7 March 2016

Lecture 5

Production of Portland Cement

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.

Reactions in lime production

- Calcining:

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

- Hydration or Slaking:

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

(volume expansion)

- Carbonation of hydrated lime:

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

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

Perspective

Historical perspectives

1750 AD | **1800 AD** | **1850 AD** | **1900 AD** | **1950 AD** | **2000 AD**

1779
1st iron bridge

1793
1st hydraulic cement building
(Eddystone Lighthouse)

1824
Portland cement
(Aspdin)

1848
Reinforced concrete
(Monier, Béton armé)

1889
Eiffel Tower,
1st reinforced concrete bridge
(Alvord Lake Bridge)

1908
Alumina cement

1929
Prestressed concrete

1936
1st concrete dam
(Hoover Dam)

1980
High performance concrete

2000
Ultra high performance concrete

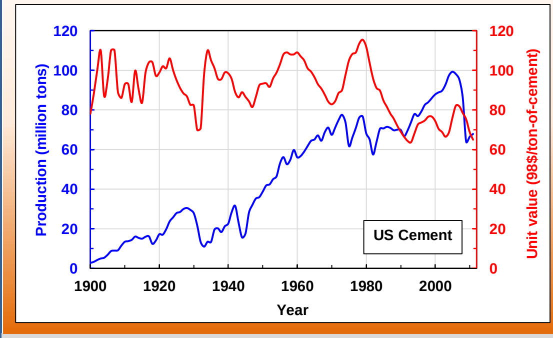
Monday, March 7, 2016 Cagla Meral – cmeral@metu.edu.tr 5

PORTLAND CEMENT

E-choice – Text to 4660

- Which country produced the highest amount of portland cement in 2014?
  - A) USA
  - B) Brazil
  - C) Turkey
  - D) China
  - E) India

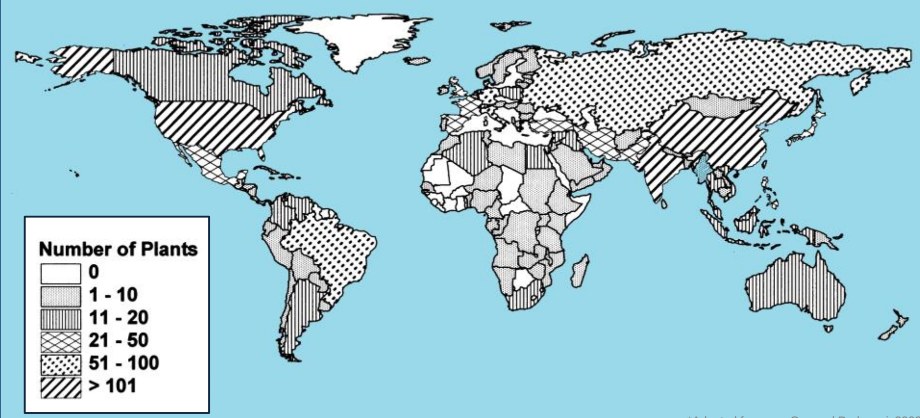
Portland Cement



	(million tons)	2012
1	China	2,150
2	India	250
3	USA	74
4	Brazil	70
5	Iran	65
6	Vietnam	65
7	Russia	60
8	Turkey	60
9	Japan	52
10	Korea	49
11	Egypt	44
12	Saudi Arabia	43
13	Mexico	36
14	Germany	34
15	Thailand	33
16	Italy	32
17	Pakistan	32
18	Indonesia	31
19	Spain	20
20	Other countries	500
	World (rounded)	3,700

