

Introduction: Cement

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International Context

- Population growth and need for new infrastructure
- Decaying existing infrastructure
- Transportation congestion
- Waste management crises
- Climate change and more frequent natural disasters inflicting damage to infrastructure

Doing something unpleasant

- World population growth
- RC structure continue to deteriorate prematurely

International Context

“Laws of Fives”

- $1 spent on design and construction
- equivalent to $5 spent as damage initiates and before it propagates
- $25 once deterioration has begun to propagate
- and $125 after extensive damage has occurred
- This course: Focus on the $1 to $5 situation, so as not to face the $25 or $125 situation
- Caution: poorly designed and/or executed repairs can worsen situation

Cement

History of Cementing Material

- Oldest cementing material: mud mixed with straw to bind un-burnt bricks (ancient Egypt). No resistance to water. Works only in very dry climates.
- Babylonians and Assyrians used natural bitumen to bind stones and bricks.
- Ancient Egyptians used gypsum in the construction of the pyramid of Cheops (3000 BC). Setting will not take place in water (non-hydraulic binder, gypsum is soluble in water).
- Lime mortars (by calcinating limestone) were used in Egypt in the Roman period and earlier in Crete, Cypris and Greece. Also non-hydraulic binders.

History of Cementing Material

This bridge, over the river Gard, is 275 meters (900 feet) long and 49 meters (160 feet) high. It was part of an aqueduct nearly 50 kilometers (30 miles) long which supplied Nimes with water

Hydraulic Lime

- Greek and Romans produced hydraulic limes by calcinating limestone containing clayey impurities
- They also knew that some volcanic deposits when ground and mixed with lime produce mortars which are not only stronger, but also resistant to water.
- Best variety was found near village of Pozzuoli in Italy, the origin of the name pozzolana

Hydraulic Mortars

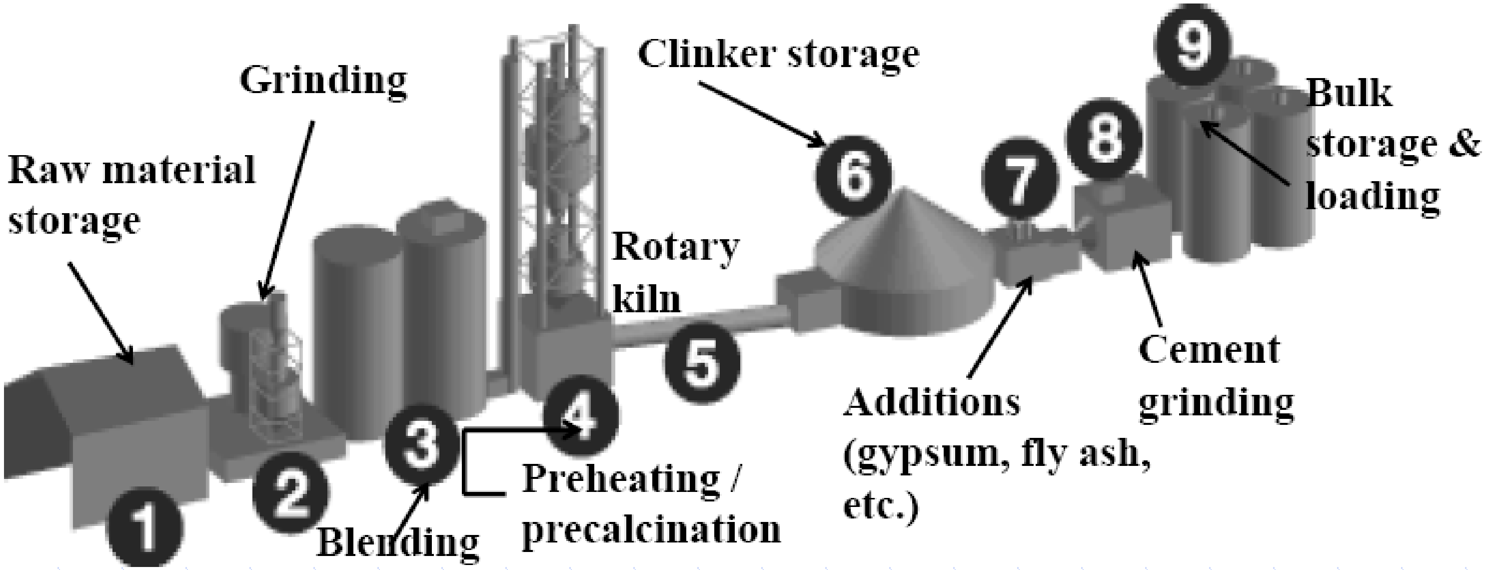
The Romans used hydraulic mortars to make a form of concrete. The Pantheon, the best preserved building of the ancient world (2nd century AD) was largely built using concrete.

Dome is 141 ft 6 in in diameter

Development of Portland Cement

- In 1776, James Parker in England patented a natural hydraulic cement made by calcinating limestone with clayey impurities.
- 1813 in France, Vicat prepared a hydraulic lime by calcinating synthetic mixtures of lime and clay.
- In 1824, Joseph Aspden, a Leeds builder took out a patent on portland cement prepared by calcinating in a kiln finely ground limestone mixed with finely divided clay.

