# Exploring the Chemical Landscape of Cement and SCMs: Phases, Reactions, Microstructure, and Their Role in Sustainable and Durable Construction

**Dipendra Kumar Das**

**PhD Research Scholar**

Building Technology, Construction Materials and Management

Department of Civil Engineering, IIT Madras

# Mini CV

- PhD in Civil Engineering (BTCM)- IIT Madras, Chennai **2023** (Pursuing)
- M.Tech (Structural engineering)- Vellore Institute of Technology & CSIR-CBRI Roorkee, Vellore, Tamil Nadu **2023**
- B.E Civil Engineering-B.M.S College of Engineering-Bangalore(VTU) **2021**

Some of the Achievements:

- ❖ **ICI** – Ultratech **Outstanding Master Thesis Award** 2023
- ❖ Futuristic Ideas by Young Scientists-A Poster Presentation at CBRI Roorkee (Consolation Award)
- ❖ **Rank holder** (MTech Structural Engineering)
- ❖ Intermediate Level (11 &12th aggregate, School Topper)
- ❖ **2013 MGSS (GOI), 2017 COMPEX Scholarship, 2021 HJBSS, 2023 ICCR**

**Projects**

**Apple Chemie**, **India** (Running)

**Sika AG**, **Switzerland** (Jan 2025 onwards)

Publication: Hydration kinetics and stability study of pure phases of cement clinker with the addition of SCMs and dopants" Recent Advances in Green Technologies and Sustainable Development (**Taylor & Francis 2023**)

## Adapted from Prof. Ravindra Gettu, Manu Santhanam & Piyush Chaunsali

# Outline

- Portland Cement Introduction
- Cement Production
- Various Types of Cement
- Hydration Reactions
- Microstructure
- Mineral admixtures
- Chemical admixture (WRA)
- Various Issues on Concrete
- Brief on LC3
- Conclusion
- References

# Portland Cement

## Cement= Clinker +Gypsum

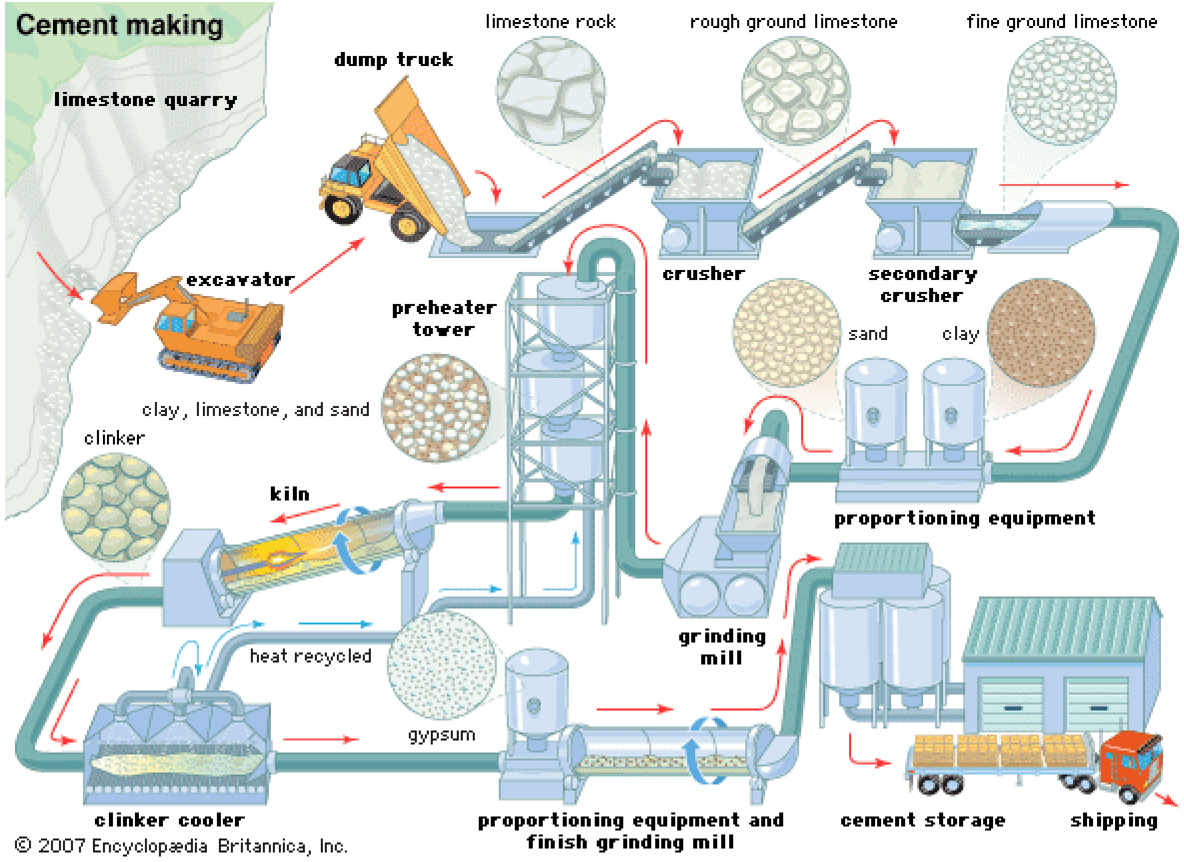
### Oxide Composition of Cement

- **CaO (C): 60-67%**
- **$SiO_2$ (S): 17-25%**
- **$Al_2O_3$ (A): 3-8%**
- $Fe_2O_3$ (F): 0.5-6%
- MgO (M): 0.1-4%
- Alkalis (eq. $Na_2O$): 0.2-1.3%

## Phase Composition of Cement

| Name | Formula | Shorthand | Weight % |
|---|---|---|---|
| Tricalcium silicate (Alite) | 3 CaO. $SiO_2$ | **$C_3S$** | ~ 55-60 |
| Dicalcium silicate (Belite) | 2 CaO. $SiO_2$ | **$C_2S$** | ~ 15-20 |
| Tricalcium aluminate | 3 CaO. $Al_2O_3$ | **$C_3A$** | ~ 5-10 |
| Tetracalcium aluminoferrite | 4 CaO. $Al_2O_3$. $Fe_2O_3$ | **$C_4AF$** | ~ 5-8 |
| Gypsum | $CaSO_4$. $2H_2O$ | **$CSH_2$** | ~ 2-6 |

# Cement Production




- Up to **700 °C** : activation of silicates
- **700 – 900 °C** : calcination of $CaCO_3$
- **900 – 1200 °C** : Belite ($C_2S$) formation
- **> 1300 °C**): reaction of belite and free lime to form alite
- Cooling stage: molten phase gets transformed to a glass

# Proportioning of Raw Materials

- Alumina Modulus (AM) = A/F (typical range: 1-1.8)

- Silica Modulus (SM) = S/(A+F) (typical range: 2-2.8)

- Lime Saturation Factor (LSF) (typical range: 0.92-0.98)

  = C/(2.8S +1.18A + 0.7F) (when AM < 0.64)

or, = C/(2.8S + 1.65 A + 0.35F) (when AM > 0.64)

