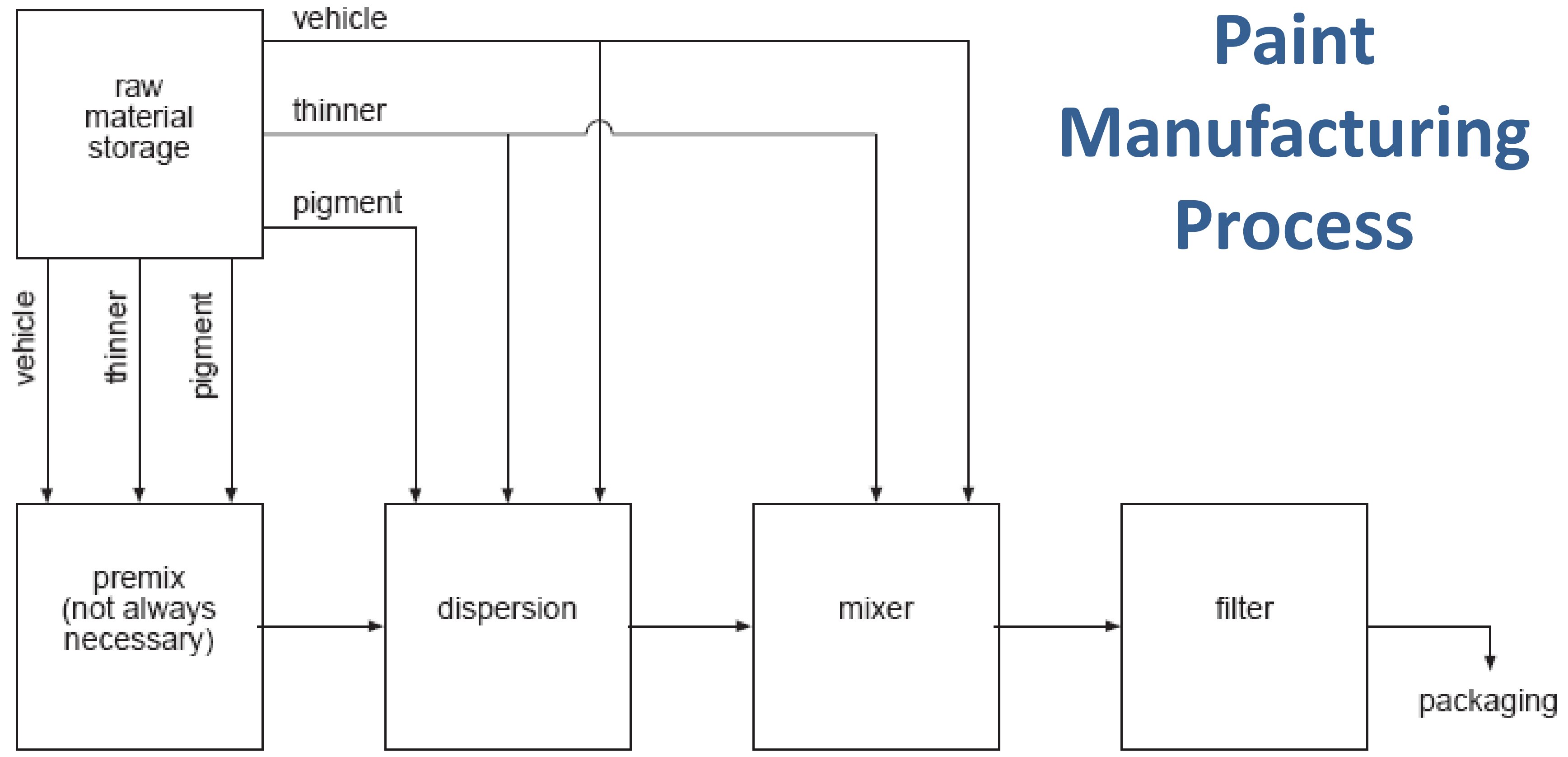
Lecture 3

Paint Manufacturing
Paint Drying Methods

Paint Manufacturing

- The manufacture of paint or coatings is a physical process that seldom involves significant chemical changes.
- Virtually all paint production employs the batch process, with continuous processing being quite rare.
- Generally, the manufacturing process consists of these steps: **Mixing → Filtration → Packaging**
  - Clear coatings, such as varnishes, are made by mixing specific ratios of resin binders with volatile solvents, using a mechanical agitator in a mixing tank. Once mixed, the batch is pumped through a filter and packaged for sale.
  - For opaque (white or colored) paints, the manufacturing process is the same as for making varnish except that pigments are first **dispersed** in a portion of the vehicle. The batch is finished by mixing the balance of the vehicle into the *pre-dispersed pigment/vehicle mixture*.

Paint Manufacturing Process



Paint production involves controlled mixing, dispersion, and finishing of pigments, binders, and thinners to produce a uniform, usable coating.

Thinner is a low-viscosity liquid (solvent or diluent) added to paint to adjust its viscosity, improve flow, and enable proper mixing and application. It does not form the final solid film but evaporates after application.

Process Description

Raw Material Storage
The main paint components—**binder (vehicle), pigments, and thinner**—are stored separately to allow controlled feeding into the process.

Premixing (Optional)
Pigments are first mixed with part of the thinner and binder to form a **premix**. This step reduces dust formation and improves wetting of pigment particles.

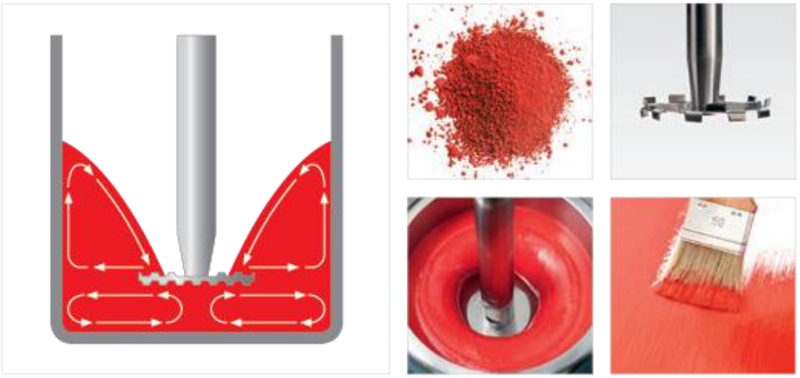
Dispersion
The premix is subjected to high-shear mixing to **break down pigment agglomerates** and achieve uniform pigment dispersion in the liquid phase.

Mixing
The dispersed pigments are blended with the remaining binder and thinner to obtain the **final paint composition** with the required color, viscosity, and consistency.

Filtration
The paint is filtered to remove **undispersed particles, gels, or impurities**, ensuring a smooth and defect-free product.

Packaging
The finished paint is filled into containers and prepared for storage, transport, and sale.

Pigment Dispersion step



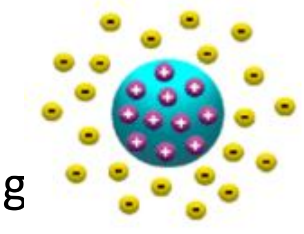
Why pigment dispersion is critical?

- Each dry pigment particle is actually a cluster of many smaller particles. The objective is to separate them from one another so that the surface of each small particle can be wetted with the vehicle and the particles can be evenly distributed throughout the paint.

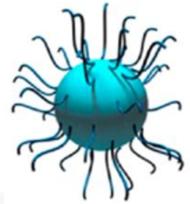
- This is accomplished by applying powerful mechanical forces using dispersion machinery of several different designs, e.g. High-speed disperser (a shaft with a disc-like toothed blade on one end.)
- When the blade is spun at high speeds in the viscous pigment/vehicle mix, shearing forces are produced at the surfaces of the blade.
- Often it is necessary to make a premixed paste of pigment/vehicle using a high-speed disperser. This paste is then fed into one of the other types of dispersion machinery.

Dispersion Stabilization

- Once dispersed, pigment particles have a tendency to associate, or flocculate, into loose clusters or to settle into a hard cake.
- **Dispersion stabilization**
  - Special additives are often necessary to enhance dispersion stability.
  - In water-thinned paint, stabilization is accomplished by imparting like electrostatic charges to pigment particles so that they repel each other.
  - In solvent-thinned paint, stabilization usually depends on steric hindrance, with molecules of binder adsorbing onto the pigment particle surfaces to form immobile envelopes around the particles. These envelopes of binder act as a physical barrier to particle association.



