2 March 2016

Lecture 4 - Lime

CE 344
Materials of Construction

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CE 344 – Tentative Outline

Week	Dates		Topic
1	22-Feb	26-Feb	**1. Introduction to materials of construction**
			2. Gypsum
2	29-Feb	4-Mar	**3. Lime**
3	7-Mar	11-Mar	4. Portland cement
4	14-Mar	18-Mar	(1st Lab around these dates)
5	21-Mar	25-Mar	
6	28-Mar	1-Apr	5. Pozzolans
	Specific date TBA		1st MIDTERM EXAMINATION
7	4-Apr	8-Apr	6. Aggregates
8	11-Apr	15-Apr	(2nd Lab around these dates)
9	18-Apr	22-Apr	7. Concrete
10	25-Apr	29-Apr	(3rd Lab around these dates)
11	2-May	6-May	
12	9-May	13-May	
	Specific date TBA		2nd MIDTERM EXAMINATION
13	16-May	20-May	8. Ferrous metals, alloys and concrete reinforcement
14	23-May	27-May	9. Polymers
			10. Clay bricks

(*) The detailed course schedule is available at the course web page.

GYPSUM

- Gypsum plaster:
  - For each 1 cm, 9-11 kg/m^2
  - 150-165 TL/ton (2014)
- Saten plaster
  - For each 1 mm, 1 kg/m^2
  - 279 TL/ton (2014)

	(1000 tons)	2012	Reserves
1	China	48,000	NA
2	Iran	14,000	NA
3	Spain	11,500	NA
4	Thailand	10,000	NA
5	United States	9,900	700,000
6	Japan	5,700	NA
7	Italy	4,100	NA
8	Mexico	3,850	NA
9	Russia	3,100	NA
10	Australia	3,000	NA
11	Turkey	3,000	NA
12	Brazil	2,800	230,000
13	India	2,750	69,000
14	France	2,300	NA
15	Saudi Arabia	2,300	NA
16	Canada	2,200	450,000
17	Germany	2,050	NA
18	United Kindom	1,700	NA
19	Algeria	1,650	NA
20	Argentina	1,200	NA
21	Poland	1,200	55,000
22	Other countries	14,900	NA
	World (rounded)	150,000	Large

Calcination of Gypsum

- Gypsum rock when heated to 100-190°C looses ¾ of its water:

$$CaSO_4.2H_2O \xrightarrow{100\text{-}190^\circ C} CaSO_4.\tfrac{1}{2}H_2O + 3/2\ H_2O \uparrow$$

Plaster of Paris

(This is low burning process called as INCOMPLETE CALCINATION.)

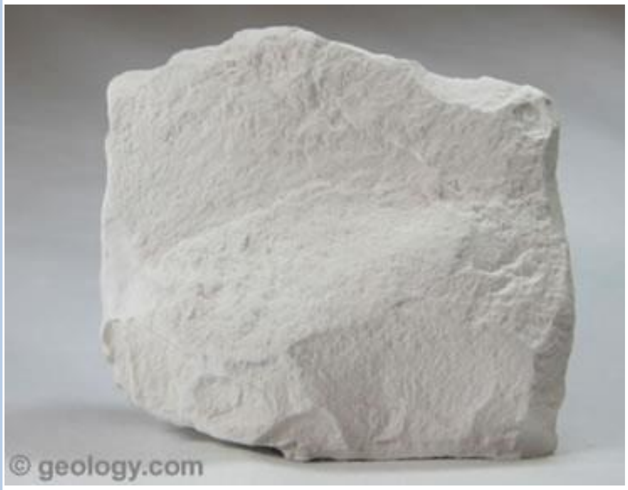
- When calcination is carried out at temperatures above 190°C all water is removed:

$$CaSO_4.2H_2O \xrightarrow{>190^\circ C} CaSO_4 + 2H_2O$$

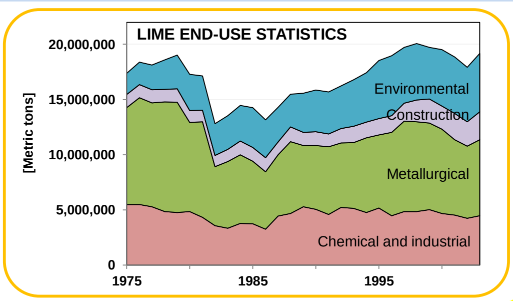
Gypsum anhydrite

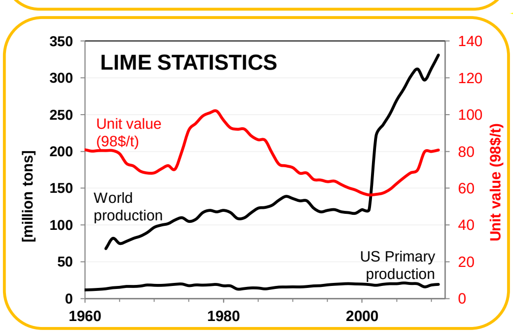
(This is high-burning process & COMPLETE CALCINATION.)