CaO (C); $SiO_2$ (S); $Al_2O_3$ (A); $Fe_2O_3$ (F)

- AM governs the melt phase (clinker liquid)
- Silica modulus controls amount of melt
- LSF dictates the amount of free lime

# Cement Classification

## ASTM Classification (ASTM C150)

- Type I: General purpose
- Type II: Moderately sulfate resistant, and moderate heat of hydration
- Type III: High early strength
- Type IV: Low heat of hydration
- Type V: Sulfate resistant
- Type IA, IIA and IIIA for air-entrained cements

## Blended cements (ASTM C595)

- Type IS – Portland blast-furnace slag cement (S < 95%)
- Type IP – Portland-pozzolan cement (P < 40%)
- Type IL – Portland-limestone cement (5% < L< 15%)
- Type IT – Ternary blended cement

Benefits:

- **Pozzolanic reaction; additional C-S-H**
- **Pore refinement**
- **Increased durability**

# Typical Composition

| ASTM Type | Compound composition (%) | | | |
|---|---|---|---|---|
| | $C_3S$ | $C_2S$ | $C_3A$ | $C_4AF$ |
| I | 45-55 | 20-30 | 8-12 | 6-10 |
| II | 40-50 | 25-35 | 5-7 | 10-15 |
| III | 50-65 | 15-25 | 8-14 | 6-10 |
| IV | 25-35 | 40-50 | 5-7 | 10-15 |
| V | 40-50 | 25-35 | 0-4 | 10-20 |

# BIS & EN Classification

## BIS Classification

- Ordinary Portland Cement – IS:269-1989 (further classified into 33, 43, and 53 grade)
- Portland Cement, Low Heat – IS:12600-1989
- Rapid Hardening Portland Cement – IS:8041-1978
- Portland-Pozzolana Cement – IS:1489-1976
- Portland-Slag Cement – IS 455-1976
- Composite Cement – IS: 16415- 2015
- Microfine Ordinary Portland Cement – IS: 16993 – 2018

## EN Classification

| | |
|---|---|
| • CEM I | Portland cements |
| • CEM II | Portland composite cements |
| • CEM III | Blast-furnace cements |
| • CEM IV | Pozzolanic cements |
| • CEM V | Composite cements |

# Bogue's Compound

## $C_3S$

- Early strength development
- High reactivity due to irregular structure – high heat of hydration

## $C_2S$

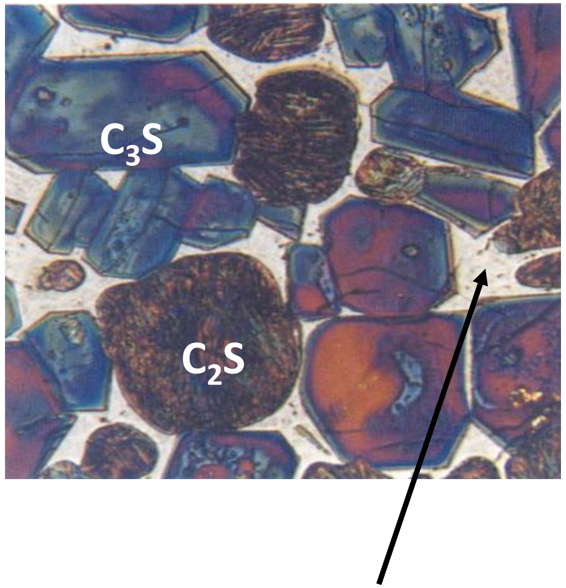
- Less irregular structure than C3S - less reactivity
- Present entirely as β-C2S

## $C_3A$

- Generally intermixed – difficult to distinguish
- highest heat of hydration for C3A

## $C_4AF$

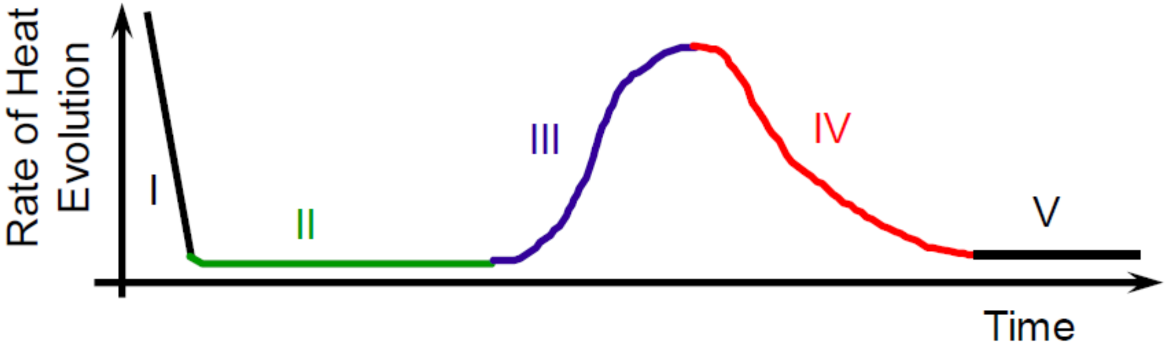
- Ferrite closely mixed with aluminates (similarity in cell parameters)
- Imparts color to cement