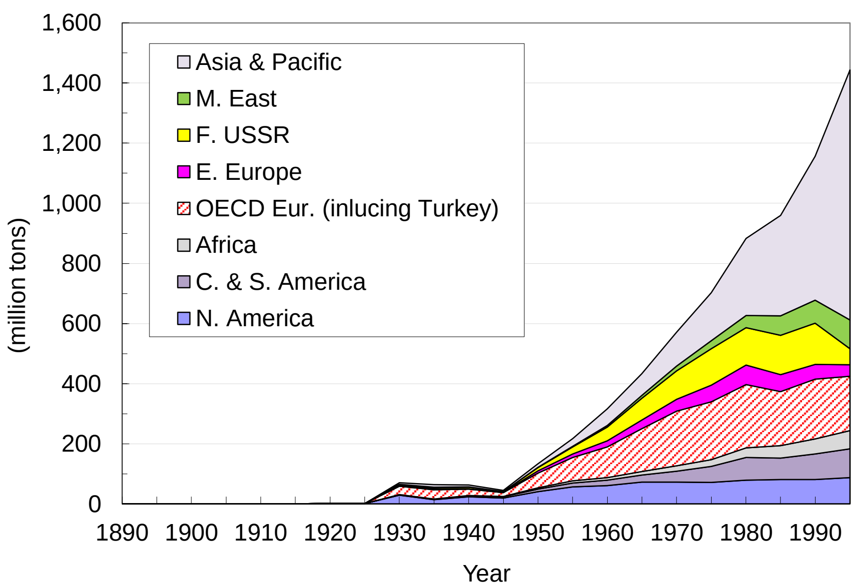
Cement plants

Cement plants all over the world…



*Adapted from van Oss and Padovani, 2002

Cement production by 1994



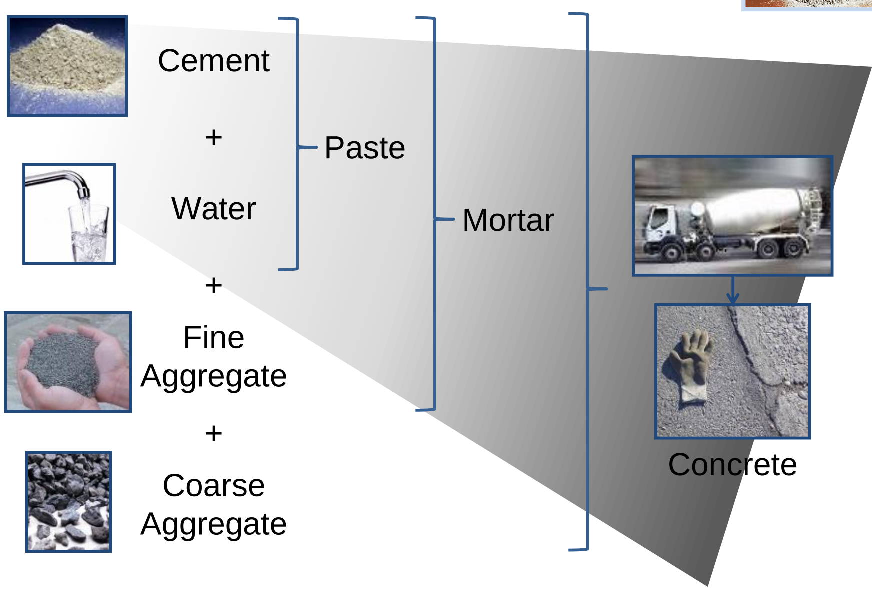
*Adapted from Marland et al., 1994

Overview

- Why we use concrete?
- History
- Raw materials
- Production steps
- Rotary kiln reactions
- Major compounds in portland cement
- Methods of determining compound composition
- Life cycle assessment of Turkish Cement Production

Concrete

Concrete



Concrete, the man made rock…

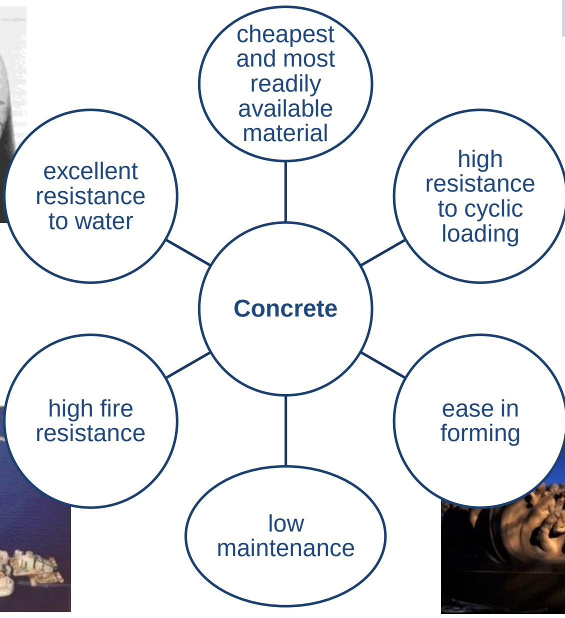
~ 12 billion tons/year of Concrete

Concrete

Why this much concrete?