LIME



Lime production





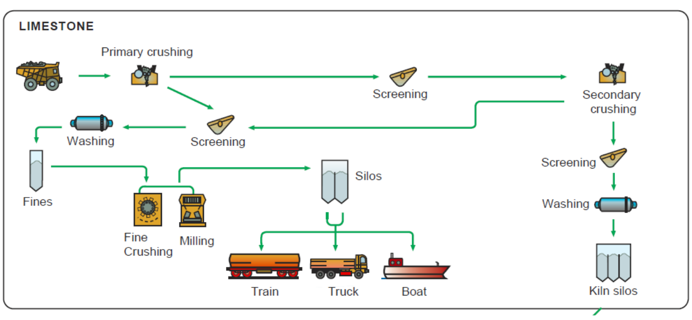
	(1000 tons)	2011
1	China	200,000
2	United States	19,300
3	India	15,000
4	Other countries	12,000
5	Brazil	8,300
6	Russia	8,200
7	Japan (quicklime only)	7,200
8	Germany	7,100
9	Italy5	6,600
10	Mexico	6,200
11	Turkey (sales)	4,900
12	Korea, Republic of	4,500
13	Ukraine	4,400
14	France	3,600
15	Iran	2,900
16	Belgium	2,200
17	Spain	2,200
18	Poland	2,000
19	Romania	2,000
20	Australia	1,900
21	Canada	1,900
22	Vietnam	1,700
22	United Kingdom	1,500
23	South Africa (sales)	1,000
	World total (rounded)	330,000

Sources of $CaCO_3$

- Limestone
- Coral
- Sea shells
- Chalk

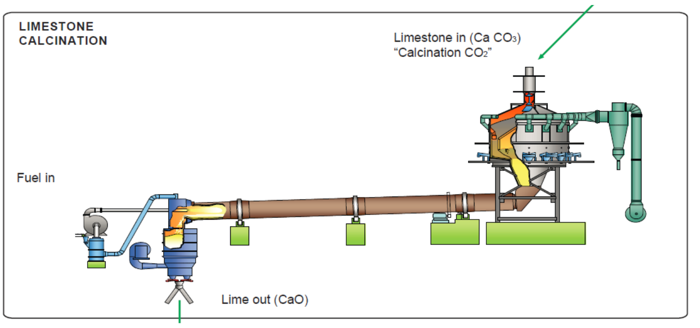
- These source materials:
  - Mainly $CaCO_3$
  - Impurities → $MgCO_3$, Al_2O_3, Fe_2O_3, SiO_2

Lime production process



- Excavation of limestone
- Crushing
- Grinding
- Calcination: Quicklime (Sönmemiş kirec)
- Pulverize Quicklime
- Mixed with water under pressure: Slaked Lime (Sönmüş kirec)
- Drying of slaked lime
- Pulverizing
- Marketing in bags

Lime production process



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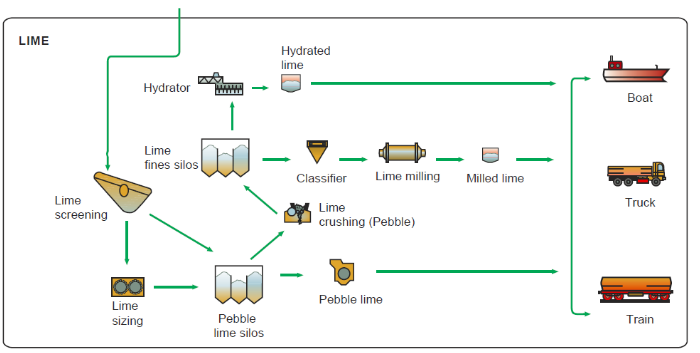

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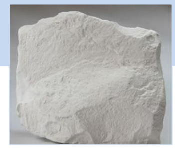
Reactions in lime production



- Calcining:

$$\underset{\text{Calcium Carbonate}}{CaCO_3} \xrightarrow{>900°C} \underset{\text{Quicklime}}{\underline{CaO}} + CO_2\uparrow$$

- Hydration or Slaking:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Heat (i.e. exothermic)}$$

(volume expansion)

- Carbonation of hydrated lime:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3$$

Calcination of $MgCO_3$

- Decomposition of magnesium carbonate to form magnesium oxide and carbon dioxide begins at a temperature slightly above 400 °C.

$$MgCO_3 \xrightarrow{>400°C} MgO + CO_2\uparrow$$

Calcination of $MgCO_3$ and $CaCO_3$

Q

- 1 ton of dolomitic limestone with 30 weight% $MgCO_3$ was calcined at 700°C. Calculate the amounts of **MgO**, **CaO** produced and **CO_2** given off by this calcination process.