Microcrystalline matrix of aluminate and ferrite

H.F.W. Taylor, 1997, D. H. Campbell, 1999

# Typical Heat of Hydration Curve

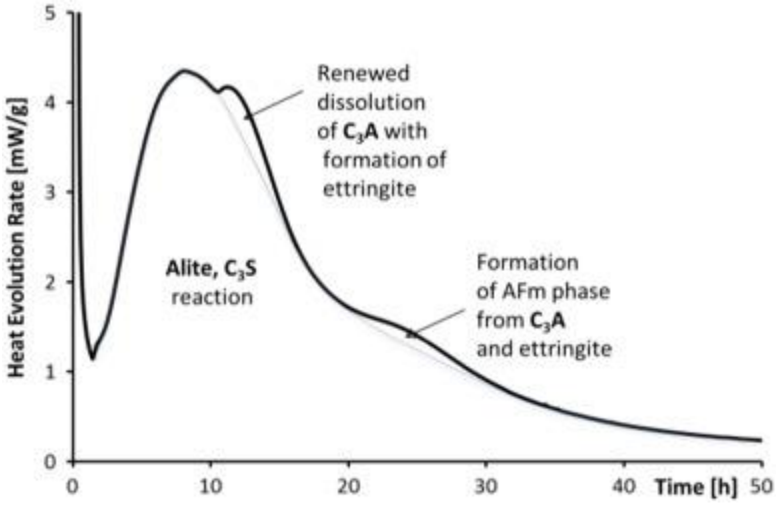


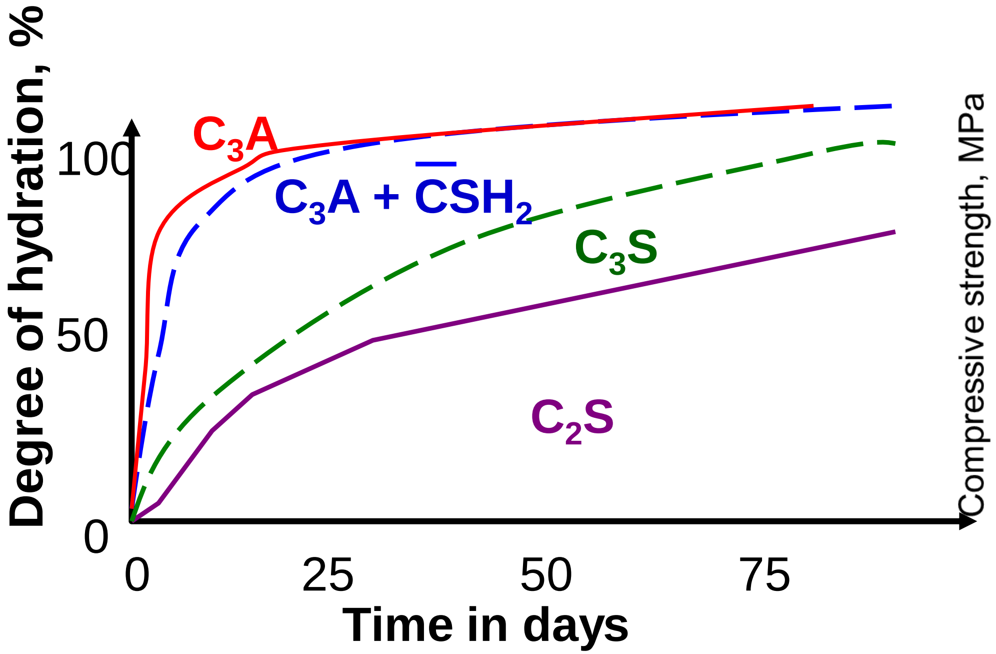

| | | | |
|---|---|---|---|
| Stage I | Rapid Heat Evolution | | (<15 mins) |
| Stage II | Dormant Period | Important for transportation | (2-4 hrs) |
| Stage III | Accelerating Stage | Begins with initial set | (4-8 hrs) |
| Stage IV | Deceleration Stage | No longer workable | (12-24 hrs) |
| Stage V | Steady State | | |

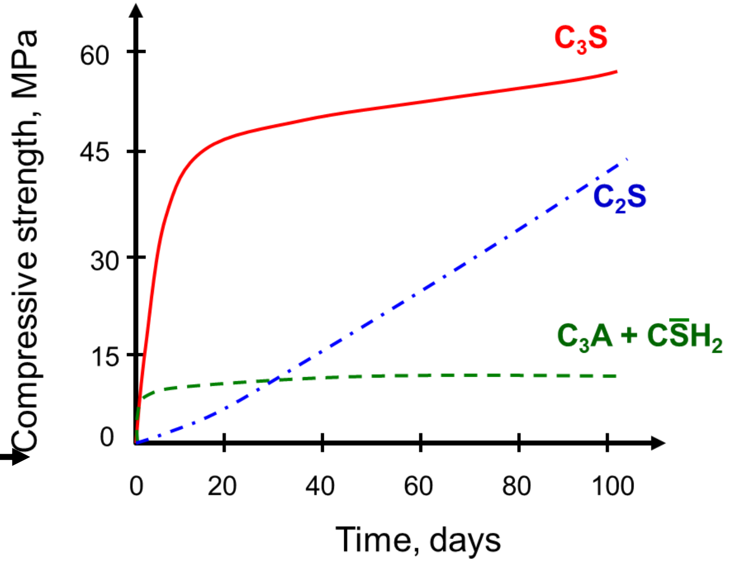
## Summary of Reaction Process

| Reaction stage | Relevance to concrete properties |
|---|---|
| Initial hydrolysis | |
| Induction period | Determines initial set |
| Acceleration | Determines final set and rate of initial hardening |
| Deceleration | Determines rate of early strength gain |
| Steady state | Determines rate of later strength gain |

# Calorimetry of Modern Portland Cement




- $C_3S$ contributes to high **early strength**
- $C_2S$ contributes to **later age strength**
- **$C_3A$ reacts immediately** with water
- **Gypsum** prevents **flash set**
- **Reactivity: $C_3A$,$C_3S$,$C_2S$,$C_4AF$**

Bullard et al., 2011

# Hydration Reactions of Cement

Calcium Silicates ($C_3S$ and $C_2S$)

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$$

C-S-H

Portlandite

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH$$

In presence of enough gypsum

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32}$$ Ettringite (AFt)

After gypsum depletion remaining $C_3A$ reacts with ettringite and forms monosulfate

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12}$$ Monosulfate (AFm)

$$2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$$ Hydrogarnet

Flash set reaction!

# Hydration Products of Cement

## C-S-H

- 50-65% of solids volume; high surface area (200-700 $m^2/g$)
- Morphology – poorly crystalline to a reticular network
- C/S ranges from 1.5 to 2
- Strength attributed to Van der Waals forces

## C-H

- 20 – 25% of the paste’s solid volume
- Hexagonal crystals

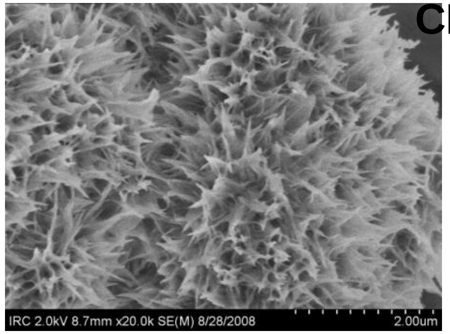
## Ettringite

- Acicular, columnar, hexagonal crystals (seen as prismatic needles)