Development of Portland Cement



Development of Portland Cement

After cooking in a kiln at about 1500 °C

The raw material becomes cement clinker

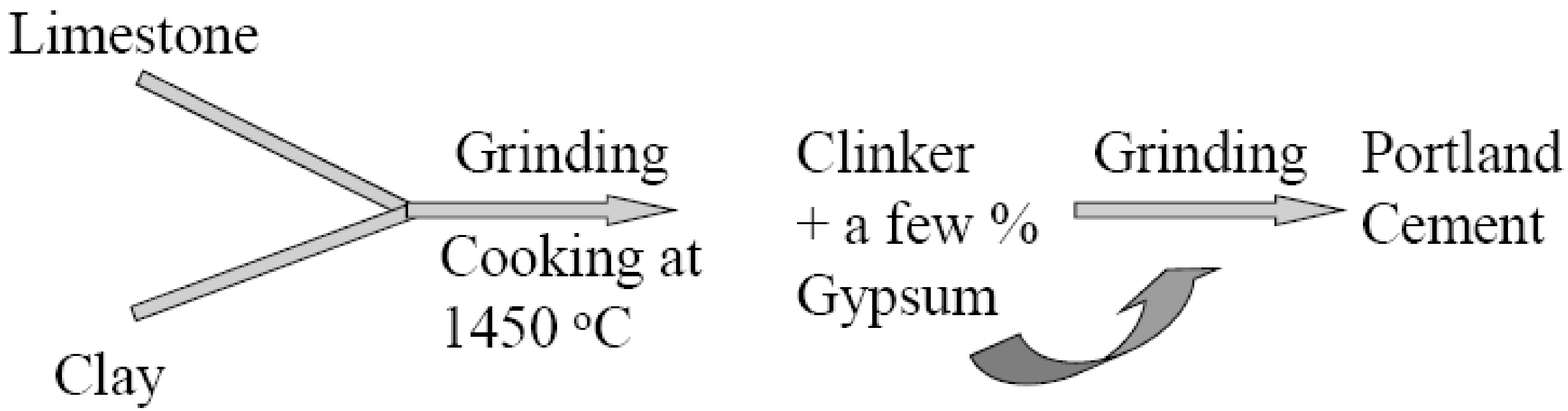
Development of Portland Cement

Clinker

Clinker is ground with small proportions of gypsum to give portland cement

Gypsum

Cement Manufacturing



Lime = CaO,

Iron = Fe_2O_3

Silica = SiO_2,

Alumina = Al_2O_3

Raw Materials for Cement Manufacturing

- Lime (CaO): limestone, marble, calcite, seashells, etc.
- Silica (SiO_2): clay, sand, calcium silicate, etc.
- Alumina (Al_2O_3): clay, shale, bauxite, etc.
- Iron Oxide (Fe_2O_3): iron ore, blast furnace dust, etc.

Impurities

- Other impurities exist in clinker: free lime, MgO, alkalis (Na_20 and K_2O), sulfates, etc.
- They lower the melting temperature & improve combination of lime.
- Their incorporation in silicates improves strength.

Typical Oxide Composition in Cement

CaO	63%	C	SO_3	2
SiO_2	20	S	K_2O and Na_2O	1
Al_2O_3	6	A	Others	1
Fe_2O_3	3	F	Loss on ignition	2
MgO	1		Insoluble residue	½

Cement Chemist Notation

Major Constituents of Cement

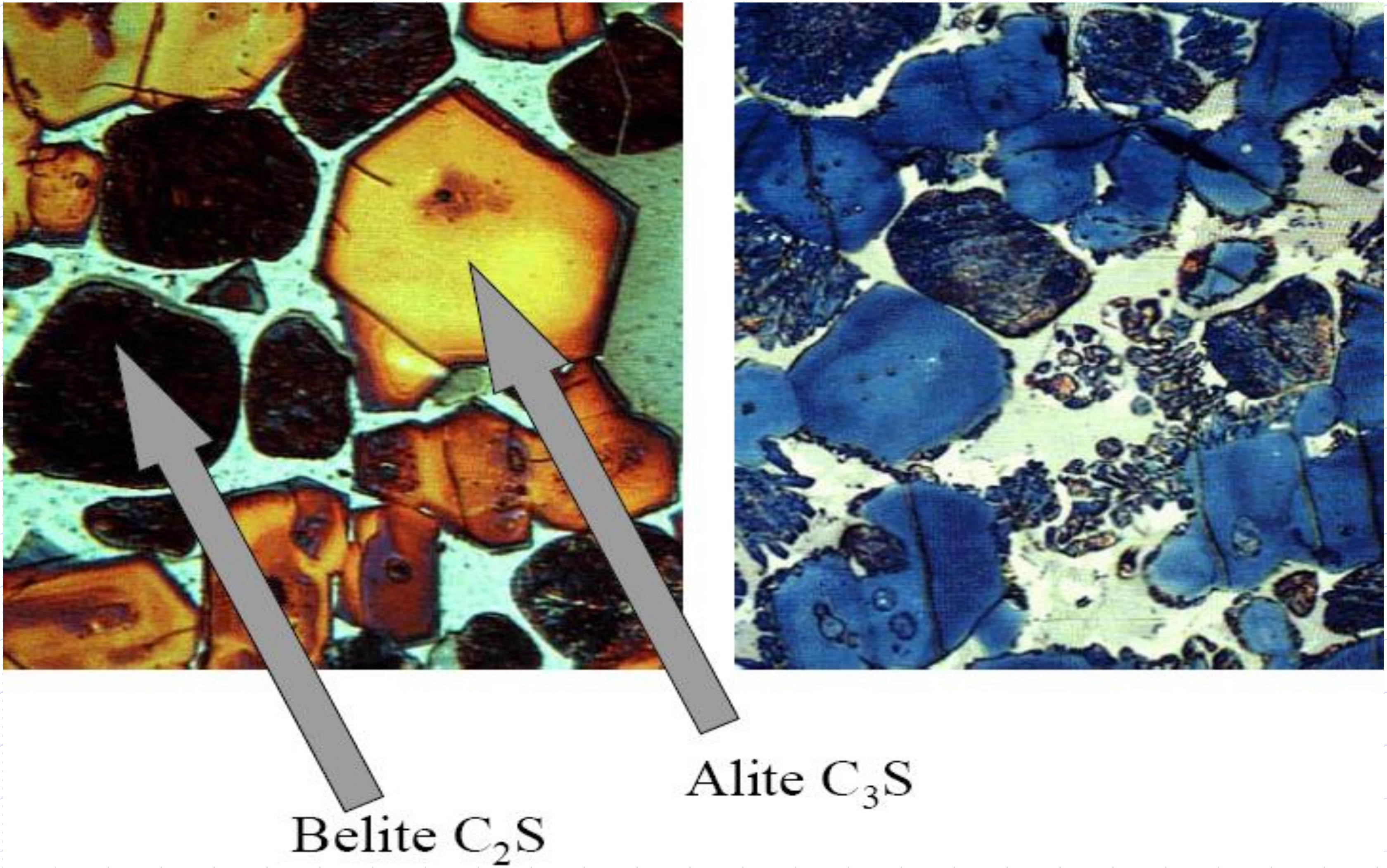
These oxides interact in the kiln to form more complex products. Upon cooling, crystallization takes place.