(Ca: 40, Mg:24, C: 12, O:16, S: 32, H:1)

Calcination of $MgCO_3$ and $CaCO_3$

Q

- If a 24g sample of a $MgCO_3$ and $CaCO_3$ mixture produces 12g CO_2, then what is the percentage by mass of $MgCO_3$ in the original mixture?

(Ca: 40, Mg:24, C: 12, O:16, S: 32, H:1)

Kilns for calcining lime

- Calcining:

$$CaCO_3 \xrightarrow{>900^\circ C} \underline{CaO} + CO_2\uparrow$$

Calcium Carbonate

Quicklime

- Calcination is carried out in various kilns:
  1. Temporary clamp kiln
  2. Permanent structure kilns
     1. Intermittent
     2. Continuous
     3. Rotary
     4. Reactor

Simplest method: Clamp kiln

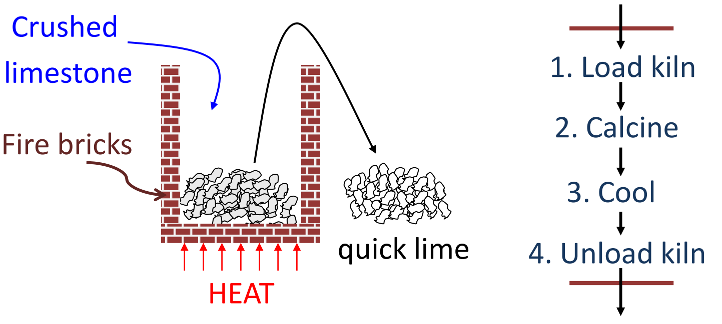
Common in Roman and medieval Britain

North West Leicestershire,
Post-mediavel clamp kiln

- Not permanent …
- Not really a kiln at all, but consisted of layers of fuel and limestone stacked together in a mound, covered with clay or turf and slowly burned in a method similar to that used in charcoal burning.
- Difficult to control the quality
- Remains of such 'kilns' comprise merely a hearth on the floor of a pit, measuring up to ϕ 2.5m and 2.0m in depth.
- Surrounding soil may show evidence of burning by a change in color and loose piles of rock may be present.

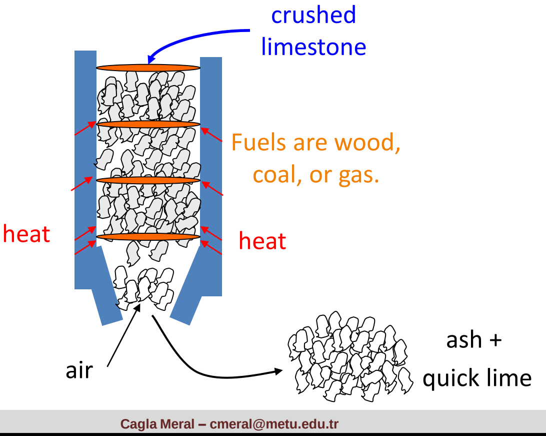
Permanent structure kilns

1. Flare (intermittent or periodic) kilns
   - loaded with a single charge of limestone and burning had to stop for this to be removed before it could be re-loaded for the next firing
   - Suitable for small scale production



Permanent structure kilns

2. Continuous (draw, perpetual, shaft or running) kilns
   - kept burning continuously while further supplies of raw material and fuel were fed in at the top and the lime was drawn off at the bottom

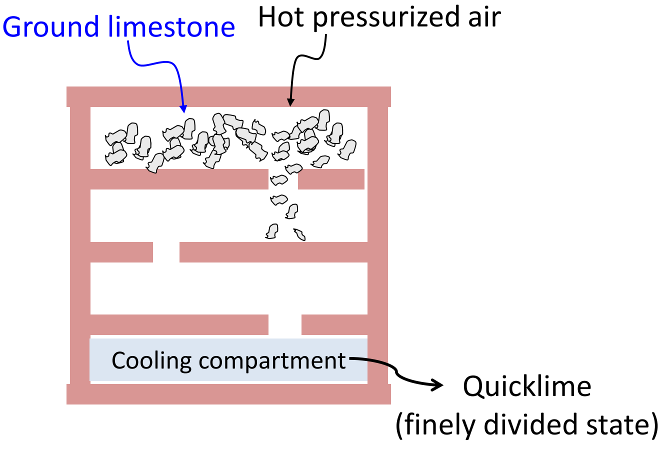


Permanent structure kilns

3. Rotary kiln

Permanent structure kilns

4. Reactor kiln



Slaking (Hydration) of lime

- Hydration or Slaking:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Heat (i.e. exothermic)}$$