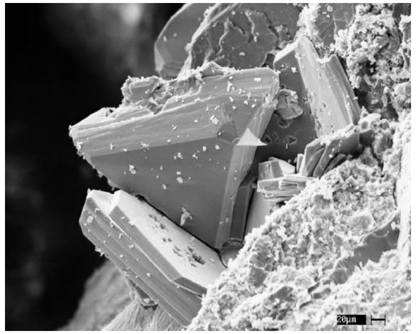
## Mono sulphate

- plain hexagonal
- Volume occupied (**Ettringite+ Mono sulphate**): 15 – 20%

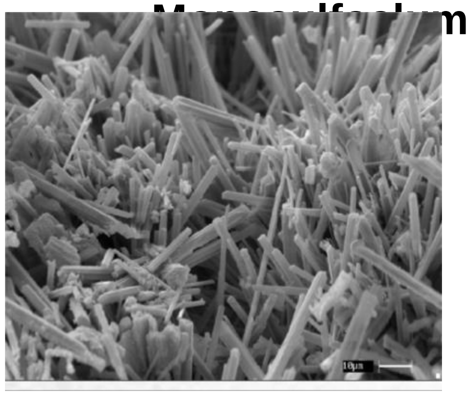
**C-S-H**



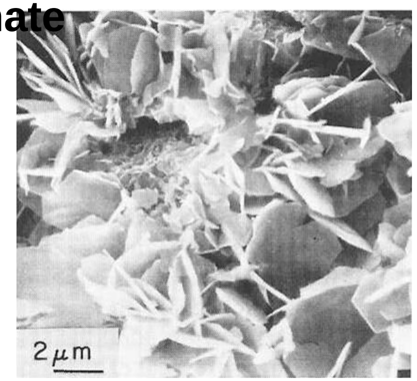

**CH**



**Ettringite**



**Monosulfoaluminate**

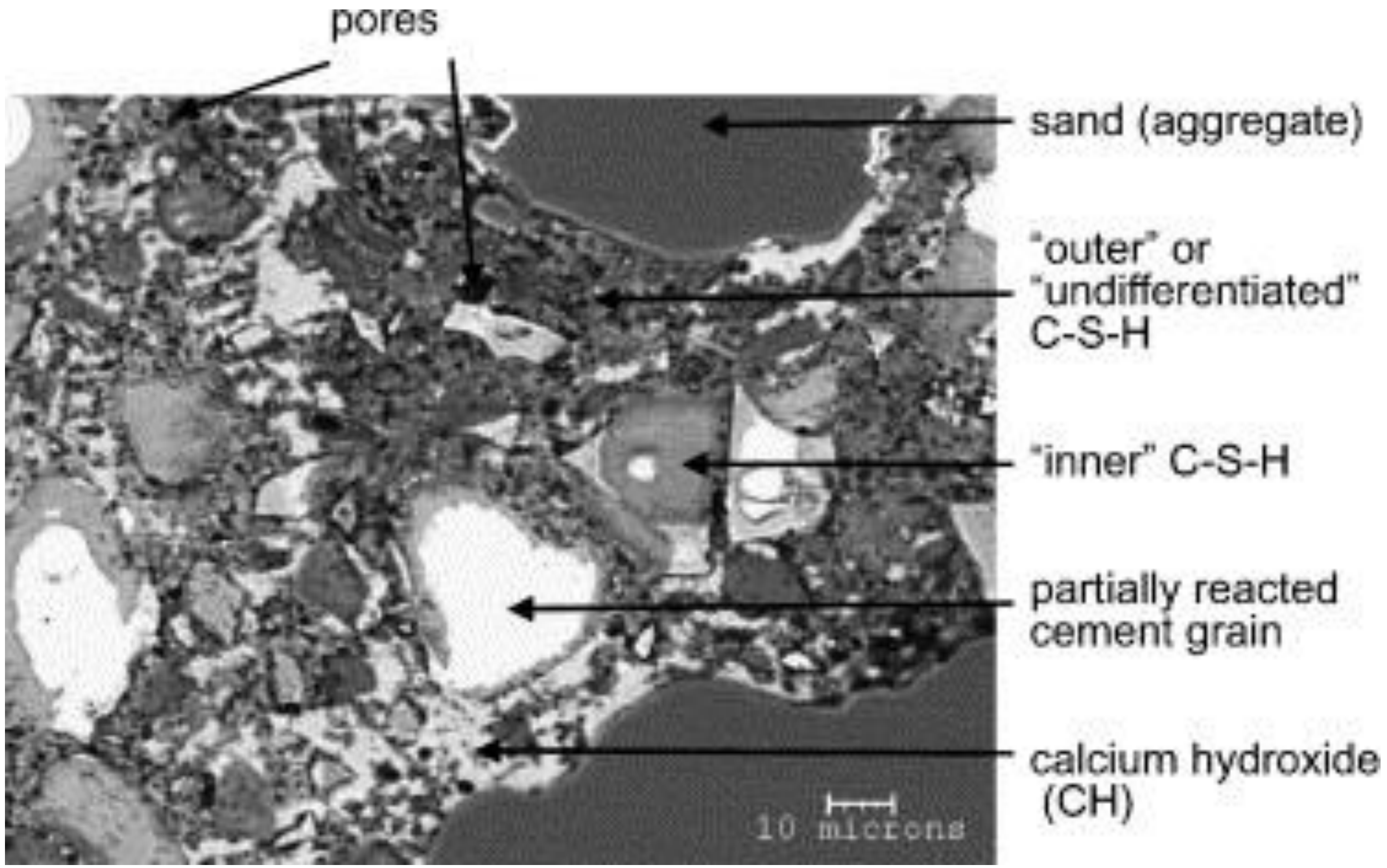



http://cementlab.com/cement-art.htm

Mehta and Monteiro, 1993, Mindess and Young, 1981

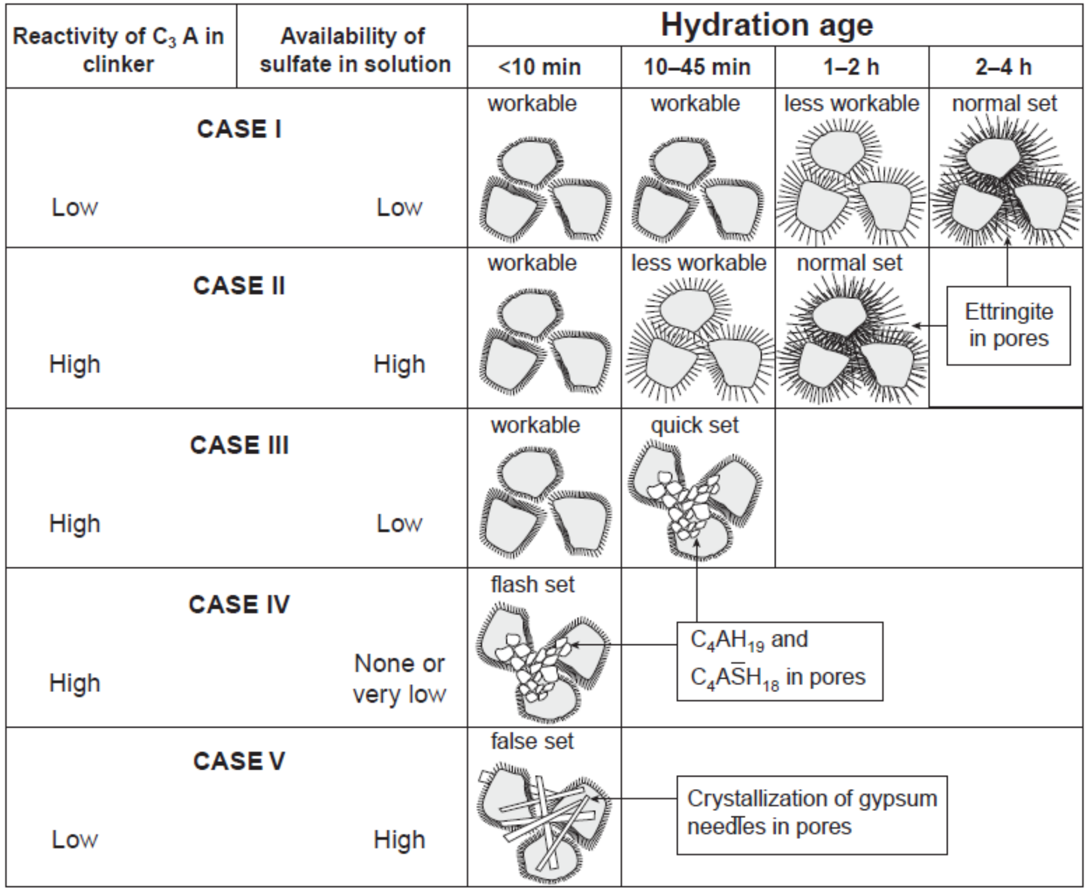
# Concrete Microstructure (BSE Imaging)