Concrete

- cheapest and most readily available material
- high resistance to cyclic loading
- ease in forming
- low maintenance
- high fire resistance
- excellent resistance to water



Concrete

Portland Cement

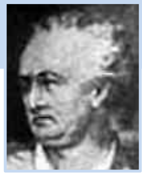
- A hydraulic cement capable of setting, hardening and remaining stable under water. It consists essentially of hydraulic calcium silicates, usually containing calcium sulfate.

Hydraulic Cement

Q

- Portland cements are "hydraulic cements." What is the meaning of the term "hydraulic cement"?

Portland Cement



Cement

- 1824 AD: Joseph Aspdin, founder of today's Portland cement industry
  - Aspdin heated a mixture of finely ground *limestone* and *clay* in a furnace and ground the mixture into a powder to create a hydraulic cement.

Limestone
source of lime

Clay
source of silica, alumina, iron

Raw materials of portland cement

mix substances containing $CaCO_3$ with substances containing SiO_2, Al_2O_3, Fe_2O_3 and heat them to a clinker which is subsequently ground to powder and mixed with 2-6 % gypsum

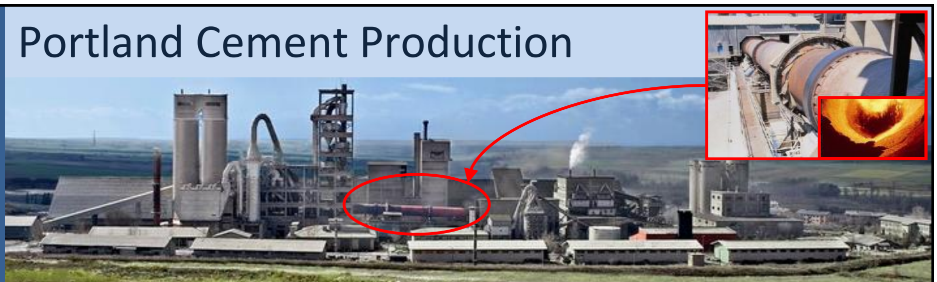
1) Calcareous Rocks ($CaCO_3$ > 75%)
   - Limestone, marl, chalk, marine shell deposits
2) Argillocalcareous Rocks ($40\% < CaCO_3 < 75\%$)
   - Cement rock, clayey limestone, clayey marl, clayey chalk
3) Argillaceous Rocks ($CaCO_3$ < 40%)
   - Clays, shales, slates

Raw materials for portland cement manufacture

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		

Portland Cement Production

Cement



Limestone + Clay
(2 parts) (1 part)

Crushing
Proportioning
Blending

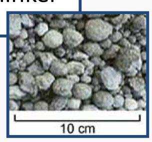
Preheating

Kiln
(~1450°C)