The four major constituents (about 90%) of cement are:

Name of compound	Oxide composition	Notation
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.\ Fe_2O_3$	C_4AF

Cement Chemist Notation

Major Constituents of Cement



Major Constituents of Cement

1) C_3S Tri-Calcium Silicate

- $3CaO \cdot SiO_2$ -"C_3S - Alite"
- Provides Early strength development
- 70% reacts by 28 days
- Usually present at 40-70%

2) C_2S Di-Calcium Silicate

- $2CaO \cdot SiO_2$ -"C_2S - Belite"
- Provides late strength development
- 30% reacts by 28 days
- Present at 20-40%

Major Constituents of Cement

3) C_3A Tri-Calcium Aluminate

- $3CaO \cdot Al_2O_3$ -"calcium aluminate"
- Generates heat in early hydration
- High C_3A not as resistant to sulfate attack
- Little contribution to strength
- Early hydration controlled by adding gypsum (no gypsum = flash set, too much gypsum = false set)

Major Constituents of Cement

4) C_4AF Tetra-Calcium Alumino Ferrite

- $4CaO \bullet Al_2O_3 \bullet Fe_2O_3$ -"calcium alumino-ferrite"
- Governs the color of the cement
- Present at 1-10%
- Iron facilitates formation of other compounds-acts as a flux
- Little contribution to strength

Percentage of Main Components of Cement

Percentages of main components are calculated using Bogue's equation. Terms between brackets represent the percentage of the given oxide in the total mass of cement.

$$C_3S = 4.071(CaO) - 7.600(SiO_2) - 6.718(Al_2O_3) - 1.430(Fe_2O_3) - 2.852(SO_3)$$

$$C_2S = 2.867\ (SiO_2) - 0.754\ C_3S$$

$$C_3A = 2.650(Al_2O_3) - 1.692\ (Fe_2O_3)$$

$$C_4AF = 3.043\ (Fe_2O_3)$$

This is a simple method provided in ASTM C150 but there are more advanced methods.

Cement Hydration

- C_3S and C_2S = ~ 75% of the weight of Portland Cement
- React with Water to form two new compounds:
  - **Calcium Hydroxide (CH)**
  - **Calcium Silicate Hydrate (CSH)**

- Hydration:

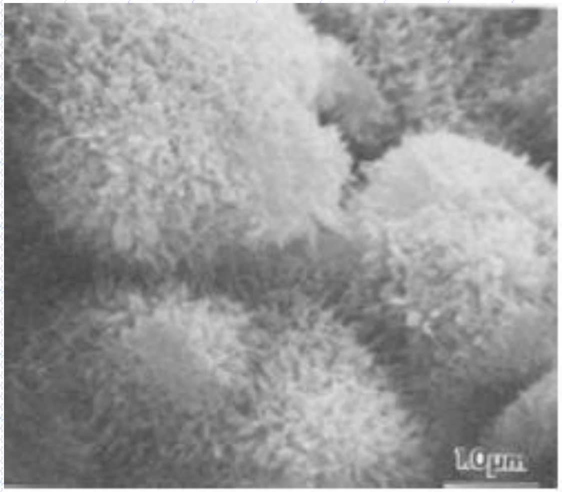
$$C_3S + H_2O \rightarrow C\text{-}S\text{-}H + CH$$

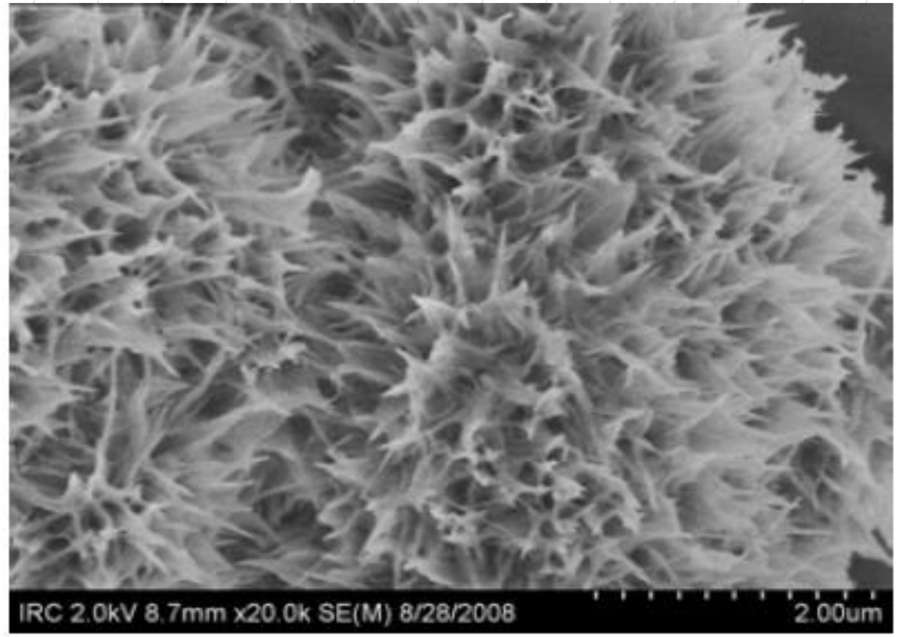
$$CH + H_2O \rightarrow Ca^{++} + OH^{-}$$

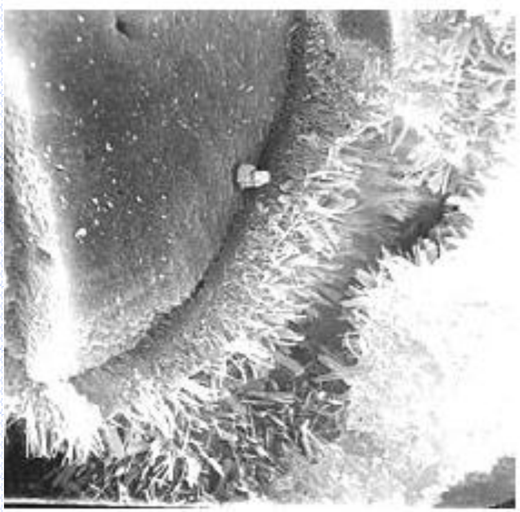
Microstructure of Hydrated Cement Product

- **CSH:** represents 50 to 60% by volume of fully hydrated cement paste. Its structure is not well known, but is believed to have a layered system. It is little crystalline (almost amorphous but polymerizes over time) and is very porous. Porosity is around 28%. Cohesion is due to van der Walls forces (high specific surface).
- **CH**: $Ca(OH_2)$ or portlandite represents 20 to 25% by volume of fully hydrated cement paste. It has a prismatic hexagonal morphology, which is influenced by temperature, impurities and the space available for CH formation.