Electrostatic

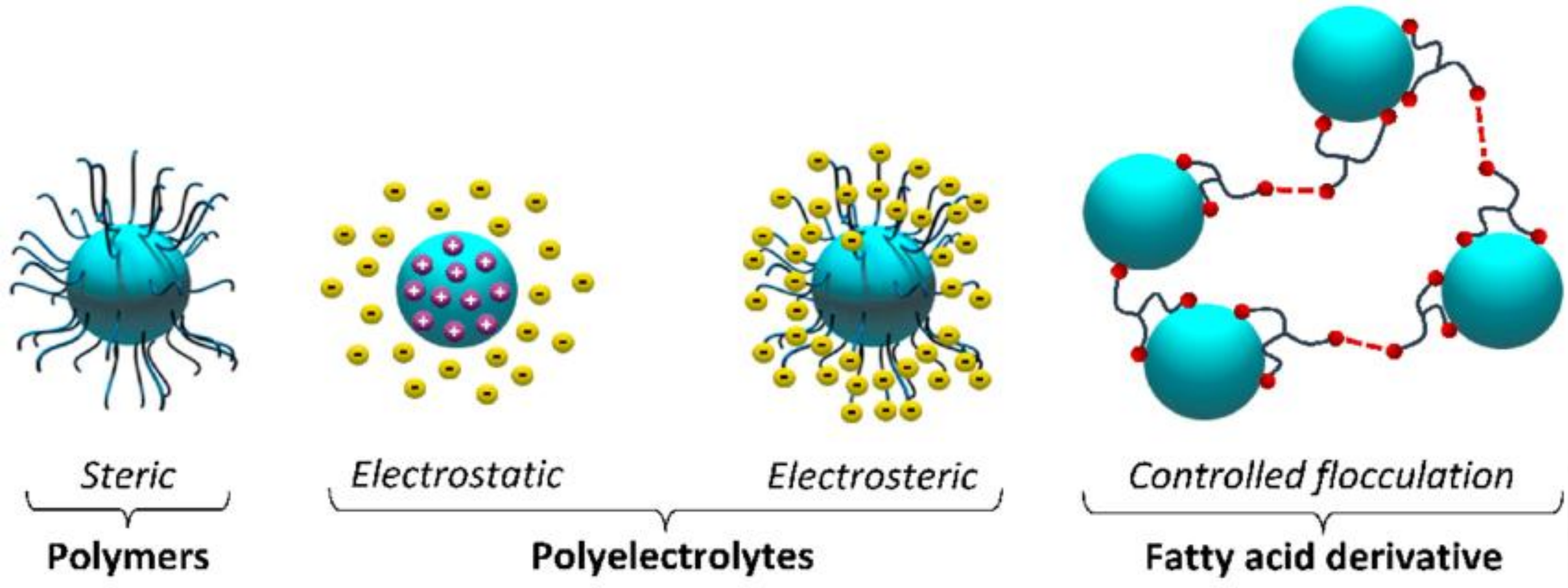


Steric

Polymers

Steric hindrance occurs when large molecules attached to a surface physically block other particles from approaching or reacting.

Mechanisms of Pigment Stabilization in Paints



Filtering & Packaging

The filtering step provides a way to remove any undispersed particles or extraneous in the batch.

Filtration methods:

- One often-used method employs **vibrating screens** with 40–300 mesh per square inch as strainers to separate the unwanted materials from the paint.
- Another filtering method allows the paint to drain through **felt bags**.
- Sometimes the paint is passed through **cylindrical cartridges of porous material**; where the paint filters through the walls of the cartridge, leaving the separated material in the container.

Once filtered, the paint batch is packaged.

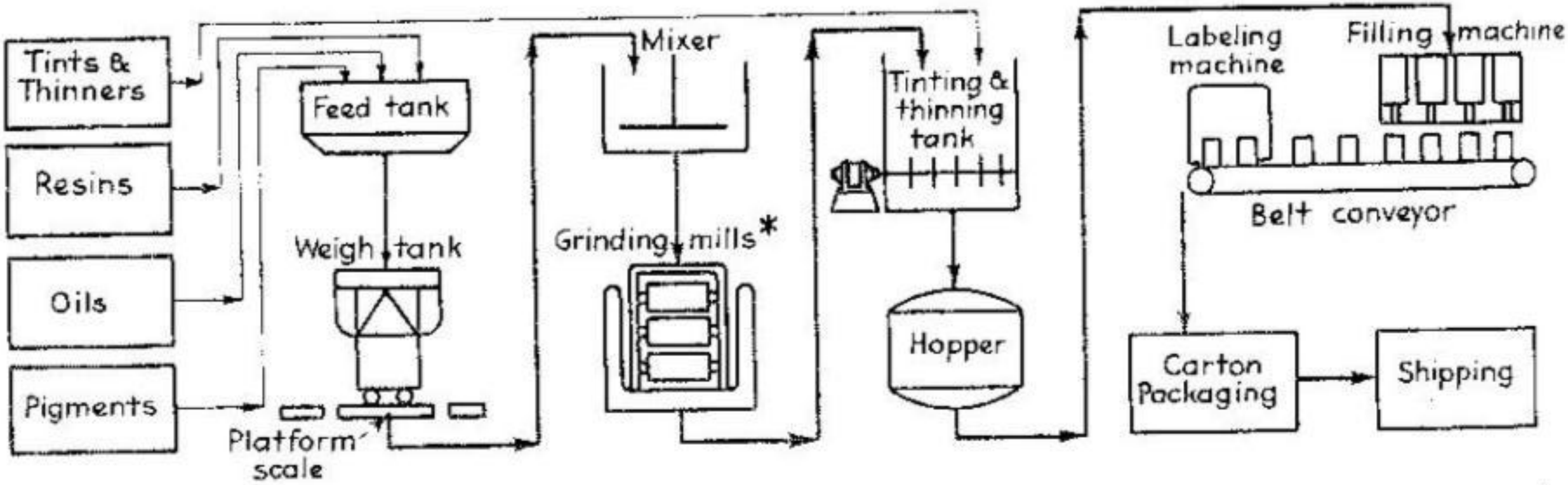


Fig. 24.1. Flowchart for the mixing of paint. NOTE: Because a complete paint factory consumes upward of 2000 different raw materials and produces ten times as many finished products, it is not possible to give yields, etc.

**Many types of grinding mills are used in the same plant, either in series or in parallel. Some of them are ball mills, high-speed dispersers, and three- and five-roll steel mills.*

Paint Drying

- The reason a paint goes dry is either due to the evaporation of the solvent or a chemical reaction to the binding medium, or a combination of both.
- The coating can be *air dried* or *force dried* at temperatures of up to 65°C. At temperatures above 65°C the drying process is called *stoving*.
- A paint can dry in one or a mixture of the following four methods:
  1. Solvent evaporation
  2. Oxidative drying
  3. Chemical curing
  4. Coalescence

1) Solvent evaporation

- Some paints can dry solely by the physical evaporation of the solvent to leave a film of non volatile solids. No chemical reaction or change does take a place.
- Typical of lacquers and many acrylic paints.
- Film can re-dissolve in the same solvent.
- These paints are referred to as ***reversible*** paints. This is because if the solvent is reapplied, then the coating will re-soften.
- **Why these paints are reversible**?
  - Because these paints possess linear or lightly branched polymers such as that **do not form chemical cross-links** during drying.
  - As a result, when the same solvent is reapplied, the solvent penetrates between the polymer chains, causing the film to soften or re-dissolve.

2) Oxidative drying

- Oxidative drying usually occurs **after initial solvent evaporation**.
- Drying occurs by reaction of the binder with oxygen from, causing **slow chemical cross-linking** within the paint film.
- This reaction is often **accelerated by driers** (metal salts) added to the paint.
- As cross-linking progresses, a hard, durable film is formed.
- Paints drying by this mechanism are **non-reversible**:
  - They do not soften or re-dissolve when the solvent is reapplied,
  - Because a chemical change has occurred in the binder.
- This drying mechanism is typical of oil-based and alkyd paints.
- Drying rate depends on oxygen availability and exposure to air.

3) Chemical curing

- Chemical curing occurs when **drying is achieved by a chemical reaction between paint components**, rather than by oxygen from air.
- The reaction leads to **polymer cross-linking**, forming a **hard, thermoset, irreversible film**.
- This process is **similar to oxidative drying**, but **uses curing agents or activators instead of oxygen**.
- Curing can be accelerated by **external energy**, such as **heat (stoving)** or **UV light**.
- Chemical curing systems are commonly:
  - **One-component systems**, activated by heat or UV,
  - **Two-component (two-pack) systems**, where the curing agent is mixed just before application.
- **Typical examples**: epoxy and polyurethane paints.

3) Chemical curing – Reaction Control

- **Driers and accelerators** are catalytic additives that **increase the rate of the curing reaction**.
- They speed up curing **without being consumed**.
- **Inhibitors** are added to **slow down or control the reaction**.
  - They react with **free radicals**, preventing premature polymerization.
  - Unlike catalysts, **inhibitors are consumed** during the process.
- **Anti-skinning agents** are **mild inhibitors** used mainly in **oxidative drying**.
  - They prevent surface skin formation,
  - Increase paint stability **inside the container** during storage.

4) Coalescence

- Coalescence occurs after initial water (or solvent) evaporation in emulsion (latex) paints.
- As the liquid phase evaporates, polymer particles move closer together and deform.
- The particles then merge (coalesce) to form a continuous, coherent film.
- No new chemical polymerization or cross-linking is required during coalescence.
- Coalescing agents (high-boiling solvents) may be added to:
  - Increase polymer particle mobility,
  - Allow film formation at lower temperatures.
- This mechanism is typical of acrylic and vinyl emulsion paints.
- Film formation requires the temperature to be above the Minimum Film-Forming Temperature (MFFT).

Minimum Film-Forming Temperature (MFFT): is the lowest temperature at which polymer particles in an emulsion paint can coalesce to form a continuous, defect-free film. Below the MFFT, the paint dries as a powdery or cracked layer instead of a smooth film.

Coalescence vs. Sintering vs. Melting

Coalescence (Paints & Polymer Coatings)

- Coalescence is a **physical film-forming process**.
- Occurs when **water or solvent evaporates** from emulsion (latex) paints.
- **Polymer particles move closer, deform, and merge** into a continuous film.
- Happens above the Minimum Film-Forming Temperature (MFFT).
- **No chemical reaction** and **no melting** occurs.

Typical applications:

- **Acrylic and vinyl emulsion paints**

Key idea:

- Soft polymer particles merge to form a film without melting.

Coalescence vs. Sintering vs. Melting

Sintering (Ceramics & Powder Materials)

- Sintering is a solid-state bonding process.
- Occurs when solid particles bond by atomic diffusion at their contact points.
- Takes place at high temperatures, but below the melting point.
- Results in reduced porosity and increased strength.
- No phase change and no chemical reaction.

Typical applications:

- Ceramics
- Powder metallurgy
- Solid catalysts

Key idea:

- Solid particles bond by diffusion while remaining solid.