Calcination
$CaCO_3 \rightarrow CaO + CO_2 \uparrow$

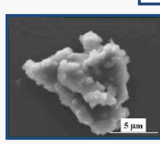
1 ton Cement
↓
0.5 ton CO_2

Clinker



Cooling

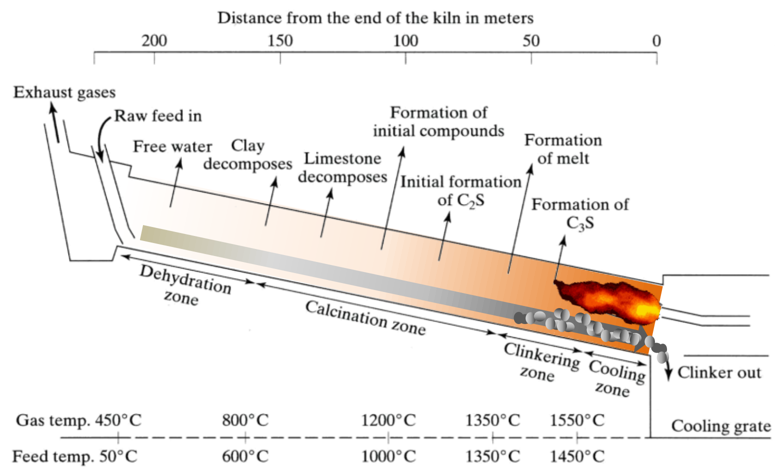
Grinding
(with ~4% Gypsum)



Portland Cement

Conditions and reactions in a dry-process rotary kiln

When suspension preheaters are used, dehydration and initial calcination takes place outside the kiln in the preheater tower.



*Adapted from Figure 3.2 from Mindess, Young, and Darwin, 2004

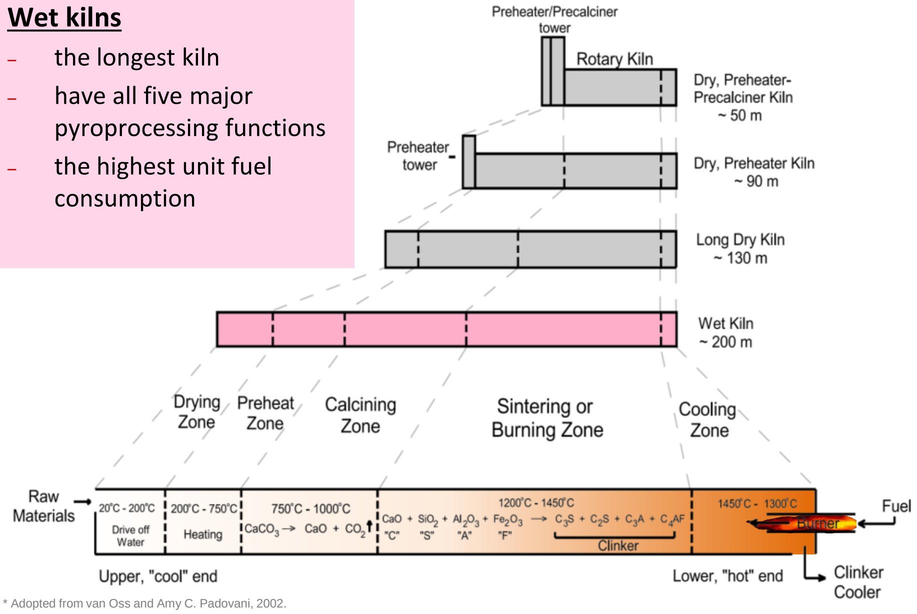
Reactions in the rotary kiln

- **~100°C** → free water evaporates.
- **~150-350°C** → Dehydration: loosely bound water is lost
- **~350-650°C** → decomposition of clay → SiO_2 + Al_2O_3
- **~600°C** → decomposition of $MgCO_3$ → MgO + CO_2 (to air ↑)
- **~900°C** → decomposition of $CaCO_3$→CaO + CO_2 (to air ↑)
- **~1250-1280°C** →liquid formation & start of compound formation
- **~1280°C** → clinkering begins.
- **~1400-1500°C** → clinkering
- (cool to **~100°C** → clinker leaves the kiln & falls into a cooler.)
- Sometimes the burning process of raw materials is performed in two stages: preheating upto 900°C & rotary kiln

Rotary kiln technologies and functional zones

Wet kilns

- the longest kiln
- have all five major pyroprocessing functions
- the highest unit fuel consumption