Microstructure of Hydrated Cement Product







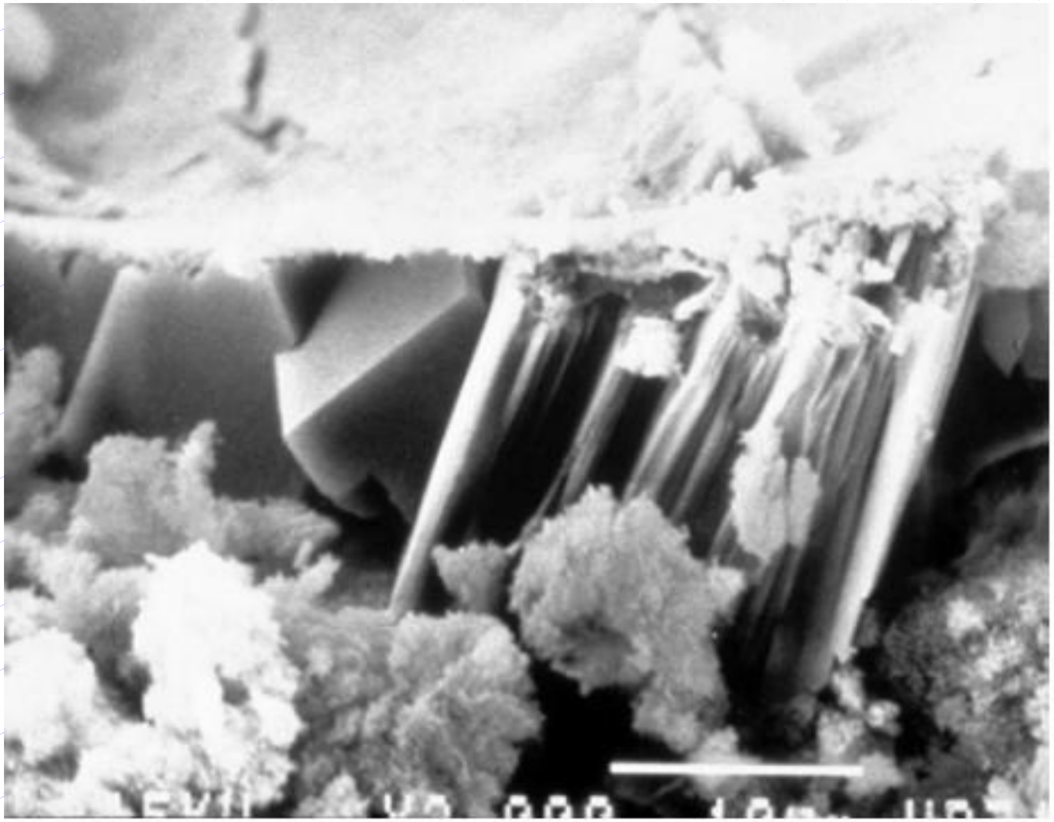
SEM micrographs illustrating CSH in HCP Hydrated cement paste

(a) Spines in 3-day old paste

(b) Honeycomb morphology in paste containing calcium chloride

(c) Coating of CSH around anhydrated cement core

Microstructure of Hydrated Cement Product



SEM micrographs illustrating calcium hydroxide (CH) also called Portlandite at acement paste-aggregate interface

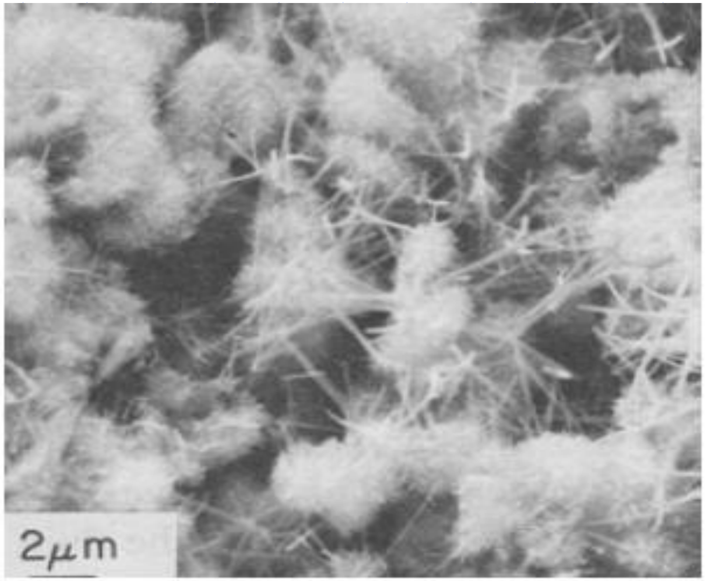
This is a week link in concrete: having low strength, high porosity, and high permeability

Microstructure of Hydrated Cement Product

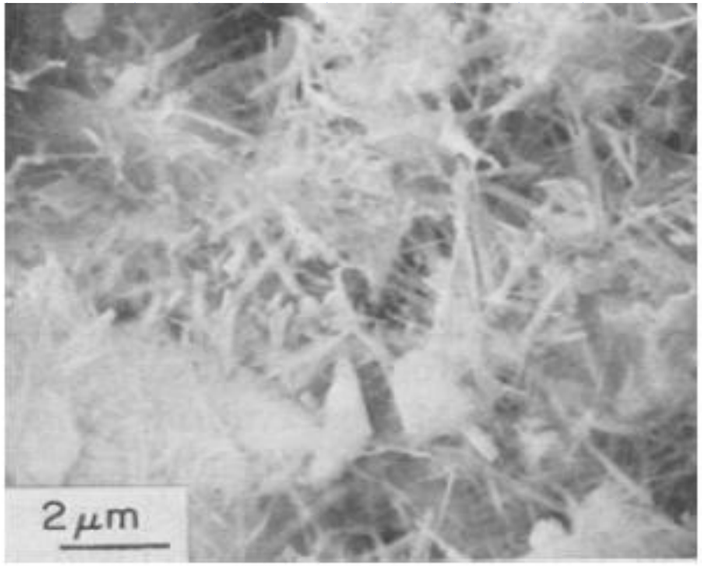
- **Calcium sulfo-aluminate**: 15 to 20% of volume of hydrated cement paste. Ettringite forms first and is in the form of short prismatic needles, which later develop into hexagonal monosulphate plates.
- **Unhydrated cement grains**: for large cement grains and especially at low w/c ratio, dense hydration products will form around such grains while their core can remain anhydrated for very long time.