(volume expansion)

- Rate of slaking and rate of heat evolution depends on:
  - Quicklime particle size
    - Finer and porous quicklimes hydrate more quickly and give off greater amount of heat
  - Chemical composition
    - Higher calcium → higher CaO → hydrate more quickly and give off higher heat%
  - Burning temperature
    - Underburned quicklimes hydrate more slowly than the ones burned at higher temperature

Calcination of Lime

Q

- How much water is necessary to slake the quicklime obtained from 10 tons of pure limestone?

(Ca: 40, C: 12, O:16, S: 32, H:1)

Slaking (Hydration) of lime

- Hydration or Slaking:

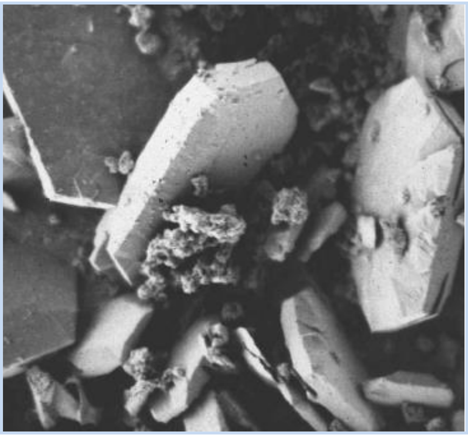
$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Heat (i.e. exothermic)}$$

(volume expansion)

- Lime can be slaked at a construction site (if necessary precautions are taken). However, a better way would be buying it from a factory; as the product would be more homogeneous & economical, and less plastic.

Calcium Hydroxide

- Slaked lime or portlandite
- Notation:
  - $Ca(OH)_2$ = CH (in cement chemistry)
- Large, weak crystals with hexagonal – prism morphology



* Image courtesy of P.J.M. Monteiro

Seasoning of slaked lime

- Hydration or Slaking:

  $CaO + H_2O \rightarrow Ca(OH)_2$ + Heat (i.e. exothermic)

  (volume expansion)

  - CaO is mixed with water in a slaking box until a "putty" has been formed.
  - The putty is then covered with sand to protect it from the action of the air & left for seasoning.
  - Time of seasoning → 1 week for mortar use

    6 weeks for plaster use

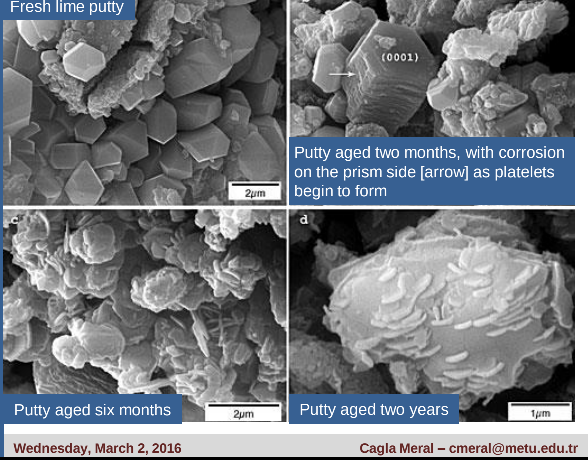
Seasoning of slaked lime

- Hydration or Slaking:

  $CaO + H_2O \rightarrow Ca(OH)_2$ + Heat (i.e. exothermic)

  (volume expansion)

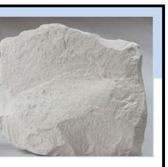
The evolution of prisms into platelets as putty ages



- If CaO is not slaked well, it will absorb moisture from air & since the volume expands upto 2.5-3 times popouts will occur.
- Seasoning for two/three weeks provides a homogeneous mass & completion of chemical reactions
- Portlandite crystals: Aging → size reduction and developing submicrometer, platelike crystals.