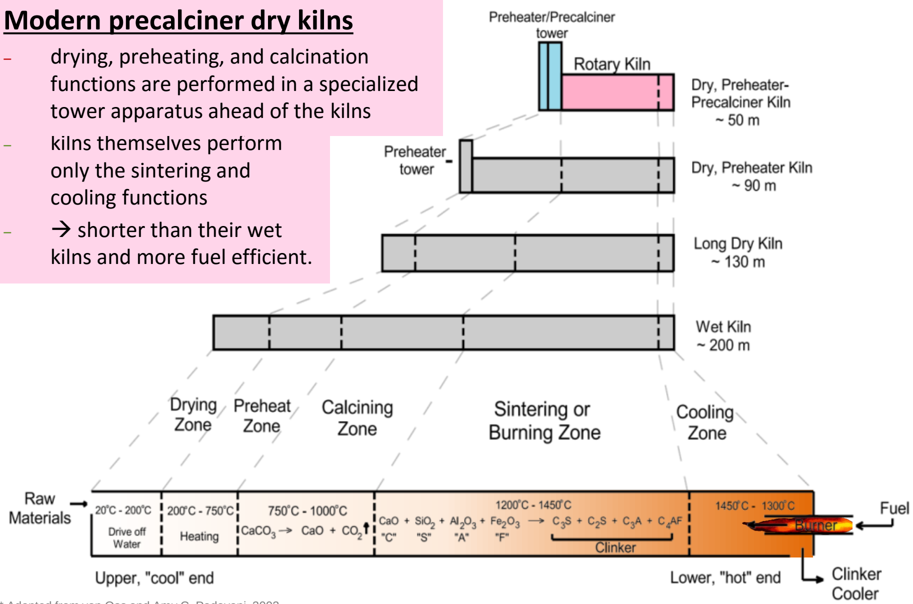


* Adopted from van Oss and Amy C. Padovani, 2002.

Rotary kiln technologies and functional zones

Modern precalciner dry kilns

- drying, preheating, and calcination functions are performed in a specialized tower apparatus ahead of the kilns
- kilns themselves perform only the sintering and cooling functions
- → shorter than their wet kilns and more fuel efficient.



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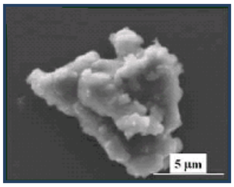
Major compounds in portland cement

Cement



Portland cement

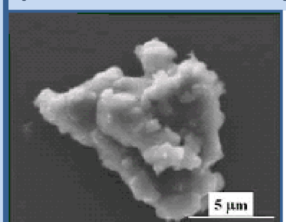
Calcium Silicates
- $3(CaO).SiO_2$
- $2(CaO).SiO_2$

Calcium Aluminates
- $3(CaO).Al_2O_3$

Calcium Aluminoferrites
- $4(CaO).Al_2O_3.Fe_2O_3$

- Portland cement is composed of four major oxides (CaO, SiO_2, Al_2O_3, Fe_2O_3 ≥ 90%) & some minor oxides.
- CaO (C), SiO_2 (S), Al_2O_3 (A) & Fe_2O_3 (F) are the major oxides that interact in the kiln & form the major compounds.
  - C_2S - Belite
  - C_3S - Alite
  - C_3A
  - C_4AF

Degree to which potential reactions can proceed to equilibrium depends on …



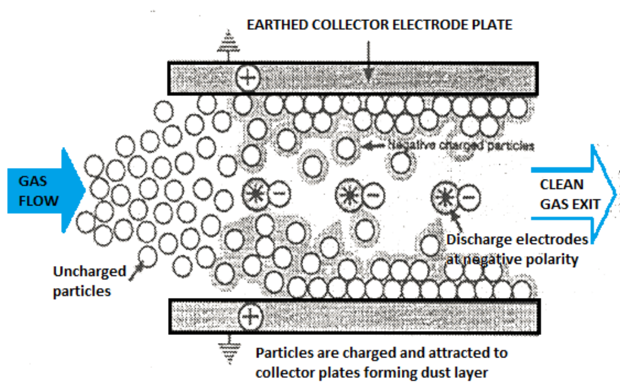
1) Fineness of raw materials & their intermixing

2) Temperature & time that mix is held in the critical zone of the kiln

3) Grade of cooling of clinker may also be effective on the internal structure of major compounds