Portland cement mortar 200 days old, *w*/*c*=0.4



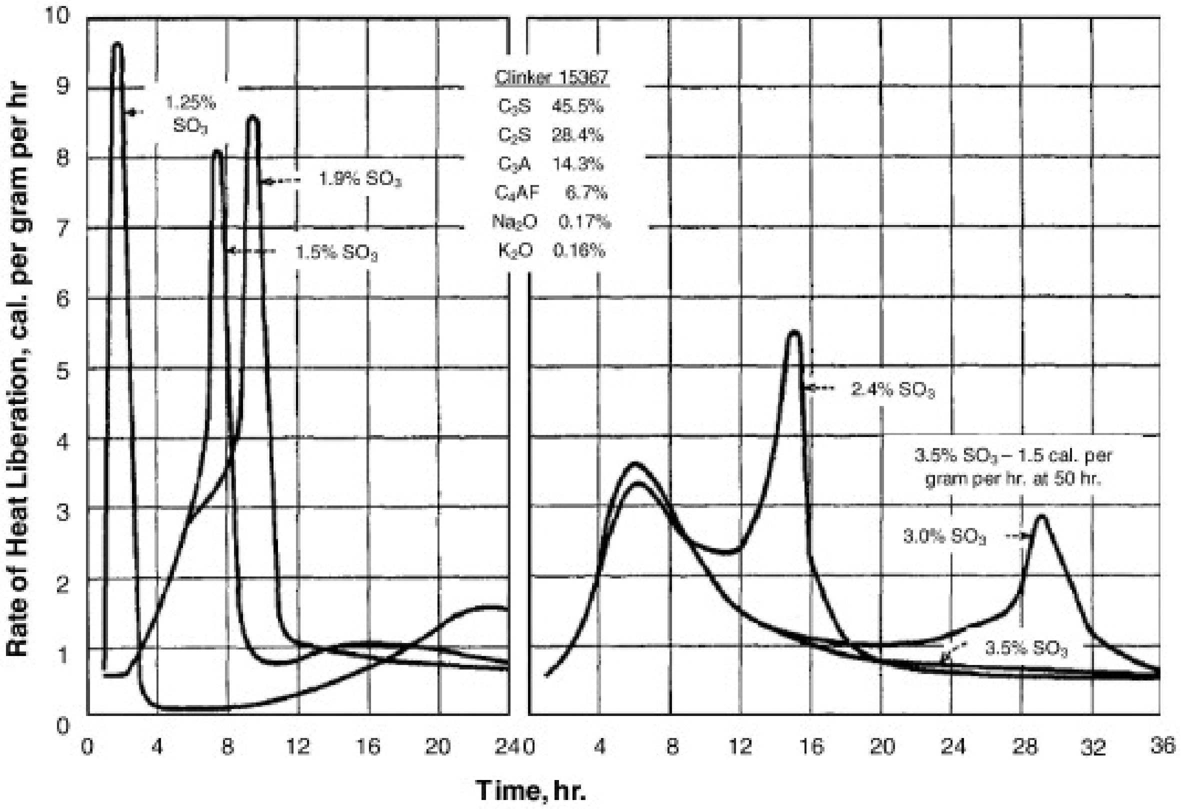

Scrivener, 2004

# Influence of $C_3A$/Gypsum Ratio




Mehta and Monteiro

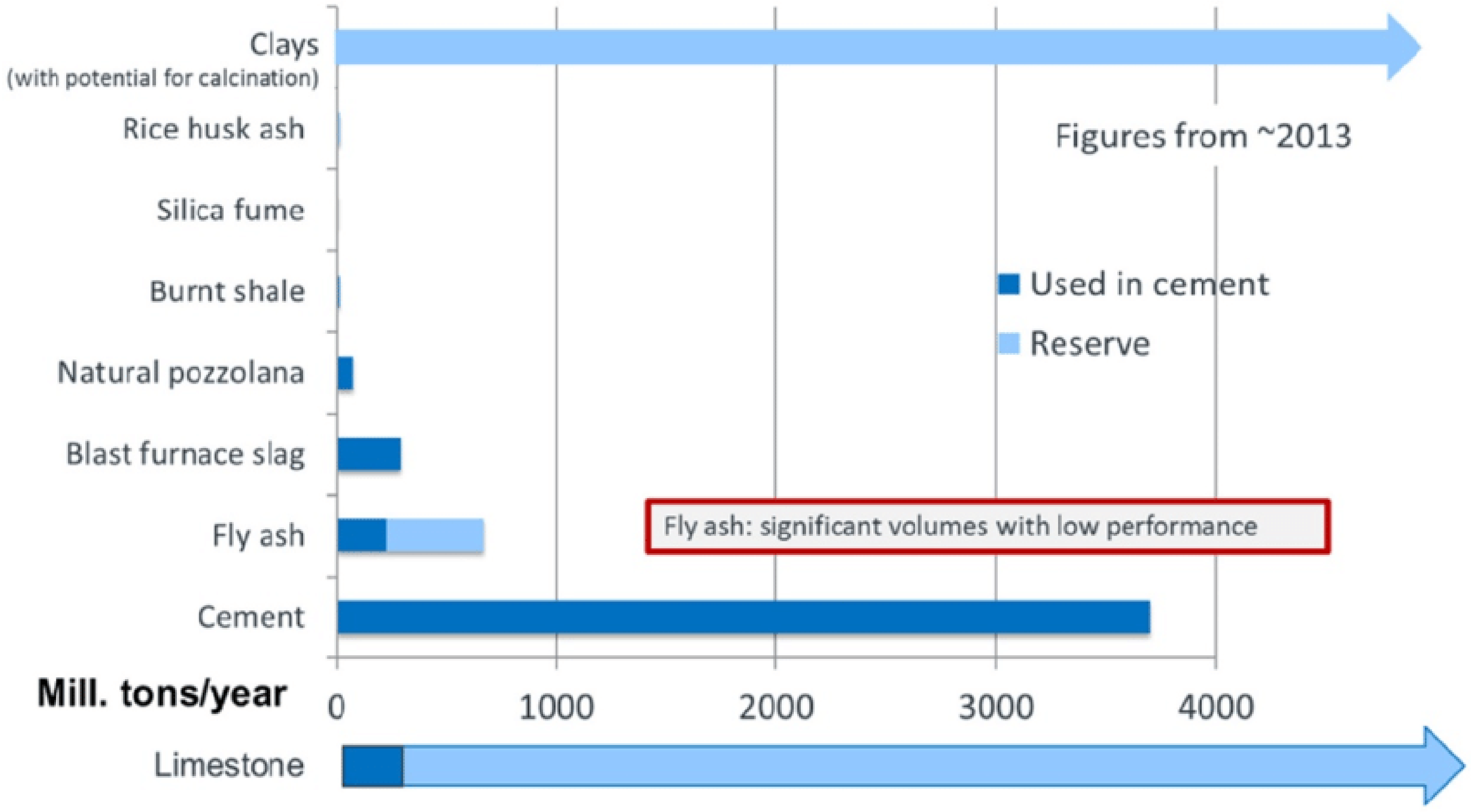
## Optimal Sulfate Content




Silicate peak suppression under-sulfated cement systems

Lerch, 1946

# Mineral admixtures (SCMs) availability




https://www.researchgate.net/figure/Availability-of-common-supplementary-cementitious-materials-SCMs-Reproduced-with_fig2_351645124