Microstructure of Hydrated Cement Product

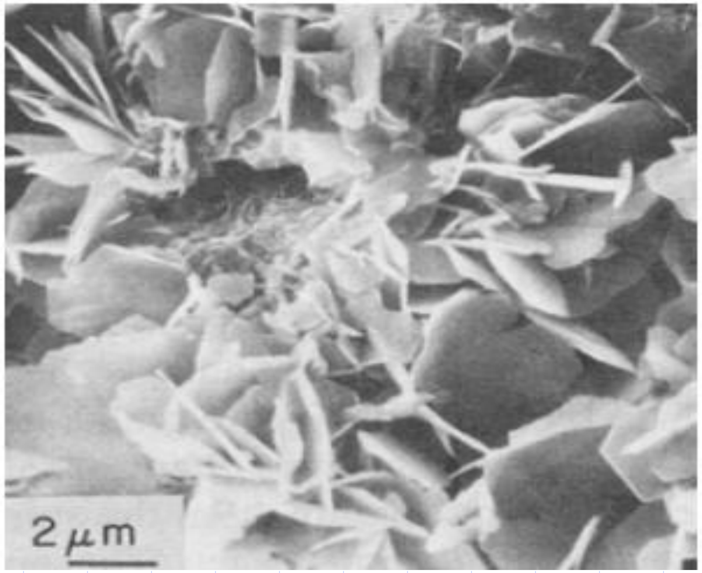
(a)



(b)



(c)



(a) Ettringite as formed from C_3A in portland cement, (b) ettringite as formed in expansive cement paste, and (c) monosulphate as formed from C_3A.

Standard Specification for Portland Cement

ASTM C150 (AASHTO 185)

I	Normal
IA	Normal, air-entraining
II	Moderate sulfate resistance
IIA	Moderate sulfate resistance, air-entraining
III	High early strength
IIIA	High early strength, air-entraining
IV	Low heat of hydration
V	High sulfate resistance

Why Five Types of Cement

What makes them different

- Different uses require different performance
- All types manufactured from similar raw materials:
  - Vary the chemical composition (proportions)
  - Vary the physical characteristics

ASTM C50: Type I (General Purpose)

- General uses
- Ready-mix is biggest customer
- IA (air-entrained)
- Most common-more than 90% of cement used is Type I or II

ASTM C50: Type II (Moderate Sulphate Resistant)

- Similar to Type I, some cements marketed as Type I/II
- Moderate sulfate resistance
- Low heat of hydration option
- IIA (air-entrained)

Type III (High Early Strength)

- Early strength means faster setting
  - Precast
  - Cold weather
  - Roadway applications
  - Repair
- IIIA (air-entrained)

Type IV (Low Heat of Hydration)

- Delayed reaction, low heat generated
- No longer common
- Other options are available for heat considerations

Niagara Hydroelectric Dam

Type V (High Sulphate Resistant)

- High sulfate resistance
  - Seawater exposures
  - Pipes
  - Industrial exposures
  - Sulfate soils
- Also has slightly lower heat of hydration

Blended Cement

a hydraulic cement consisting of two or more inorganic constituents, which contribute to the strength gaining properties of cement.

ASTM C595

Blended cement (center) surrounded by (right and clockwise) clinker, gypsum, portland cement, fly ash, slag, silica fume, and calcined clay.

Blended Cement

ASTM C595

Type IS	Portland blast-furnace slag cement
Type IP	Portland-pozzolan cement
Type P	Portland-pozzolan cement for use when higher strengths at early ages are not required
Type I(PM)	Pozzolan-modified portland cement
Type S	Slag cement for use in combination with portland cement in making concrete and in combination with hydrated lime in making masonry mortar.
Type I(SM)	Slag-modified portland cement

Benefits of Blended Cement

- Require less energy to manufacture
- Less CO_2 emissions
- Beneficial use of by-products
- Reduce solid waste
- Improved concrete performance

World Production of Cement

- World production around 500 million tonnes.
- Percentage of use varies between 3 and 57% (of total production).
- Percentage of use in concrete is 7 to 96% (of total used depending on location).
- In North America, 12 to 15% (of total production) is used in concrete, in Europe about 10%.

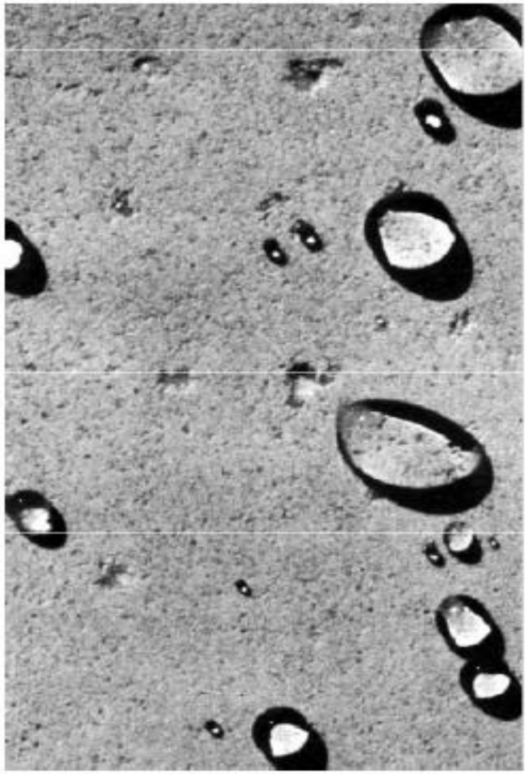
Special Cement

Special Cements

- White--primarily architectural and decorative concretes
- Safety

Special Cement

- Water-repellent--reduces the amount of water entering the concrete, mortar, or block
- Does not resist hydrostatic pressure