Coalescence vs. Sintering vs. Melting

Melting (Phase Change)

- Melting is a physical phase change from solid to liquid.
- Occurs when temperature reaches the melting temperature (Tm).
- Solid structure is lost and material flows as a liquid.
- No chemical reaction involved.

Typical applications:

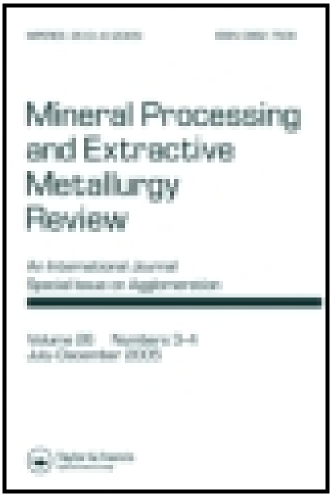
- Thermoplastics
- Metals
- Wax, ice

Key idea:

- Solid becomes a true liquid at its melting point.

Comparison Summary

Feature	Coalescence	Sintering	Melting
Phase change	❌ No	❌ No	✅ Yes
Particle state	Softened solids	Solid	Liquid
Main mechanism	Particle deformation & merging	Atomic diffusion	Thermal motion
Temperature level	Low–moderate	High (below Tm)	At or above Tm
Typical field	Paints	Ceramics & metals	Materials



Mineral Processing and Extractive Metallurgy Review: An International Journal

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmpr20

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To cite this article: Z. S. H. Abu-Hamatteh & A. M. Al-Amr (2008) CARNALLITE FROTH FLOTATION OPTIMIZATION AND CELL EFFICIENCY IN THE ARAB POTASH COMPANY, DEAD SEA, JORDAN, Mineral Processing and Extractive Metallurgy Review: An International Journal, 29:3, 232-257, DOI: 10.1080/08827500801997894

To link to this article: http://dx.doi.org/10.1080/08827500801997894

Mineral Processing & Extractive Metall. Rev., 29: 232–257, 2008

ISSN: 0882-7508 print/1547-7401 online
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CARNALLITE FROTH FLOTATION OPTIMIZATION AND CELL EFFICIENCY IN THE ARAB POTASH COMPANY, DEAD SEA, JORDAN

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Arab Potash Company (APC) was formed to develop minerals from the Dead Sea. Currently, APC is producing potash for agriculture and industrial potash for the chemical industry, industrial salt, bromine, and NPK (Nitrogen, Phosphorus, Potassium) fertilizers. The flotation unit at APC is a significant part of the overall processes, which end up separating halite from the carnallite in the mixture. The Dead Sea is the main and only source for the potash industry in the form of potassium chloride. The Dead Sea salts are converted into a final saleable product in the form of potassium chloride, which is commercially known as potash. The current study aims to provide plantoperators with a better understanding of flotation process. In this investigation, several laboratory experiments were conducted that covered several parameters and the best cell efficiency was achieved in terms of halite removal and carnallite recovery. Agitator speed, pulp density, reagent quantity, conditioning time, temperature effect, pH effect, additives effect, size distribution, and wet screening tests were performed. The conclusion is based on analyses of the obtained results incorporated with direct observation from APC flotation cells. The obtained results indicate that considering certain significant experimental parameters will reduce the loss and the overall cost and, consequently, will increase the overall production.

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***Keywords*: carnallite, crystallization, Dead Sea, froth flotation, Jordan, potash, potassium chloride**

1. INTRODUCTION

The Dead Sea is the world's saltiest natural lake. Its salinity (approximately 345 g/l) is 10 times higher than that of the normal ocean water (Abu-Hamatteh et al. 2005). The chemical contents of the Dead Sea's brine (average density 1.235 g/cc) holds a unique assemblage of salt minerals such as sodium chloride, potassium chloride, magnesium chloride, calcium chloride, and magnesium bromide (Al-Zoubi and ten-Brink 2001; Elsom and Longhurst 2004). The estimated total amount of these salts is over 43 billion tons. Salts are believed to have originated when soluble salts from the surrounding area leached through the geologic time (Bender 1974; Quennell 1958; Weber et al. 2000). These salts accumulated from water under dry conditions in a closed area, referred to by many workers as a great aquifer of water (Al-Zoubi and ten-Brink, 2001;Elsom and Longhurst, 2004; Hall, 1993; Lovelock, 1984). These aquifers were found stored in the surrounding rocks, which began with the Dead Sea water level descending. The average concentrations of the ions (wt %) and rare elements (PPM) in the Dead Sea are given in Table 1.

The study area is part of the so-called Ghor area, which is below the main sea level and is where the Jordan River and the Dead Sea lie, has an

Table 1. The average concentrations of the anions, cations (wt%), and rare elements (PPM) in the Dead Sea

Elements	PPM	Anions	Wt%	Cations	Wt%
U	0.30	Cl^-	18.18	Mg^{++}	3.69
I	4.00	Br^-	0.50	Ca^{++}	1.39
Ni	3.00	SO_4^-	0.039	Na^+	2.83
Co	20.0	HCO_3^-	0.03	K^+	0.637
Zn	13.0				
Sr	270				
B	42.0				
Mn	4.00				
Rb	400				
Li	15.0				

altitude of 197 and 392 m below sea level in the northern Ghors and the Dead Sea, respectively. Climatologically, the Ghor area is very similar to a subtropical region. It is extremely hot during summer, with an average daily temperature of 39°C and 51°C the highest temperature recorded in the Dead Sea area. In winter, the average daily mean temperature is 15°C, with 9°C as an average daily minimum temperature (*Jordan Climatological Data Handbook* 1988).

The Jordanian Government founded the Arab Potash Company (APC) in 1956 (Amira and Barajakely 2000) to utilize two of Jordan's most abundant natural resources, i.e., solar energy and the mineral-rich brine of the Dead Sea. The location of the site complex is about 110 km south of Amman and 200 km north of Aqaba. The company operates one of the largest man-made solar pond systems within an area of 131 km^2 (built on land reclaimed from the Dead Sea). The precipitated carnallite in the pond has the chemical formula $KCl \cdot MgCl_2 \cdot 6H_2O$, which exists in combination with approximately 14% NaCl. The solar ponds feed three processing refineries to produce potash at an annual capacity of 1.9 mmt. Commercial potash production started in 1983 and has since progressed with intensive development and expansion. The original design annual capacity of the plant was 1.2 mmt, which was upgraded to reach 1.4 mmtpy by 1990 after a series of modifications in both the refinery and solar pond systems. The cold crystallization plant was added to the system in 1994 with a design capacity of 0.4 mmtpy increased to 0.5 mmtpy by 1999. This made the total potash production capacity 1.8 mmtpy. Further expansion of both refineries and the solar pond system are progressing in order to bring the total capacity to 2.5 mmtpy. The APC produces three grades of potash; standard, fine, and granular (compacted material) and recently has successfully produced industrial potash at the design capacity of 100,000 tpy.

The current investigation aims to examine the various parameters affecting the froth flotation process. Therefore, there have been several and comprehensive laboratory and field experiments, such as agitator speed test, pulp density, reagent quantity, conditioning time, temperature effect, pH effect, additives effect, size distribution, and wet screening tests. The laboratory tests covered the most significant parameters in order to achieve the best cell efficiency in terms of halite removal and carnallite recovery. Tests were conducted at the Al-Balqa' Applied University Froth Flotation laboratory in cooperation with the APC Technical and Production Departments. The main objective of this study is to minimize the cost and loss and, consequently, to increase the overall production.

Records show that the Dead Sea level is decreasing gradually (at 1810 record as −399.1 below Aqaba datum) and this decrease in level was caused due to severe shortages in water supply to the Dead Sea, evaporation due to a hot climate all year around (100 million m^3 estimated yearly) and continuous pumping from Jordan and Israel. For instance, in 2000 and 2001 the APC pumped 540 million m^3 (Omari and Sharayea 2001). In the 1980s the drop average was 79 cm/year and in the 1990s the ratio was 82.5 cm/year (Omari and Sharayea 2001). Its expected that evaporation from the Dead Sea will stop at the 450-m BSL (below sea level) due to decreasing the surface area with the decreasing of the sea level, adding to that an increase in the salinity, which will lead to decreasing vapor pressure and decreasing of the evaporation average per unit area. Therefore, increasing the concentration of the solution will lead to hydrophilic and absorbance of the water from the air (Omari and Sharayea 2001; Soub 1996).

2. THE DEAD SEA

The Dead Sea is the terminal lake at the southern end of the River Jordan, which for centuries has been receiving the waters of the river and very slowly concentrating the salts into what has become one of the greatest mineral reservoirs known to man. The water level of the Dead Sea has been on the decline since the beginning of the 20th century. This variation in level has happened before in the 12,000 years of the life of the Sea and there is reason to believe that nature and man will soon take measures to halt the fall of the water level, and perhaps to reverse this fall (APC 2007).

The origin of the Dead Sea in terms of plate tectonics can be traced to the movement of the great plates into which the lithosphere, the rigid outermost shell of the earth, is divided. The Dead Sea lies on the Syrio African Rift, along which two plates have been sliding past each other for some 10 million years. Immense layers of salt and gypsum on the Rift Valley floor reveal that, during the Pliocene Epoch, the valley was in effect a great lagoon connected at times to the ocean to the west. Tectonic movements one or two million years ago disrupted the marine connection (Al-Zoubi and ten-Brink 2001; APC 2007).

Thereafter, a succession of lakes occupied the valley. Perhaps 12,000 years ago, the valley and the Dead Sea attained what is essentially their present shape, but the water level of the Sea has continued to fluctuate slightly. The chemical character of the Dead Sea brine evolved along with the lake and its basin. The brine holds a unique assemblage of salts; calcium, magnesium, potassium, sodium, and bromine. Efforts to determine the age of the brine lead to the belief that the Dead Sea salts are as old as the lake itself. The origin of the salts is believed to be leaching of soluble salts from the surrounding areas through the ages, and their concentration in this 500-km^2 hypersaline lake. Close examination reveals that most of the salts are actually brought into the sea not by the major river system, but by local springs and seepages (Abu-Hamatteh et al. 2005; APC 2007).