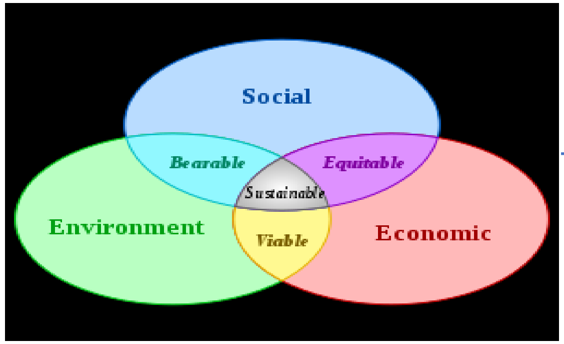
# Impact of Mineral admixtures

- 6 – 7 % of total greenhouse gas emissions come from cement production
- 1 ton Cement ≈ 1ton $CO_2$

***Corrosion repairs cost nearly 5% of developed nation's GDP***

Improved long term durability
Reduced potential for cracking

Use of waste or by-products
Reduced cement clinker usage




Increased benefit to cost ratio
Longer service life

Also called 'Supplementary Cementing Materials' (SCM)

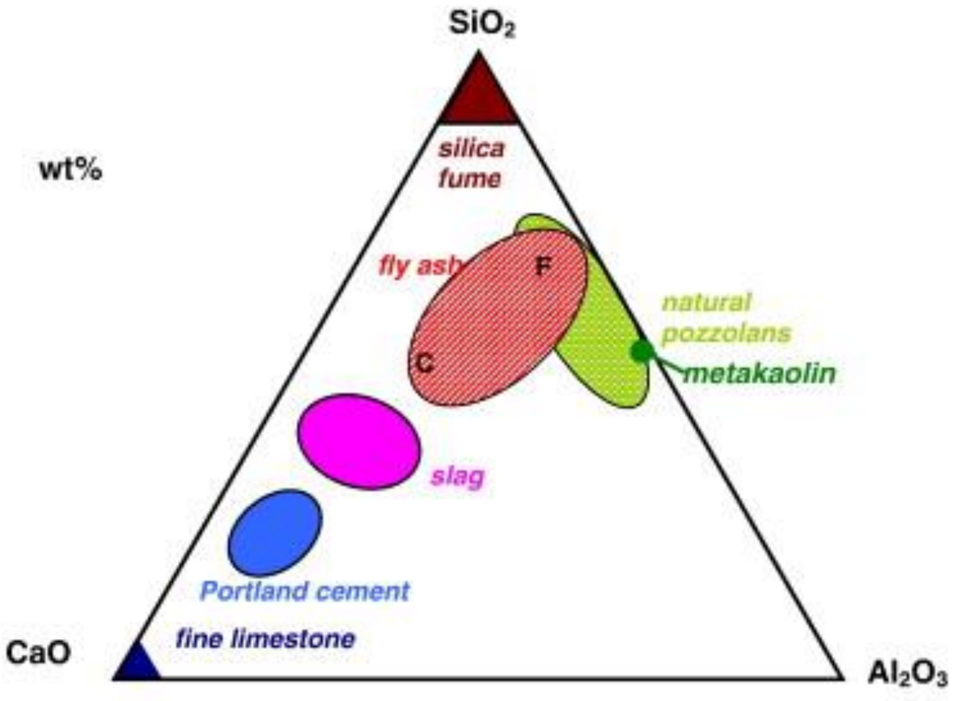
**Amorphous silica (Al)** + **$Ca(OH)_2$ (from cement hydration) → Additional C-S-H**

Sometimes, high CaO ➔ cementitious and pozzolanic

Additional mechanism of action – as filler

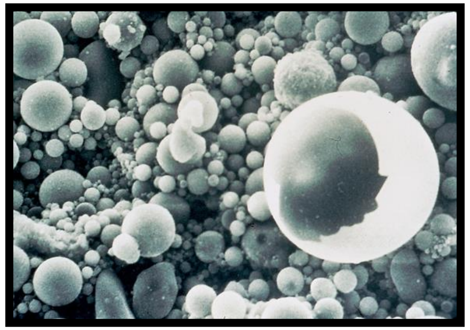
# Supplementary Cementitious Materials

- Fly ash
- Slag
- Silica fume
- Metakaolin: obtained from calcination of kaolinite clay
- Limestone



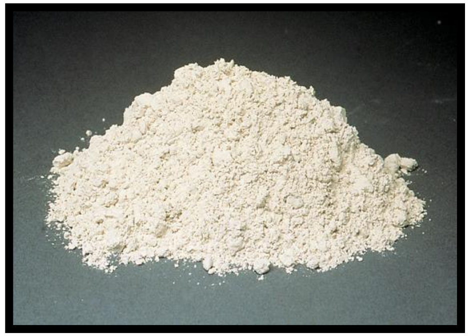
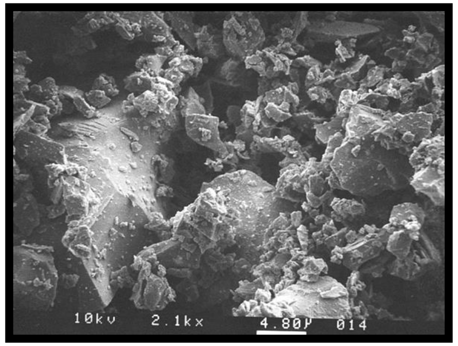