Note 1: Cement kiln dust

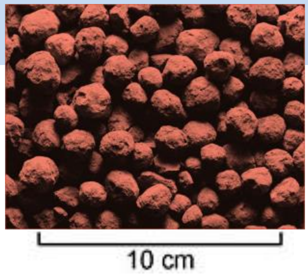
- Release of cement kiln dust (CKD) is carefully controlled
- Can be precipitated and used in concreting
- Very high alkali content



Note 2: Fuels Used

- Fuel used for cement manufacture = 6-8% of the world's fuel consumption!
- Fuel costs = ~40-60% of the manufacturing costs → fuels are often selected on an economic basis, although other considerations may also be made.
- Acquisition of the raw materials =~10% of the cost
- Fuels used include:
  - natural gas (2%)
  - oil (7%)
  - coal (70%+)
  - trash, including wood chips, tires, rice husks, oil-soaked Fuller's earth, etc. (20%+)

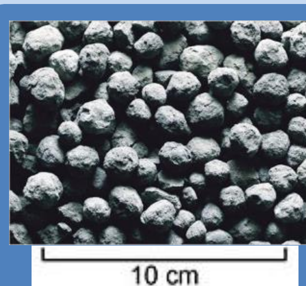
Note 3: Clinker cooling rate



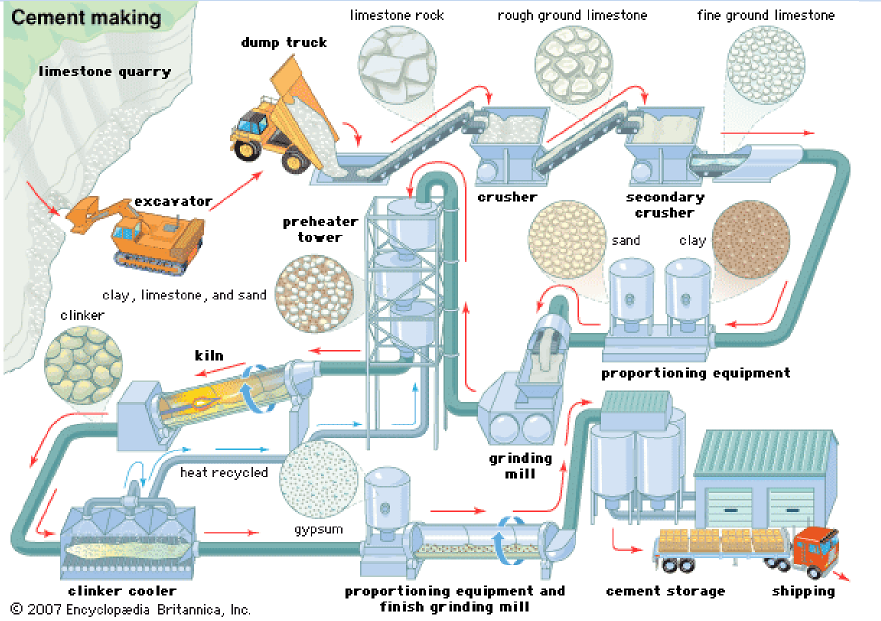
- As the clinker cools, the main liquid phase crystallizes to form aluminate phase, ferrite and a little belite.
  - Fast cooling:
    - more hydraulically-reactive silicates and lots of small, intergrown, aluminate and ferrite crystals.
  - Slow cooling:
    - less hydraulically-reactive silicates and produces coarse crystals of aluminate and ferrite - over-large aluminate crystals can lead to erratic cement setting characteristics.
  - Very slow cooling:
    - Alite (C_3S) to decompose to belite (C_2S) and free lime (CaO).