The Dead Sea is devoid of life due to an extremely high content of salts, which include calcium, magnesium, sodium, potassium, and bromine. These salts provide the raw material for fertilizers, bath salts, and cosmetic products, which are marketed worldwide, as well as the basis for a complex chemical industry. With an average salinity of 345 g/L, compared with the average of other oceans of 34 g/L, the Dead Sea is the world's saltiest natural lake. The local climate of the Dead Sea is extremely arid and hot but water evaporation is relatively slow due to the lower vapor pressure over the surface. Over 43 billion tons of salts are thought to be available in the Dead Sea, of which almost 2 billion tons are potassium chloride (APC 2007).

3. MINERAL-PROCESSING METHODS USED AT APC

3.1. Solar Pond Systems

The solar-evaporation pond system is meant to prepare the raw material (carnallite) to be fed to the refineries. The Dead Sea brine is delivered to the first part of the solar pond system at a yearly average rate of 300 million tons. The brine flows to the salt ponds (sp-op, sp-oa, sp-1, sp-2, sp-3), which are connected serially including the carnallites ponds. The level inside the pans is controlled depending on the overall level and brine density. The first pond has the highest evaporation rate within the system. In these ponds, the initial concentration of Dead Sea brine has a density of 1.235 g/cm^3. Due to high evaporation and solubility of NaCl, most of it is deposited and the water content of the brine is reduced, bringing the final density of the brine to approximately 1.3 g/cm^3 (Rwashdeh 2002).

At the end of the salt ponds, the brine is transferred by gravity to another pond, known as the precarnallite pond (pc-2). The main function of this pond is to act as a control pond in order to make a proper composition of the brine feeding to the carnallite ponds. The KCl content at this stage is around 2%. The brine is then pumped to

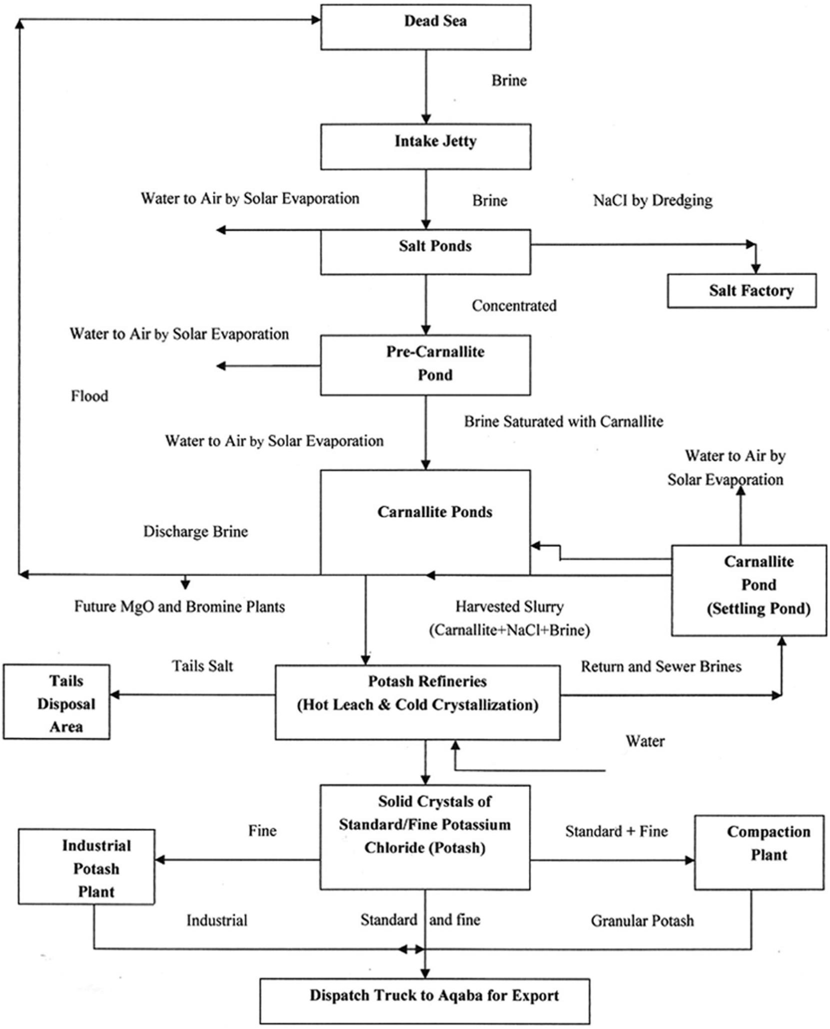

Figure 1. Flow sheet illustrating the carnallite loop.

C-3, which by gravity flows to the rest of the caranallite ponds in a series of seven carnallite ponds (C-3, C-2, C-1, C-5, C-6, and C-7) excluding C4, which is fed by the return brine from both refineries; hot and cold crystallization plant (Rwashdeh 2002). Further evaporation occurs and then carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) salt is crystallized. Carnallite that reaches to the carnallite ponds from salt ponds through a pumping station with an approximately $1.3\,g/cm^3$ density is usually harvested at 300–400-mm height. Brine from the last stage pond, C-7 (which contains a lower KCl content of approximately $0.4–0.5\,g/cm^3$), flows by gravity to the flood channel and back to the Dead Sea. The C-4 pond is fed by refinery return brine in order to improve the overall recovery of the pond system. The solar-evaporation pond system is capable of producing 10–11 mmtpy carnallites (Figure 1).

The Dead Sea water is pumped to solar pans (salt pans, precarnallite pans, and the carnallite pans subsequently). Therefore, due to evaporation, the carnallite precipitates in carnallite pans and then the harvesters pump it to both plants, the hot leaching plant and cold crystallization plant (Figure 2).

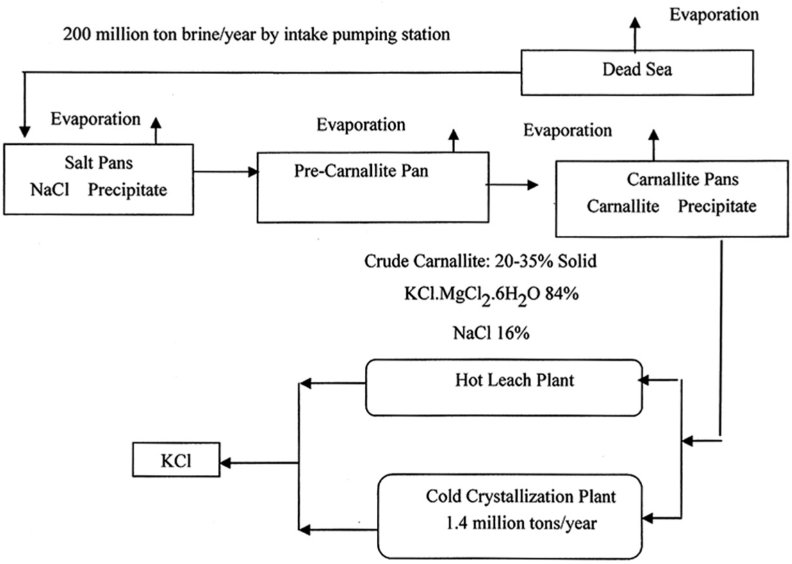

Figure 2. General process flow diagram.

3.2. Harvesting

300–400 mm of carnallite salt is crystallized and accumulated in the carnallite ponds with 84% pure carnallite and 16% sodium chloride as the average chemical composition. The carnallite bed is harvested beneath the brine in slurry form and is delivered to the process refineries via a series of pumps through steel pipes. APC has six tailor-made floating-type harvesters for this operation. the digital global positioning system (DGPS) is utilized for proper and precise harvesting guidance. This system has enhanced navigation and has been translated into higher productivity (Omari and Sharayea 2001).

3.3. Hot Leaching Plant

In this plant, the carnallite is received in main storage tanks, where the cake is separated from the liquid by centrifuges and is sent to decomposition tanks to get red out of the magnesium chloride by adding process water. Furthermore, the cake is sent again (which will be sylvinite) to the filtration unit. The next step is the hot leaching and crystallization unit (under vacuum pressure), followed by dewatering and drying the final product (Figure 1). The hot leach plant is operating at a design production rate of 1.4 mmtpy. In the hot leach process, the carnallite slurry delivered to the refinery is dewatered. Process water is used to decompose the resulting solid or cake (a mixture of NaCl and KCl known as sylvinite). The sylvinite slurry is dewatered and washed (Omari and Sharayea 2001). The dewatered cake is then introduced into hot leach plant tanks in two stages: heated brine is used for leaching potassium chloride and the hot brine is then saturated with KCl while the NaCl salt remains in a solid phase.

The saturated brine from hot thickener overflow (o/f) is cooled successively in six stages draft tube baffle vacuum crystallizers system from 93°C to 42°C. Upon cooling, KCl salt crystallizes under controlled conditions. The underflow from the last-stage crystallizer is transferred to hydro-cyclones, then to centrifuges for final dewatering (Rwashdeh 2002). The cake is dried in a rotary dryer in which fuel oil is used for drying. Product from the dryer is introduced into a screening section where two types of product are produced: standard and fine. Also, granular product is produced by compacting fine material. Anti-caking material is added to all products to reduce the caking tendency and to maintain free-flowing properties. Effluent dust and gases are passed through a number of cyclones and bag filters.