Lothenbach et al., 2011

# Contd.

**Fly ash**

**Molten slag**

**GGBS**

**Type C**: High Calcium fly ash, and possesses both cementitious and pozzolanic properties.

**Type F**: This is also called Low Calcium fly ash, and is a normally pozzolanic material.

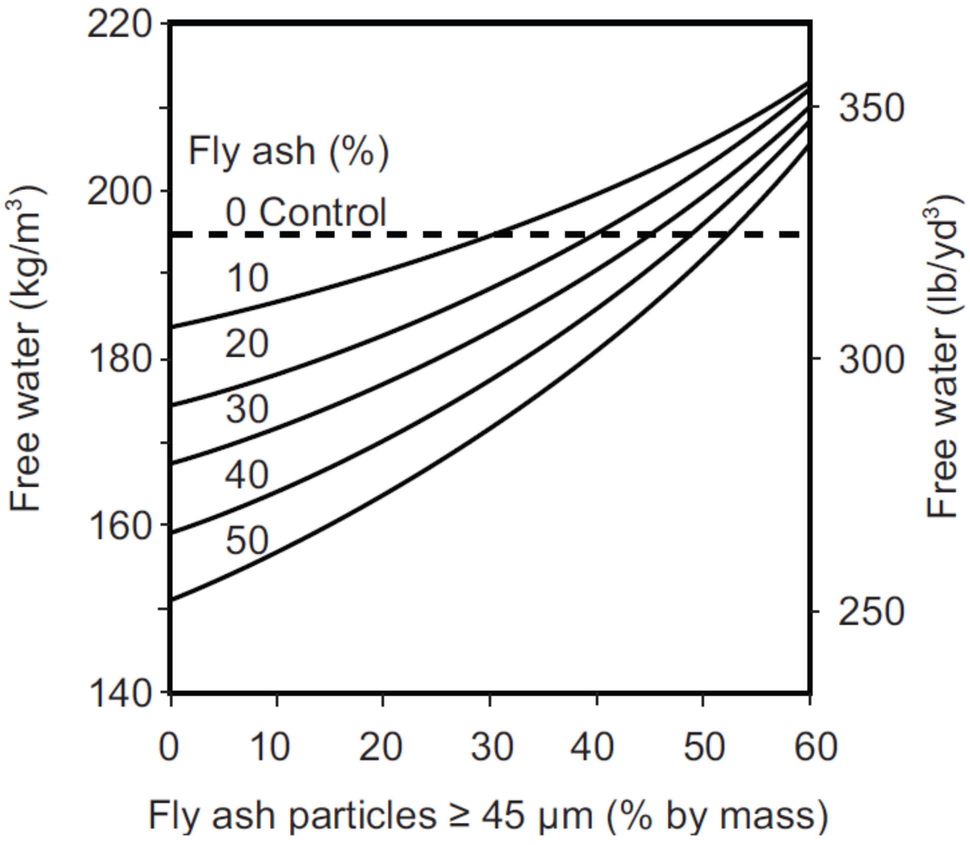
Portland Cement Association

Courtesy: M. Alexander

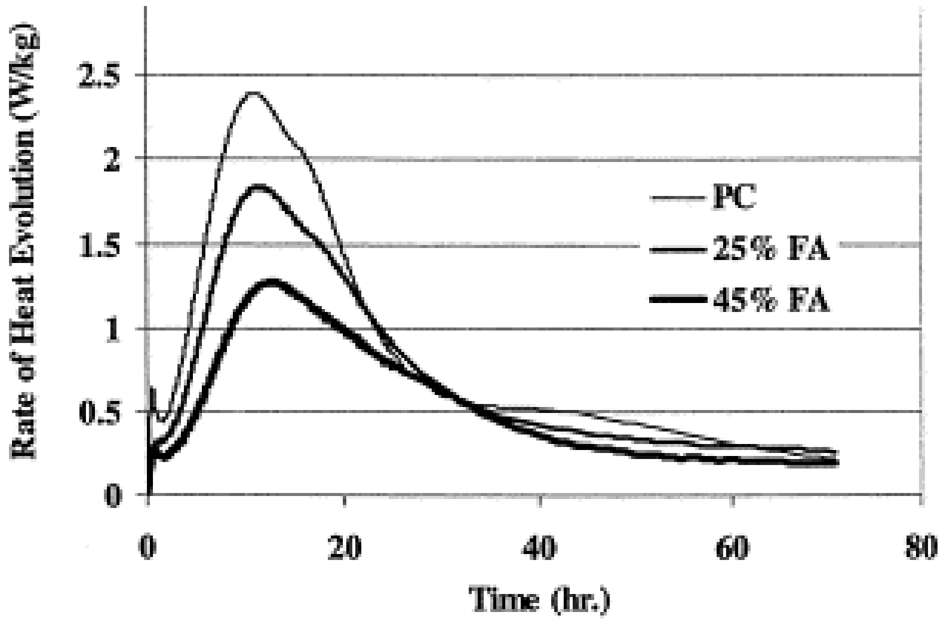
# Properties of SCMs

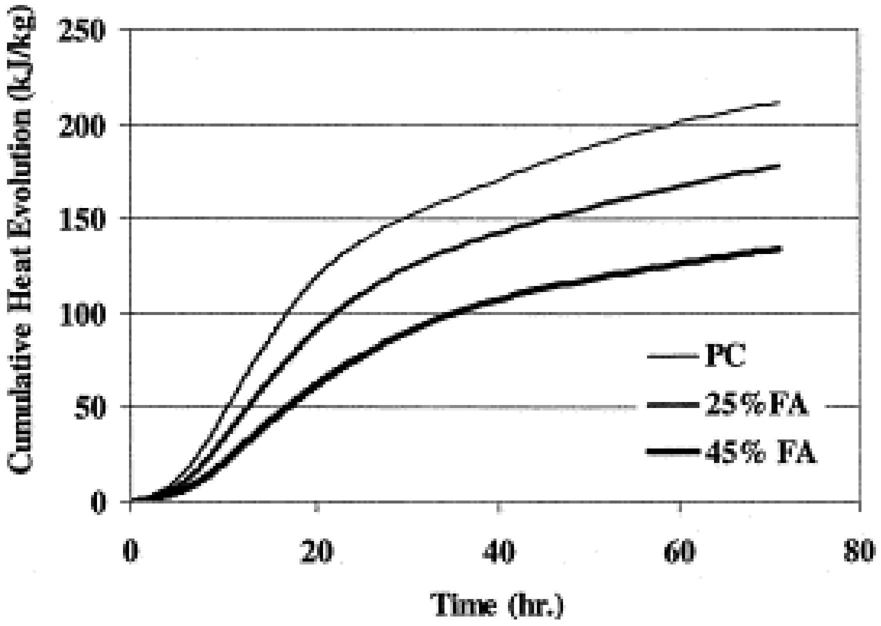
## Fly ash, GGBS and other SCMs

- Reduce the **carbon footprint of concrete**
- Small size and glassy texture
- **Water demand** reduction(~3% reduction in water demand for 10% fly ash)
- Improved **workability**
- Increased **setting time**
- **Bleeding and segregation** reduced
- Denser **microstructure**
- **Heat development** is lowered
- Resistance against **corrosion**
- Resistance to **sulphate attack** (↓ CH & permeability)
- **Alkali aggregate** reactivity ↓
- Increase the durability of concrete