Note 4: Too hot clinker

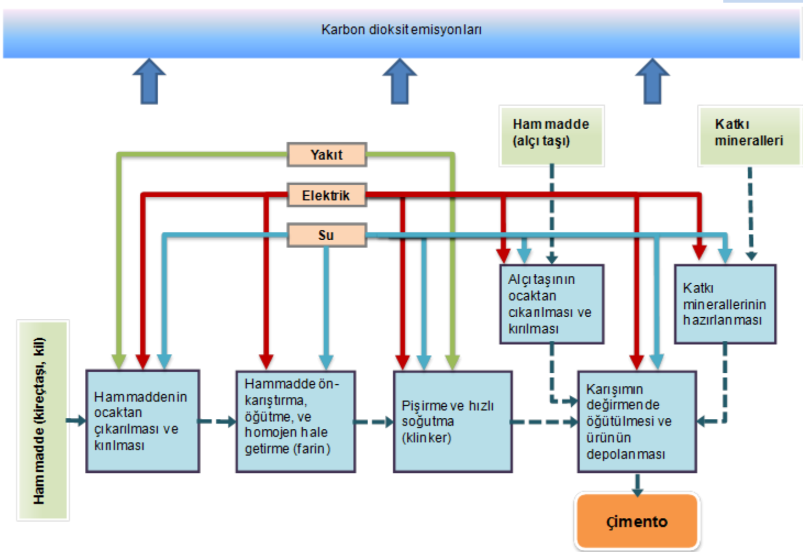
- Dehydration of gypsum when it is interground with too hot clinker can produce hemihydrate or anhydrite.
- When such cements are mixed with water the hemihydrate and anhydrite hydrate to gypsum.
- A plaster set takes place with resulting stiffening of the paste



Life Cycle Assessment of Portland Cement Production



System boundaries



Gursel and Meral 2012

Main inputs in cement production

Gursel and Meral 2012

Main inputs for Turkish cement production

Inputs	Amount	(±)	Unit
Raw materials			
Limestone	1,025		kg/ton.clinker
Marl, clay	528		kg/ton.clinker
Other (bauxite, iron ore, sand, vb)	48		kg/ton.clinker
Secondary materials			
Gypsum	50		kg/ton. CEM-I cement
Electricity	110	(± 5)	kWh/ton.cement
Fuel	800	(± 50)	kcal/kg.clinker

Average fuel mix for Turkish cement production

Fuel type	Calorific value	Average fuel consumption (%)		
	(kcal/kg)	2003	2004	2005
Pet-coke	7,500	47.49	39.23	42.68
Imported coal	6,500	34.29	28.72	26.52
Local coal	4,500	18.22	32.04	30.80

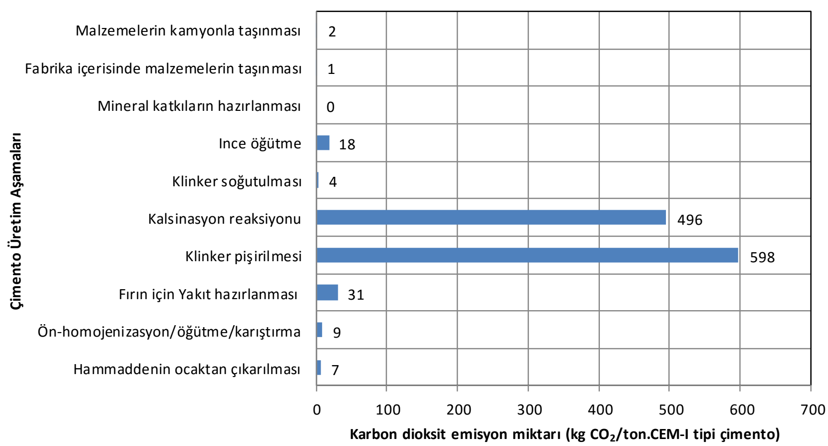
Average electricity mix for Turkish cement production

Energy source (%)	2003	2004	2005
Natural Gas	33.65	35.99	36.58
Hidro	35.34	34.34	33.25
Coal	23.15	22.53	23.49
Oil	7.68	6.98	6.51
Biomass	0.08	0.08	0.07
Geothermal	0.04	0.04	0.06
Wind	0.05	0.05	0.05

Turkey's CEM-I Production CO_2 emissions (kg CO_2/ton.CEM-I)

Gursel and Meral 2012

- In Turkey:
  - ~30 million ton CEM-I is produced at 2011
  - 1 ton CEM-I → 1.165 ton CO_2



Next lecture

- Hydration of portland cement