3.4. Cold Crystallization Plant

The cold crystallization plant is operating at a design production capacity of 0.5 mmtpy. This plant runs independently from the hot leach refinery and is operated at ambient conditions with fewer energy requirements. The process can be summarized as follows.

The carnallite salt that is delivered to the refinery first is beneficiated by wet screening to separate high-grade from low-grade carnallite. This stream is directed into flotation units where high-grade carnallite is obtained as a sink and NaCl as a float. Both streams (containing the high-grade carnallite and the sink product, after dewatering) are transferred into a two-stage cold crystallizer. Water is being added where $MgCl_2$ goes into solution, whereas KCl is crystallized, leached (in two stages), and dewatered. Centrifuges are utilized for the final dewatering. Then, the cake is dried in a rotary dryer (where fuel oil is used). The product is then classified as standard or fine material. Effluent gases and dust are directed into a series of high-efficiency cyclones.

In this plant, the flotation cells are used in order to remove or float the halite and to recover the carnallite. The carnallite is sent to atmospheric pressure and temperature crystallizers. Finally, dewatering and drying are used to create the final product. The general process is illustrated in Figures 2, 3, and 4. Technical data and specifications of the salt flotation cells used at APC are given in Table 2. The reagent used for flotation cells has a trade name of Armoflot-619 and contains the collector, frother, and modifier within the same formula. The quantity of the reagent is related directly to the size of the particles, as well as the mud that is pumped off the pans, which makes the ratio variable (N-alkylmorpholine; appearance at 20°C = liquid; color = yellow; boiling point = 130–170°C

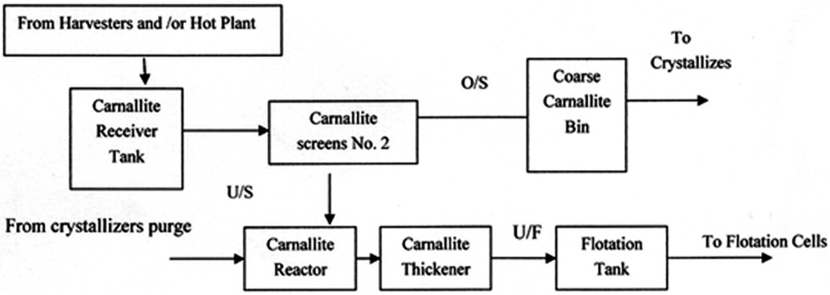

Figure 3. Carnallite processing in a cold crystallization plant.

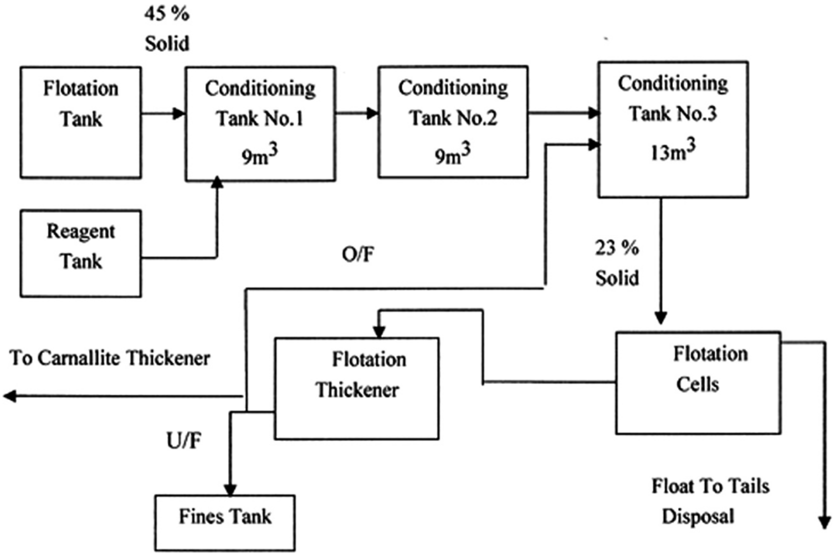

Figure 4. Flotation cells feed diagram.

(400 pa); flash point = >100°C Pensky-Martin closed cup; specific gravity = 0.87 at 25°C; viscosity = 30 mPa.s at 25°C; dosage = 0.0159 m^3/hr or 15.9 L/hr.

Hot leach and cold crystallization processes produce the same wastes of solids and dust (Figure 2). Sodium chloride is the only solid waste produced upon the application of potash-producing processes (approximately 1.9 mmtpy: 3tons sodium chloride per each ton of produced potash). Sodium chloride is pumped as a slurry mixture from both plants to a tails site. The tails area is able to accumulate all the solid wastes that result from 100 years of production. It constitutes a salty soil (inconvenient for flora) that was part of the Dead Sea floor. The topographical nature of this area assists the flow of the brine from the tails area to the Dead Sea through the truce channel. Limited quantities of the waste salt (NaCl) are sold. APC has utilized the salt material to construct a solid base layer (22 cm thick) that covers the ground at the newly established carnallite pan C-4.

4. MATERIALS AND METHODS

Two samples were taken from the main source (the flotation tank) for the flotation cells (Figure 4), in order to fix all parameters for performing the

Table 2. Flotation cells specifications

Test name	Changeable parameters	Fixed parameters
Agitator Speed	Agitator speed 700, 900, 1100, 1300, and 1500 rpm	Pulp density 23%; conditioning time 3 min; 250 g/t NaCl reagent
Pulp Density	16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, and 27% pulp density; this requires changing the solid and brine weights for both stages	Agitator speed 1100 rpm; conditioning time 3 min; 250 g/t NaCl reagent
Reagent Quantity	160, 190, 220, 250, 280, 310, and 330 g/t NaCl in feed	Pulp density 23%; conditioning time 3 min; agitator speed 1100 rpm
Conditioning Time	3, 4, 5, 6, and 7 min conditioning time	Pulp density 23%; agitator speed 1100 rpm; 250 g/t NaCl reagent
Temperature	20, 25, 30, 40, and 50°C for the process using a water path	Pulp density 23%; conditioning time 3 min; agitator speed 1100 rpm, 250 g/t NaCl reagent
Kerosene Addition	10, 20, 30, and 40% of total volume of the reagent and regent quantity	Pulp density 23%; conditioning time 3 min; agitator speed 1100 rpm
Diesel Addition	10, 20, 30, and 40% of the total volume for the reagent and regent quantity	Pulp density 23%; conditioning time 3 min; agitator speed 1100 rpm
pH	pH of the media	Pulp density 23%; conditioning time 3 min; agitator speed 1100 rpm, 250 g/t NaCl reagent

required experiments. One sample is kept with variable parameters in order to optimize the difference in the cell performance, using the same chemical specifications to optimize the differences in the cell performance. The measurement of particles size was performed by using laser ray diffraction. The objective is to intensively study the parameters that could affect the flotation process. The parameters that are considered during the experiments are shown in Table 3 by using a laboratory flotation cell apparatus and some field experiments. The chemical analyses had been carried out using an atomic absorption spectrometer, whereas

Table 3. Fixed and changeable experimental parameters

Manufacturer	Wemco, France
Number of cells	5
Unit cell volume	28.3 m^3
Froth area	11.34 m^2
Circulation rate	2740 m^3/hr
Circulation velocity	1.67 m/s
Air transfer	628.26 m^3/h
Air-slurry mixing residence time	1.106 s
Impeller speed	170 rpm
Froth paddle speed	21 rpm
Total assembled dimensions (meters)	18.55 L, 5.67 W; 4.96 H
Total retention time	7 min
Salt-removal efficiency	78.4%
Carnallite recovery	95%

the physical analyses used laser master sizer (Malvern) devices and wet screening techniques.

5. RESULTS AND DISCUSSION

5.1. Flotation

Flotation experiments were conducted in the laboratory flotation cell (Denver) and samples of 880 grams were initially conditioned at a pulp density of 16, 17...27% solid by weight at agitator speeds of 700, 900, 1100, 1300, and 1500 rpm, with conditioning times of 3, 4, 5, 6, and 7 minutes. A mix of sample and reagent was prepared at reagent quantity of 160, 190, 220, 250, 280, 310, and 330 gram/ton NaCl in cell feed. A series of tests were run in order to determine the optimum agitator speed, pulp density, quantity of reagent, conditioning time, temperature, quantity of additives (kerosene and diesel), and pH. The froth product (float) and sink was filtered, dried, grinded, and chemically analyzed. The cell efficiencies are shown in Figures 5–16. The flotation parameters used in the present study are shown in Table 3.