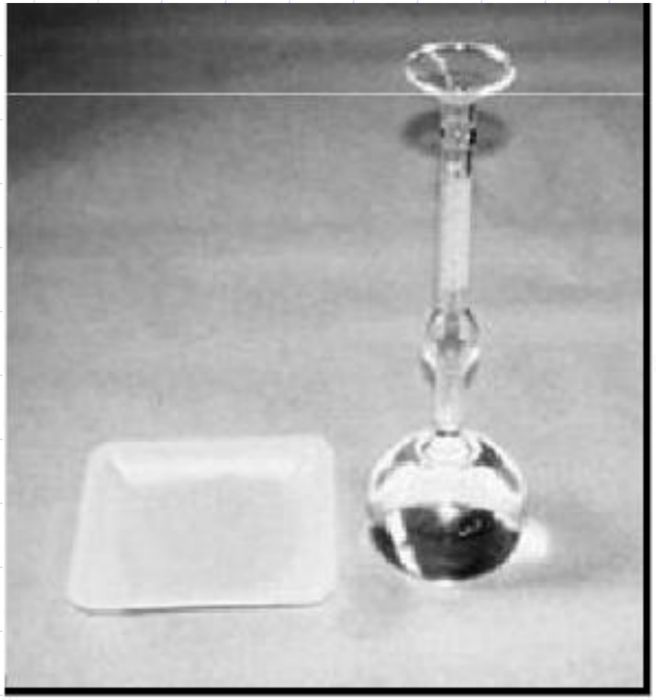
Special Cement

- Masonry--cements specifically formulated for use in masonry mortars
- Mortar--cements like masonry cements that include limits on max air content and min strength (for structural applications)

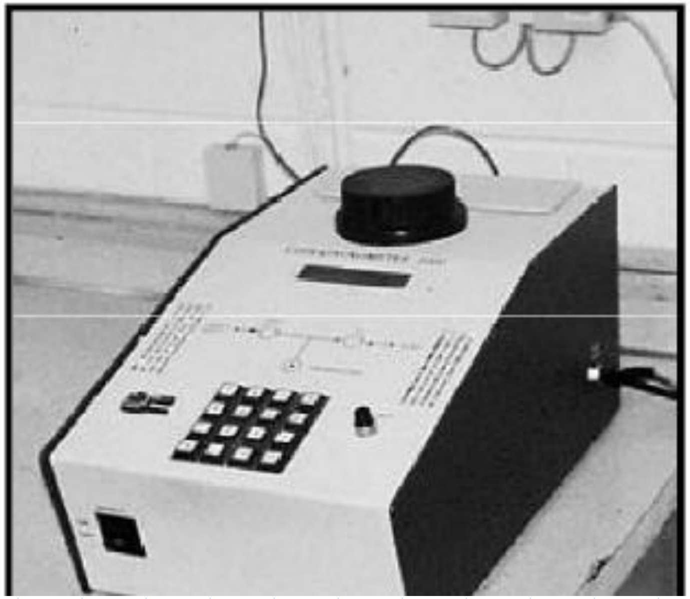
Quality Tests on Cement

- Quality control
  - Chemical aspects
  - Physical aspects
- Factors that affect performance of cement/concrete
  - Fresh properties influence placing and workability
  - Hardened properties influence strength and durability

Density of Cement



Le Chatelier flask (ASTM C 188 or AASHTO T 133)



Helium pycnometer

Bulk Density

Bulk density of cement varies between

830 kg/m^3 (52 lb/ft^3)

and

1650 kg/m^3 (103 lb/ft^3).

Chemical Tests on Cement

- ASTM C 114
  - Chemical analysis to determine oxides
  - Use this to calculate potential compound composition
    - C_3S
    - C_2S
    - C_3A
    - C_4AF

Cement Fineness Tests

Blaine, ASTM C 204 (m^2/kg)

Measures time to pass air through cement sample (porous “bed”)

Wagner, ASTM C 115 (m^2/kg)

Pass light through suspension of cement particles, measure intensity

Modern Fineness Tests

Nitrogen adsorption
Surface area

Laser diffraction particle
size analysis

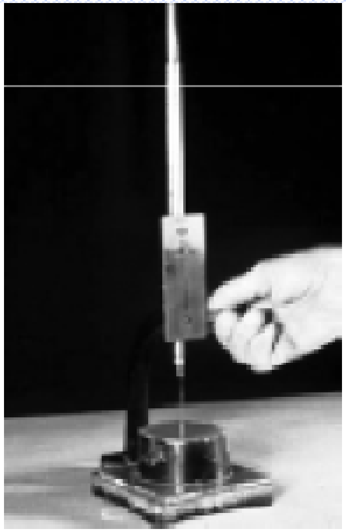
Cement Fineness

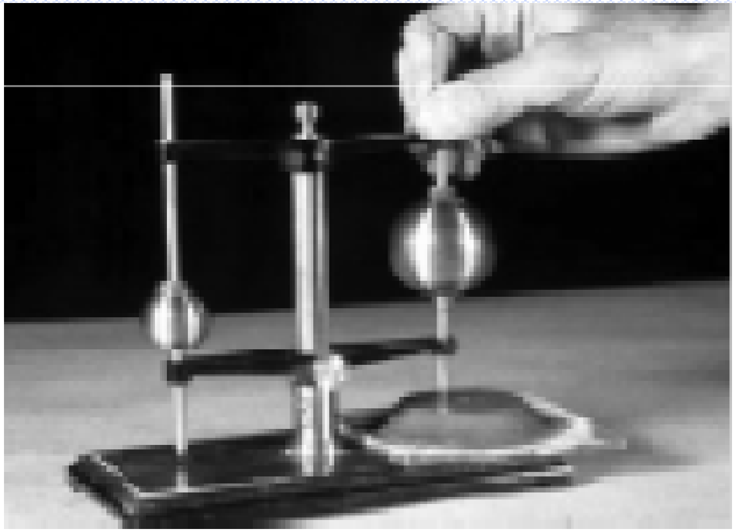
- 300 m^2/kg (Blaine) - 1950's Type I
- 370 m^2/kg (Blaine) - Today's cements
- Finer = faster hydration, more heat generation, higher early-age strength less long-term gains