* J. Am. Ceram. Soc., 81 [11] 3032–34 (1998)

Classification of quicklime



1. <u>According to Particle Size</u>
   - Lump Lime (10-30 cm lumps)
   - Pebble Lime (2-5 cm)
   - Granular Lime (~0.5 cm)
   - Crushed Lime (~5-8 mm)
   - Ground Lime (passes #10 sieve, by grinding crushed lime)
   - Pulverized Lime (passes #100 sieve)

Classification of quicklime

2. <u>According to Chemical Composition</u>
   - High-Calcium (CaO ≥ 90%)
     - Slakes faster
     - Hardens faster
     - Have greater sand carrying capacity
   - Calcium (75% < CaO < 90%)
   - Magnesian (MgO ≥ 20%)
   - High-magnesian (dolomitic, MgO ≥ 25%)

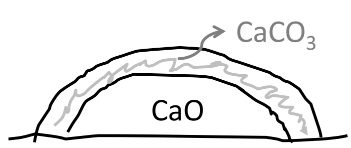
Classification of quicklime

3. <u>According to Intended Use</u>
   - Mortar Lime (Sand + Lime + Water)
     - used for masonry construction until the advent of portland cement in mid-1800s.
     - now used in the conservation of buildings originally built using lime mortar
     - Two types:
       - Non-Hydraulic
       - Hydraulic
   - Plaster Lime
     - Lime + Water
   - Lime wash

Air slaked lime (Bayat kireç)

- When quicklime (CaO) is left uncovered it picks up moisture and CO_2 from air & becomes partly $CaCO_3$.

  - $CaO + \overset{air}{H_2O} \rightarrow Ca(OH)_2$ → Expansion observed
  - $Ca(OH)_2 + \overset{air}{CO_2} \rightarrow CaCO_3 + H_2O$



Setting/Hardening of lime mortar

- $Ca(OH)_2 + CO_2 \xrightarrow{\text{air}} CaCO_3 + H_2O$ → SLOW!

- Higher the moisture
- Lower the CO_2
- Lower the calcium

} longer the setting time

Plasticity of lime mortar

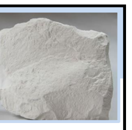
- Plasticity of lime mortar = spreading quality of mortar
  - If it spreads easily and smoothly → plastic
  - If it sticks to the trowel or cracks, curls up and drops behind the trowel → non-plastic

- Adding enough sand

} Increases plasticity
Reduces drying shrinkage
Results in cheaper mortar

- Adding too much sand → non-plastic mortar

Strength of lime mortars

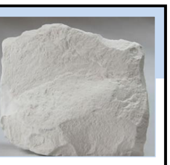


- Chemical composition of lime
  - Magnesian Limes > Calcium Limes
- Sand amount & properties
  - Adding sand decreases strength
  - Too little sand → shrinkage cracks in the mortar → reduced strength
  - Mortars with fine sand > Mortars with coarse sand
- Amount of water
  - Voids are formed after evaporation
- Setting conditions
  - Lower humidity & higher CO_2 → higher strength

Lime pops (Kireç topakları)

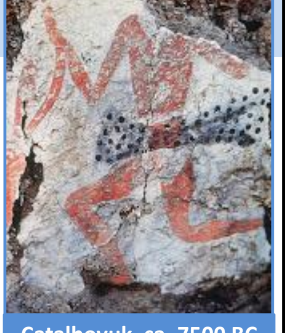
- If quicklime is not mixed completely with water, some CaO will be carried to construction stage.
- In its final stage it will absorb water & CO_2 from air and will expand upto 2.5-3 times.
- This will cause cracking & pop-ups in the structure.

Properties of lime mortars



- Lime + sand → Lime mortar
  - Modern mix: 1 to 3 by weight
  - Historical mix: 1 to 2 by weight
- Adding sand:
  - Adjusting plasticity → otherwise too sticky
  - More economical → sand is cheaper than lime
  - Decreasing shrinkage effects → horse hair can be also added

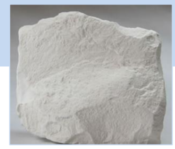
Why use lime mortar?



Catalhoyuk, ca. 7500 BC

- Plaster mortars → sets slower than gypsum
- White-wash (badana)
- Lime mortar is soft and porous
  - Better with softer building materials as masonry mortar: natural stone, terracotta…
  - Good for repairs of older, stone-built structures and restoration of historical buildings (Portland cement is good for brick and concrete construction)
- In production of masonry blocks
  - Slaked lime + sand + pressure

Durability of limes



- Not resistant to moving water

  ↓
- Not for outside use

  ↓
- Hydraulic binder?

Hydraulic lime

- A lime obtained by calcination of siliceous or clayey limestone at higher temperature

- It differs from quicklime:
  - Burned at higher temperature
  - It contains lime silicates
  - It can set & harden under water

like portland cement

Next lecture…

- Portland Cement