5.2. Sample Preparation

Two samples were taken from the flotation cell feed (Figure 4). After filtrating and drying, the samples were placed in an oven for 10 hours

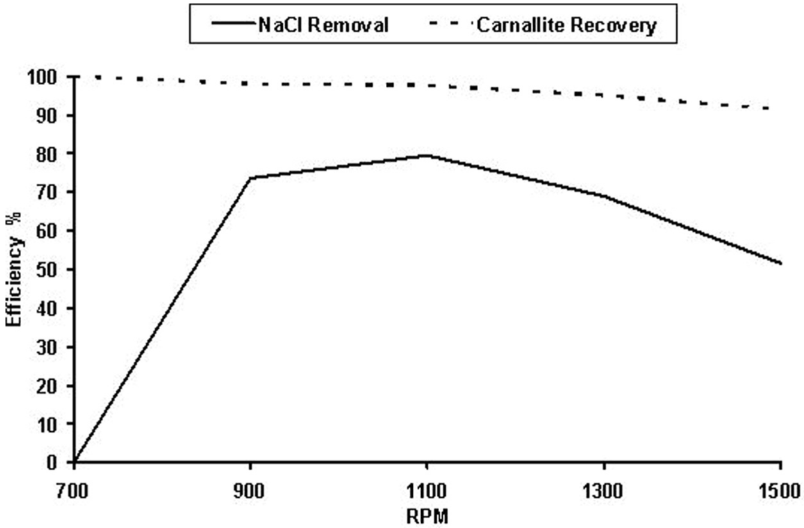

Figure 5. Binary diagram showing the result of an agitator-speed test.

at 90°C, in order to avoid losing the crystalline water from the carnallite crystals (Lide 1992; Stoev et al. 1992; Alford 1992; Bergh and Yianatos 1994; Ozkan 2002). The two samples were chemically analyzed for

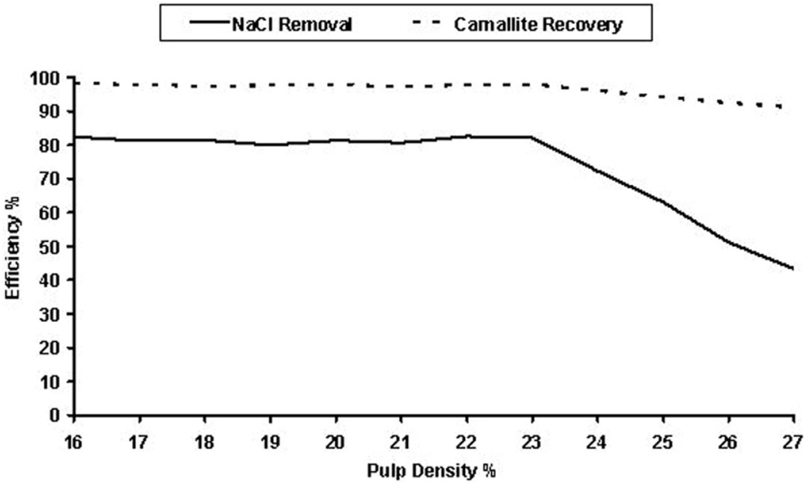

Figure 6. Binary diagram showing the result of a pulp-density test.

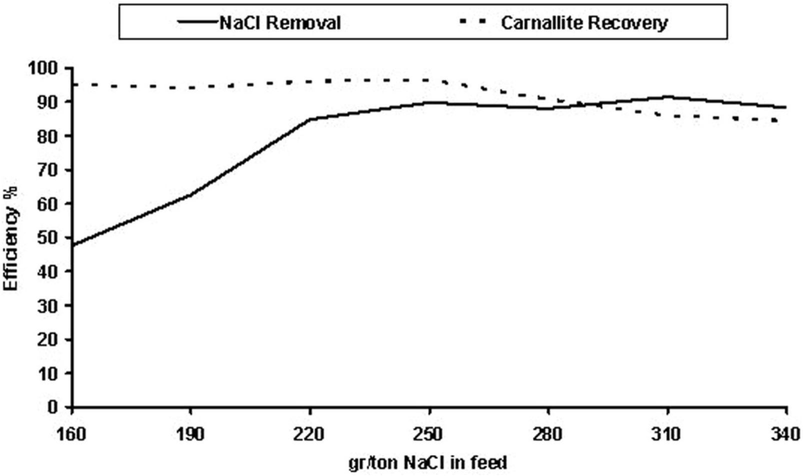

Figure 7. Binary diagram showing the result of a reagent-quantity test.

percentages of NaCl, KCl, $CaCl_2$, and $MgCl_2$. The results of the two samples are NaCl: 10.04% and 17.09%; KCl: 21.39% and 18.04%; $CaCl_2$: 0.60% and 0.58; and $MgCl_2$: 30.20% and 27.29 for samples 1 and 2, respectively.

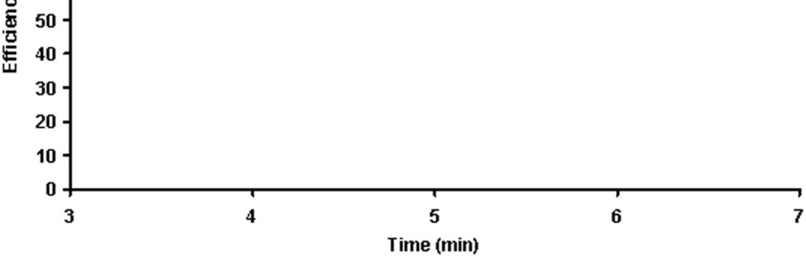

Figure 8. Binary diagram showing the result of a conditioning-time test.

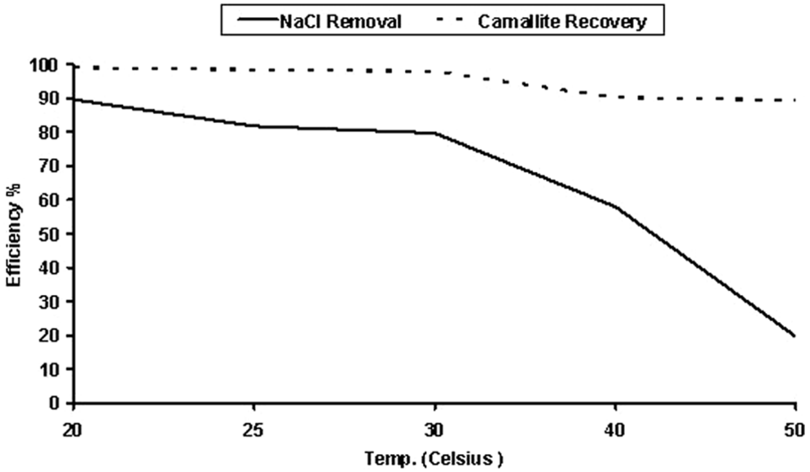

Figure 9. Binary diagram showing the result of a temperature test.

5.3. Flotation Parameters

5.3.1. Agitator-Speed Test. The main objective of this test is to determine the best speed for the cell agitator in relation to the cell's efficiency. The test requirements are: 1) 880 g of the sample; 2) 1076 g flotation thickener o/f brine (conditioning); 3) 1870 g flotation thickener o/f brine

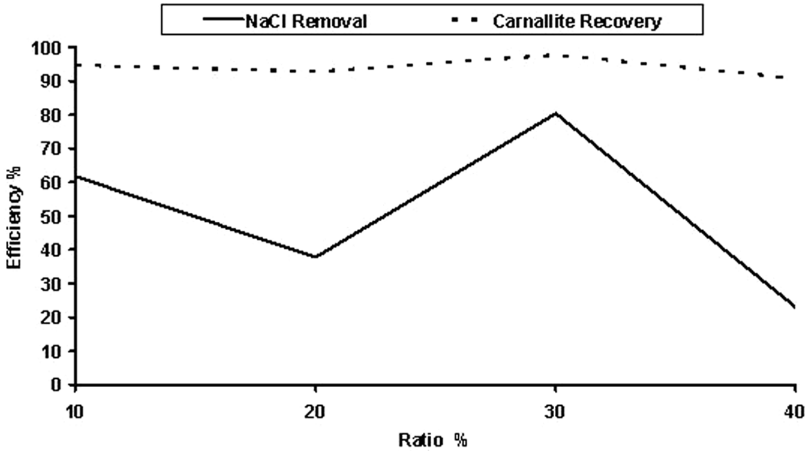

Figure 10. Binary diagram showing the result of a kerosene test.

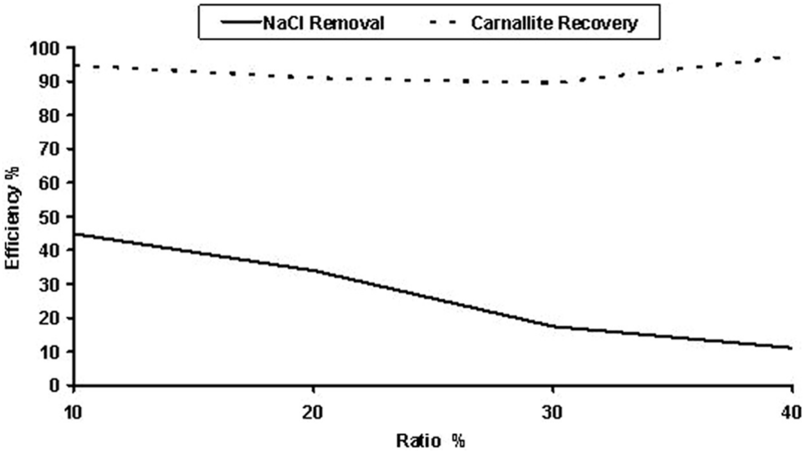

Figure 11. Binary diagram showing the result of a diesel test.

(dilution); and 4) preparation of the required quantity of reagent. The reagent was calculated in accordance with the plant design, which is 250 g/t NaCl in feed. Therefore, the required quantity was calculate to be $0.02629\,\mathrm{cm}^3 = 26.30\,\mu\mathrm{L}$.

1076 g of the flotation thickener brine was added to the cell container and the agitator was adjusted at a speed of 1500 rpm. Thereafter, 880 g of

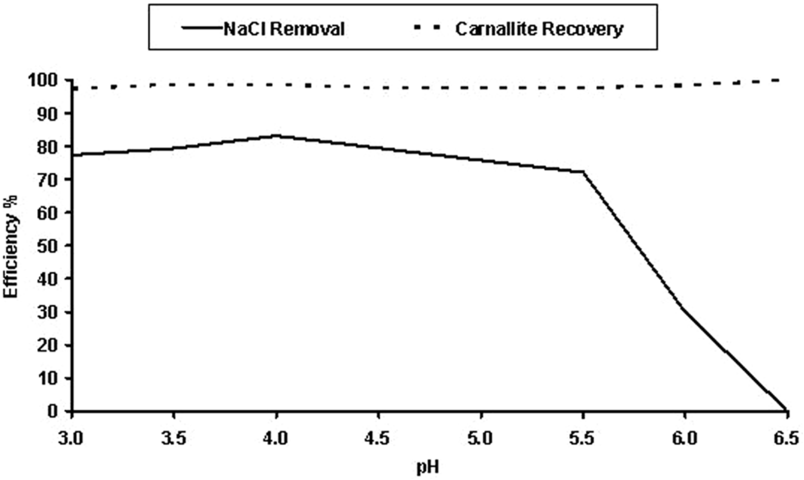

Figure 12. Binary diagram showing the result of a pH test.