Setting Behaviour of Cement

- Initial Set - From 1 to 4 hours
- Final Set - From 3 to 6 hours
- False Set - Rapid setting without much heat liberation, can be remixed (too much gypsum)
- Flash Set – Very rapid setting with significant heat liberation, can't be remixed (not enough gypsum)

Setting Behaviour of Cement Tests





Vicat, ASTM C 191, time

300g needle with 1 mm diameter

Initial set: 25-mm penetration

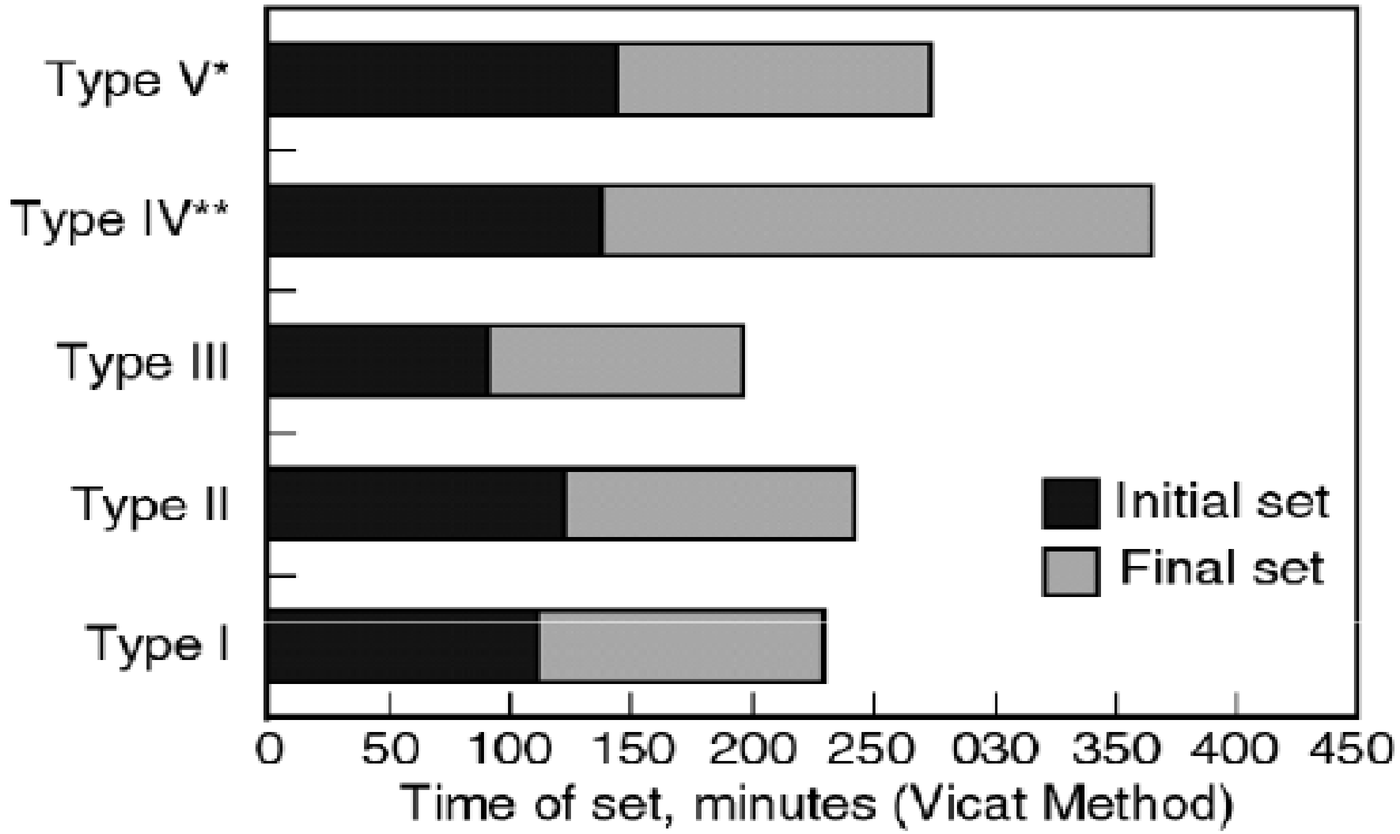
Final set: zero penetration

Gillmore, ASTM C 266,

Initial set: 2 mm diameter needle, 113 g

Final set: 1 mm needle, 454 g

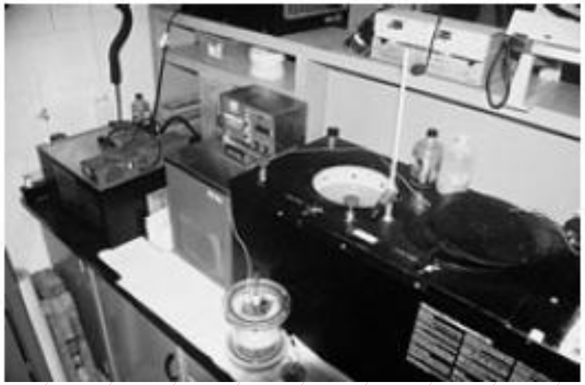
Setting Time for Portland Cement

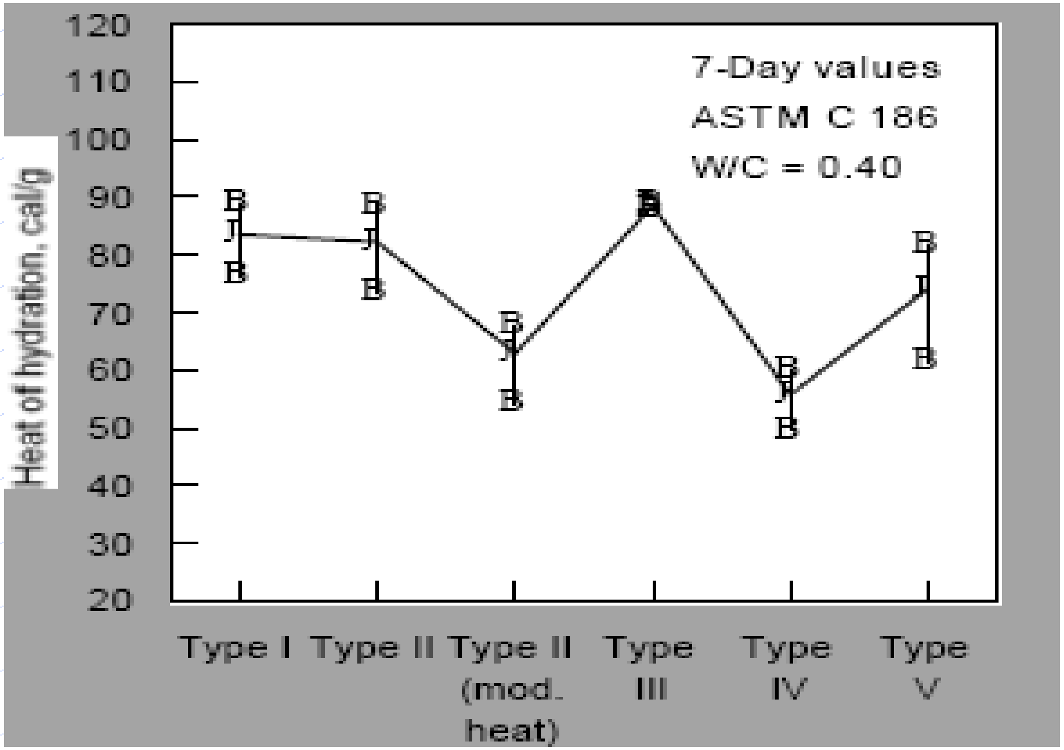


*Average of two values for final set
**Average of two values for initial set; one value for final set

Heat of Hydration Test

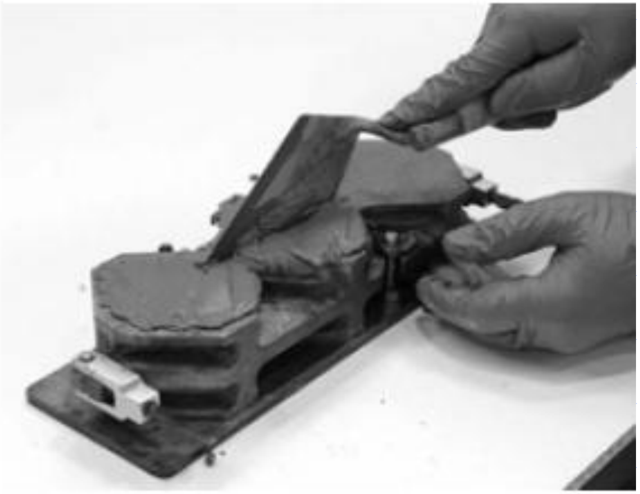
- ASTM C 186
  - Measure heat generated from cement as it hydrates