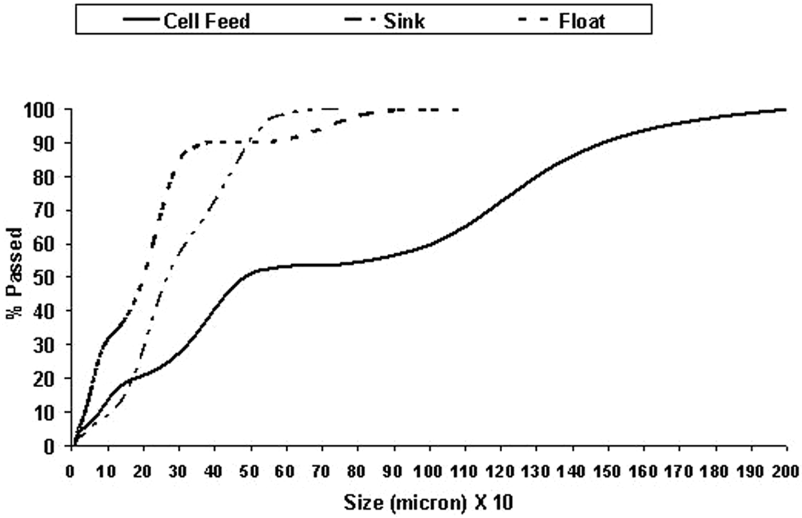

Figure 13. Size distribution versus accumulative pass chart.

the carnallite sample was added, along with 26.29 μm of the reagent. It was kept for 3 min in order to achieve the conditioning for the sample at pulp density 45%. After 3 min, 1870 g of flotation thickener brine was added to reduce the pulp density to 23% and to keep for 1 min.

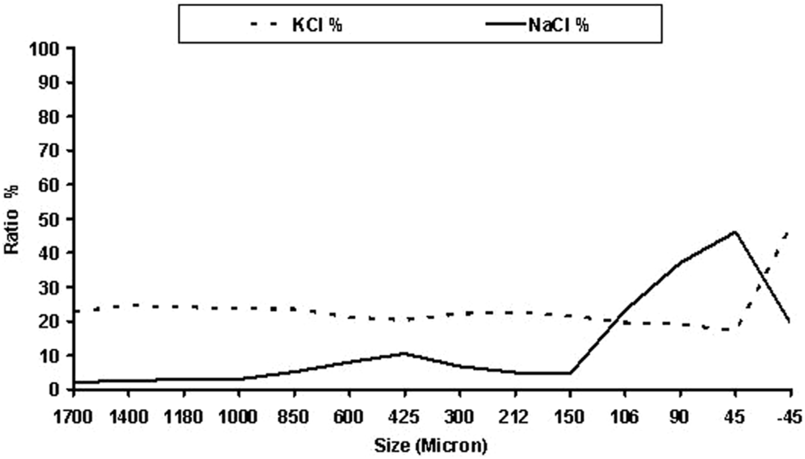

Figure 14. Cell feed sample wet screening analysis chart.

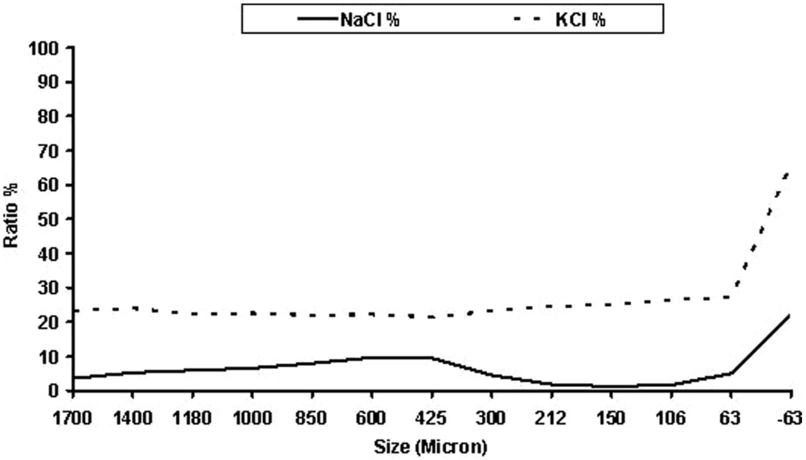

Figure 15. Sink sample wet screening analysis chart.

Finally, the feed entered into the first cell. The air valve opened and started skimming the froth for 90 sec, then the agitator was turned off. The sink and float were filtered individually and the samples were kept in an oven for 3 h at 90°C. Samples were milled in order to reduce the dried sink and float size prior to analyses. The objective of the milling process is to get a representative sample. The experiment was repeated

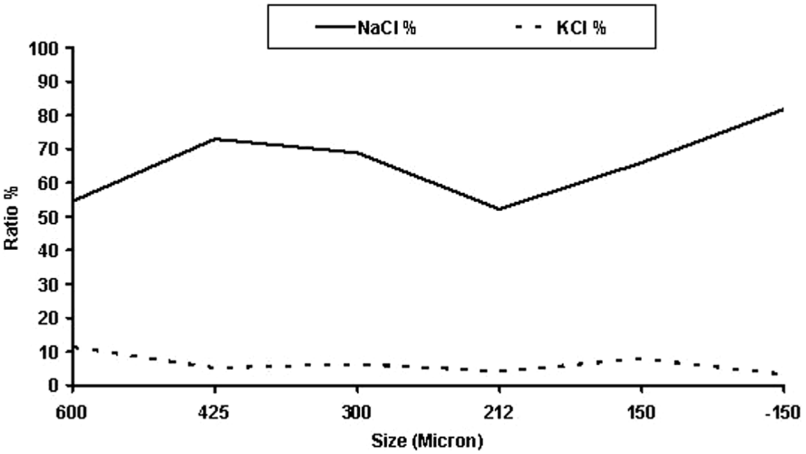

Figure 16. Float sample wet screening analyses chart.

under similar conditions except for the agitator speed, which is the only changeable parameter. Figure 5 shows the efficiency chart of the agitator-speed test, where the efficiency equations are:

$$\text{Carnallite recovery} = \frac{(Feed_{KCl} - Float_{KCl}) * Sink_{KCl}}{(Sink_{KClz} - Float_{KCl}) * Feed_{KCl}}\,100\%$$

$$\text{NaCl removal} = \frac{(Feed_{NaCl} - Float_{NaCl}) * Sink_{NaCl}}{(Sink_{NaClz} - Float_{NaCl}) * Feed_{NaCl}}\,100\%.$$

5.3.2. Pulp-Density Test. The pulp density test was performed to determine the best pulp density for the best cell efficiency. The agitator speed was kept at 1100 rpm with a similar time duration, where the quantity of reagent was based on 250 g/t NaCl in the feed. The cell efficiency is illustrated in Figure 6.

5.3.3. Reagent-Quantity Test. The reagent-quantity test is conducted in order to determine the optimum quantity required for best cell efficiency. The chemical analyses indicate that the sample ratio is 17.09% for NaCl and 18.04% for KCl, which means that the weight of NaCl in the tested sample is 150.39 g. The agitator speed 1100 rpm with fixed time and 23% pulp density. The reagent quantity is calculated as grams per ton of NaCl in the feed (Figure 7).

5.3.4. Conditioning-Time Test. This test is intended to determine the effect of conditioning time on the efficiency of the cell. At APC, the designer assigns the time according to the volume of tanks and the flow rate for the cell feed. In this experiment, we tried to find the behavior of the efficiency versus time (Figure 8). The cell feed sample was comprised of 17.09% NaCl, 18.04% KCl, and 43.22 μL reagent required for all tests. The pulp density remained as 23%, where the addition brine for conditioning and dilution is the same and constant agitator speed is 1100 rpm.

5.3.5. Temperature-Effect Test. Temperature plays an important role in the flotation process (Hanumanth and Williams 1992; Pal and Masliyah 1989, 1990;Schulze, 1984). The temperature-effect test evaluates the temperature effect on the flotation process by increasing and decreasing the temperature for the cell and media. The experiment was performed on five different temperature readings. The parameters are fixed for this test as that of the agitator speed, with the temperature as the only variable parameter. The sample weight was 880 g containing a 10.04% ratio of NaCl, with similar NaCl weight in the sample (91.52 g). An agitator speed is set at 1100 rpm and the reagent quantity is based on 250 g/t NaCl in the feed (Figure 9).

5.3.6. Additives-Effect Test. The relevance of the hydrocarbons, kerosene, diesel oil, and fuel oil or organic compounds in this process is that they act as extenders for the ionizable organic compounds that actually work as collectors. They interact with the desired mineral by establishing an insoluble compound that will cover the surface of the mineral and maintain the surface tension property of the used oil, which will lead to an increase in the contact angle. This experiment has been divided into two parts, i.e., kerosene and diesel additions. The tested ratios were 10%, 20%, 30%, and 40% for both tests. All parameters remain without any significant change with1100 rpm agitator speed and 23% pulp density, whereas the reagent ratio was 250 g/t and the quantity of both kerosene and diesel was calculated from the total volume. The cell-efficiency chart for the tests of kerosene and diesel are illustrated in Figures 10 and 11, respectively.

5.3.7. pH Effect Test. One of the most important factors in the flotation process is the pH (Schulze 1984; Ahmed and Jameson 1985; Crawford and Ralston 1988; Stoev et al. 1992; Tuteja et al., 1995; Ozkan 2002). In the site, the working pH is (5.2–5.4), however, in this experiment we tried to study the behavior of the cell performance in acidic and basic environments. HCl and NaOH were used to perform the pH effect test. The experiments were done with pH that varied from 3.0 to 6.5 with 0.5 constant increments. Other parameters remained constant with agitator speed set at 1100 rpm, pulp density 23%, reagent ratio 250 g/t, conditioning and flotation time 1, 1.5, and 3 min. The obtained chemical analyses are presented the in pH efficiency chart (Figure 12).

5.3.8. Size-Distribution Test. Classification of the particles sizes and their ratio in the tested samples was done to choose the proper screens for the wet screening process; therefore, a size-distribution test was conducted. Three samples have been taken from three different streams, i.e., flotation cells feed, flotation cells sink, and flotation cells float. The samples were tested by the Laser Master Sizer and the results are presented in Figure 13.

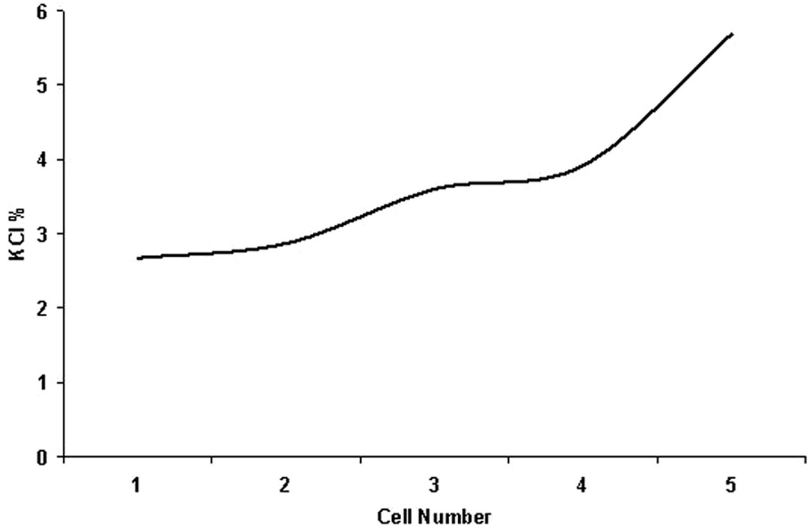

Figure 17. Relationship between KCl float percentage and various cells at APC.

5.3.9. Wet-Sieving Test. The main purpose of this test is to obtain the different sizes of solid particles and the ratio of KCl and NaCl for every chosen sieve. This test has been carried out on three samples collected from the cell feed, sink, and float. After the screening process, the residuals were filtrated, dried, and chemically analyzed. Figures 14–16 show the ratio of KCl and NaCl Vs screen size.

5.3.10. Samples from APC Flotation Cells Float Fraction. Six tests have been done on the flotation cells float from all five cells on-site, indicating the highest ratio of KCl from the last two cells, i.e., 4 and 5 (Figure 17).

5.4. Observations of APC Flotation Cells

The flotation cells' performance during the year 2002 is given for comparison (Table 4). The flotation cells performances after raising the density to 26% and 28% are given in Tables 5 and 6, respectively. A thorough investigation of the samples' raw materials was carried out in order to conduct the experiments. Samples of flotation feed materials were obtained from APC. Information about the physical properties and chemical composition of the samples provide important clues for proper

Table 4. Flotation cells performance during 2002

Month	Feed NaCl %	Float KCl %	Sink NaCl %	Efficiency % Carnallite recovery	Efficiency % NaCl removal
Jan	12.19	5.81	5.55	97.7	59.4
Feb	10.78	4.45	5.89	97.9	62.3
Mar	13.08	4.35	5.07	97.5	70.5
Apr	13.57	5.11	4.68	97.4	69.5
May	13.22	5.01	4.79	97.6	67.5
Jun	14.12	5.14	4.93	97.3	69.2
Jul	14.49	5.33	4.78	97.0	71.2
Aug	14.77	4.77	4.83	97.3	71.4
Sep	13.64	4.91	4.63	97.5	69.9
Oct	14.34	4.73	4.82	97.4	70.5
Nov	12.22	4.78	4.37	98.0	67.6
Dec	12.69	4.59	4.30	97.9	69.7
Average	13.26	4.92	4.89	97.54	68.23

planning of the experimental program; the chemical analysis of the main samples for the experiments was carried out at the APC plant. The sample recovery of the flotation-process characteristics depends greatly on the grain-size distribution. The sample grain size in the current study was carried out at APC using Laser Master Sizer (Malvern) device. The grain-size distribution chart for the flotation cells is given in Figure 13.

5.4.1. Agitator Speed Versus Cell Efficiency. As shown in Figure 5, the efficiency of our separation process shows that the lowest efficiency is 51.58% in term of NaCl removal and 91.35% in term of carnallite recovery at an agitator speed of 1500 rpm, whereas the heights efficiency

Table 5. Flotation cells performance at 26% pulp density

Time	Feed rate t/h	Reagent g/t NaCl	Feed NaCl %	Sink NaCl %	Float KCl %	Carnallite recovery %	NaCl removal %
9:00	220	399.4	11.88	3.12	8.18	95.4	63.9
11:00	210	163.2	13.71	5.66	7.58	96.0	59.1
13:00	210	198.1	13.80	7.79	11.50	93.9	41.8
15:00	220	184.2	14.17	7.98	7.20	97.0	50.7
17:00	200	374.5	13.94	9.29	7.29	97.7	41.8
Average	212	263.88	13.50	6.77	8.35	96.00	51.46

Table 6. Flotation cells performance at 28% pulp density

Time	Feed rate t/h	Reagent g/t NaCl	Feed NaCl %	Sink NaCl %	Float KCl %	Carnallite recovery %	NaCl removal %
9:00	160	441.3	11.09	5.63	6.35	97.9	51.7
11:00	160	506.1	9.67	2.83	6.50	97.5	64.6
13:00	100	537.4	14.57	4.05	9.20	93.2	62.7
15:00	150	500	13.5	4.0	10.2	89.37	56.18
17:00	150	457	9.90	4.60	12.08	94.7	41.6
19:00	170	368.2	12.51	6.10	10.08	95.1	47.6
21:00	135	572.6	10.13	5.0	6.90	97.9	50.5
Average	146.43	483.23	11.62	4.60	8.76	95.10	53.55

was recorded as 79.49% in terms of NaCl removal and 97.63% in terms of carnallite recovery at an agitator speed of 1100 rpm.

5.4.2. Pulp Density Versus Cell Efficiency. Pulp density has a great influence on the efficiency of the flotation process (Figure 6), indicating that the best efficiency of the flotation process was nearly constant in both terms until the pulp density reached 23%, which started to reduce substantially with an increase in the pulp density.

5.4.3. Reagent Quantity Versus Cell Efficiency. Another benefit obtained from the presence of reagent during the flotation process is the considerable variations in efficiency that were observed depending on the quantity of reagent added. A sample made from 160 g/t NaCl in feed had a comparatively low efficiency observed at 47.67% in terms of NaCl removal. The highest efficiency in terms of NaCl removal was achieved on a 310-g/t NaCl sample, which was 91.46% but the carnallite recovery was 86%, as shown in Figure 7. However, the sample of 250 g/t shows better efficiency in terms carnallite recovery and NaCl removal, i.e., 96.53% and 89.81%, respectively.

5.4.4. Conditioning Time Versus Cell Efficiency. The conditioning time also has a great influence on the efficiency of the flotation process, as shown in Figure 8. The best efficiency was observed with 6 min of conditioning time. It was recorded as 96.75 % and 85.09% in terms of carnallite recovery and NaCl removal, respectively. The lowest efficiency was recorded at 7 min of conditioning time.

5.4.5. Temperature Versus Efficiency. Temperature plays an important role in the flotation process. Figure 9 shows that the efficiency is reduced substantially with increasing temperature. The lowest value is observed at 50°C and the highest value was obtained at 20°C.

5.4.6. Additives Versus Efficiency. Figure 10 illustrates that the best efficiency is obtained through the addition of 30% kerosene. The efficiency of the flotation process ranged between 11% (lowest) with 40% addition ratio and 45% (highest) with 10 % addition ratio, in terms of NaCl removal of diesel (Figure 11).

5.4.7. pH Versus Efficiency. Figure 12 shows that the efficiency of the flotation process is reduced substantially with increasing pH. The highest value of efficiency was observed at 4.0 pH.

5.4.8. Particle-Size Distribution Versus Chemical Composition. Figure 13 shows that 60% of the cell feed passed from a 1000-μm screen. On the other hand, Figure 14 indicates that the particular range in size has a low ratio of NaCl.

5.4.9. Number of Cells Versus KCl% in Float. Figure 17 shows the increase of KCl ratio in the float fraction, which means that the lost quantity of carnallite is increasing from cell one to cell five.

5. CONCLUSION AND RECOMMENDATIONS

The optimum efficiencies of the flotation process in the current study were achieved after investigating several parameters, which led to the best conditions. They are 1100 rpm agitator speed, 22% pulp density, 250 g/t NaCl reagent quantity, 6 min conditioning time, 20°C temperature; 30% of kerosene, and 4.0 optimum pH. Sizes greater than 1000 μm need no flotation and the highest ratios of KCl in float exist in the last cells. The results obtained during this investigation could help to achieve maximum efficiency at a lower cost, taking into consideration the following recommendations:

- Separating the particles greater than 1000 μm before entering the flotation cells
- Increasing the conditioning time

- Replacing the first conditioning tank with a new bigger tank (27 m^3)
- Recycling the float from cells four and five (scavenger)
- Studying the consequences of adding acid to the cells in order to reduce the working pH from 5.2–5.5 to 4.0–4.5, but the outputs of the cells need to be neutralized.

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