Strength Tests

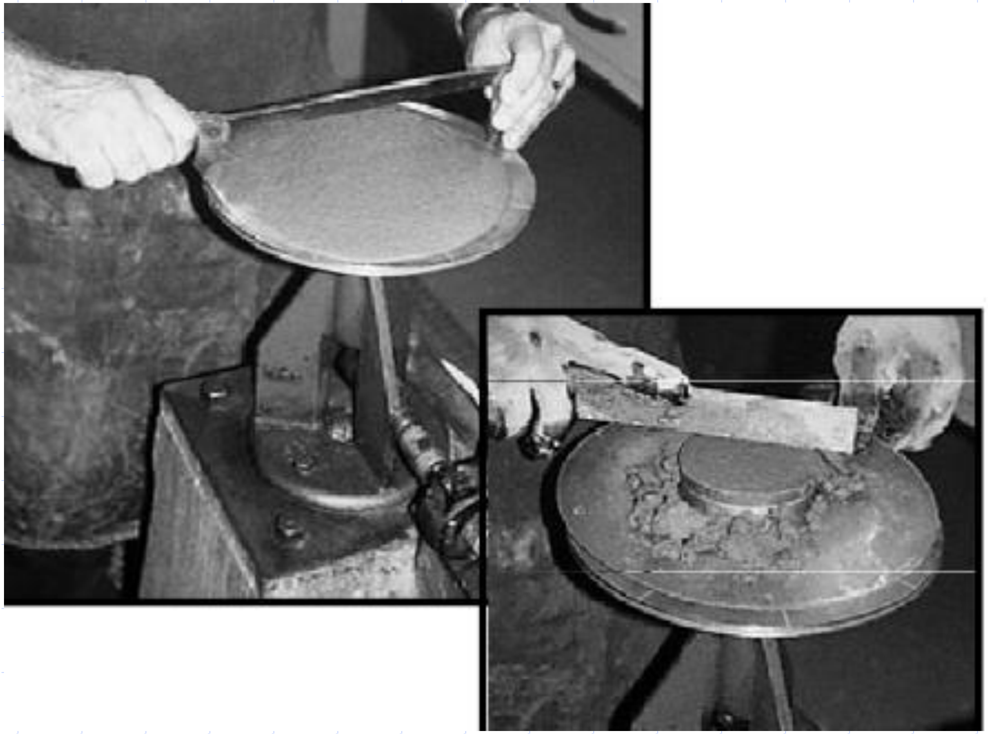
- ASTM C 109
  - 50-mm (2-in.) mortar cubes
  - Made from 1 part cement, 2.75 parts sand
  - In molds for 1 day, lime water till testing
  - Results in MPa/psi



Air Content Test

- ASTM C 185
  - Air content of mortar from a unit weight measurement
  - Used to ensure that cement does not entrain undesired air
  - Used to ensure that additions are present in correct quantity

Consistency Test



ASTM C 230 (AASHTO M 152) and ASTM C 1437

Flow table

Thermal Analysis

- Thermogravimetric analysis (TGA)
- Differential Thermal Analysis (DTA)
- Differential Scanning Calorimetry (DSC)

Transporting Cement

Questions and Assignment

- Discuss various types of Cement available in Pakistan and its Characteristics. (*Note*: *Put colour pictures of aggregates*)
- Different tests on Cement
- Report and Power point Presentation
- Need to submit in Group