# Influence of Fly Ash on Heat of Hydration



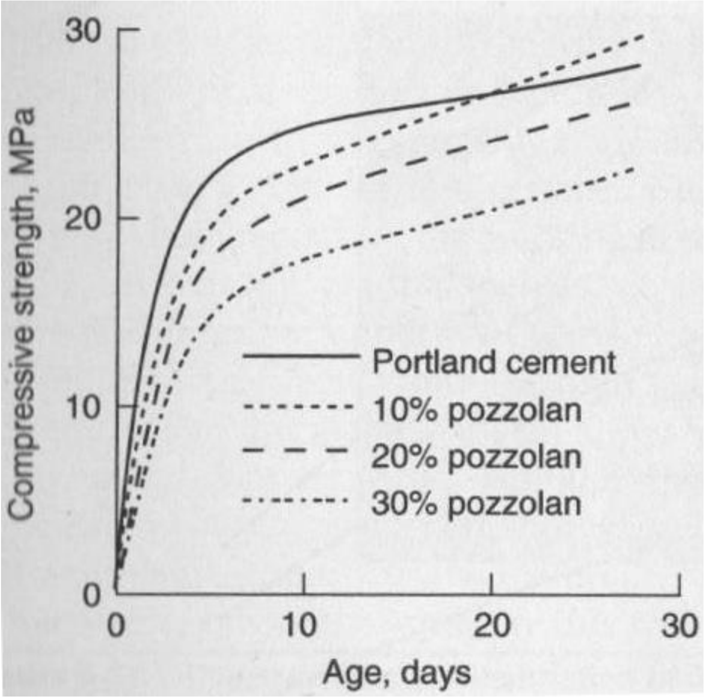



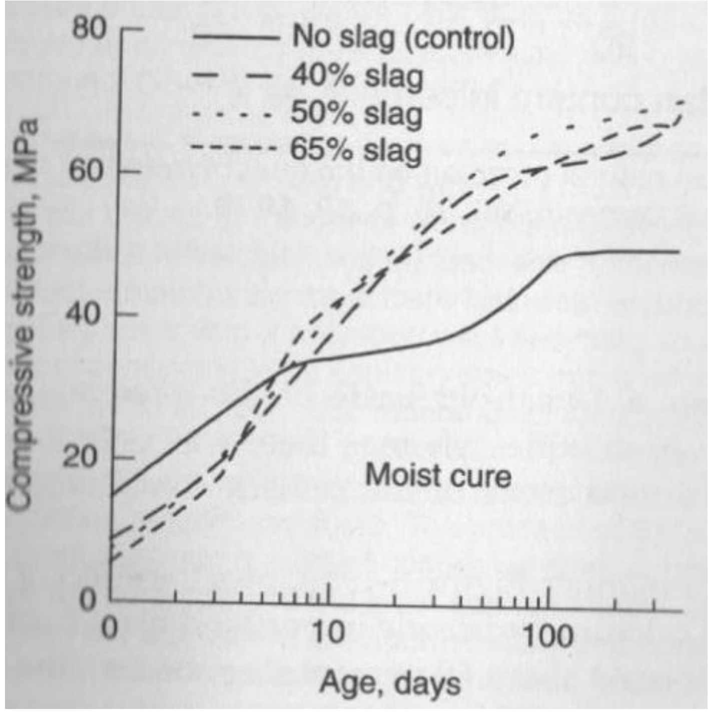

**PC**: Highest **early hydration peak**

**FA**: Lower **heat release**, Lower **cumulative heat**; **slower strength** development but beneficial for **long-term performance, reducing thermal cracking**

Poon et al., 2000

# Strength of Blended Cements

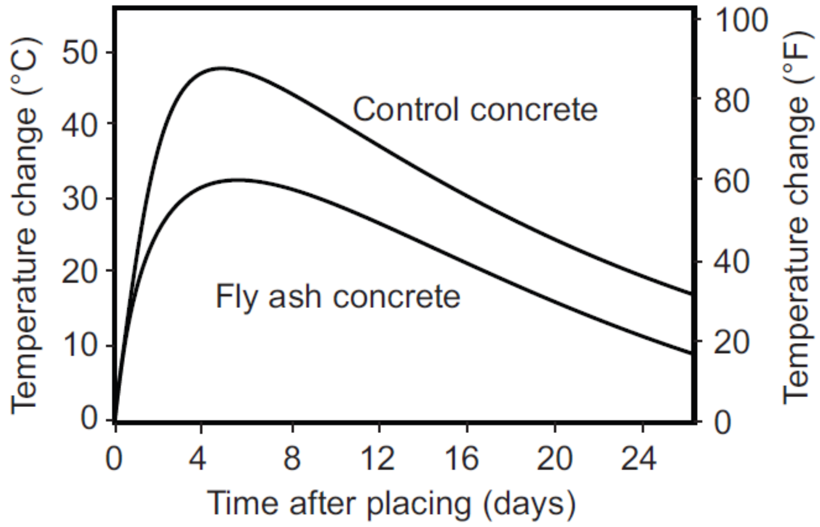


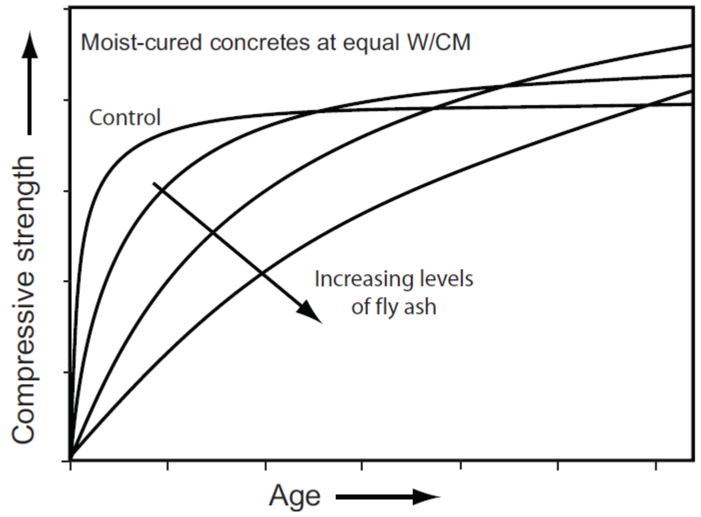



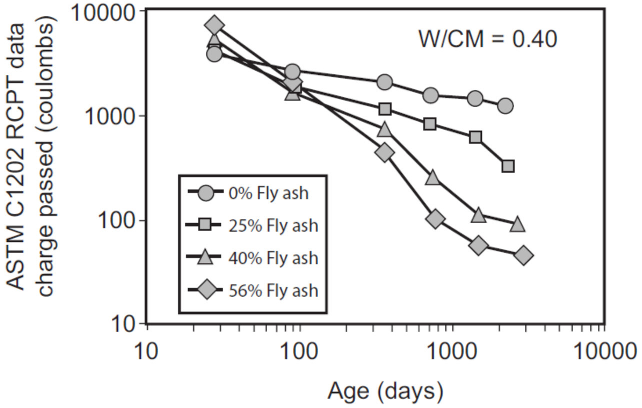

Strength decreases initially with higher pozzolan content but **improves** over time.

Strength increases with slag content, particularly at later ages, under moist curing conditions.

Mehta and Monteiro



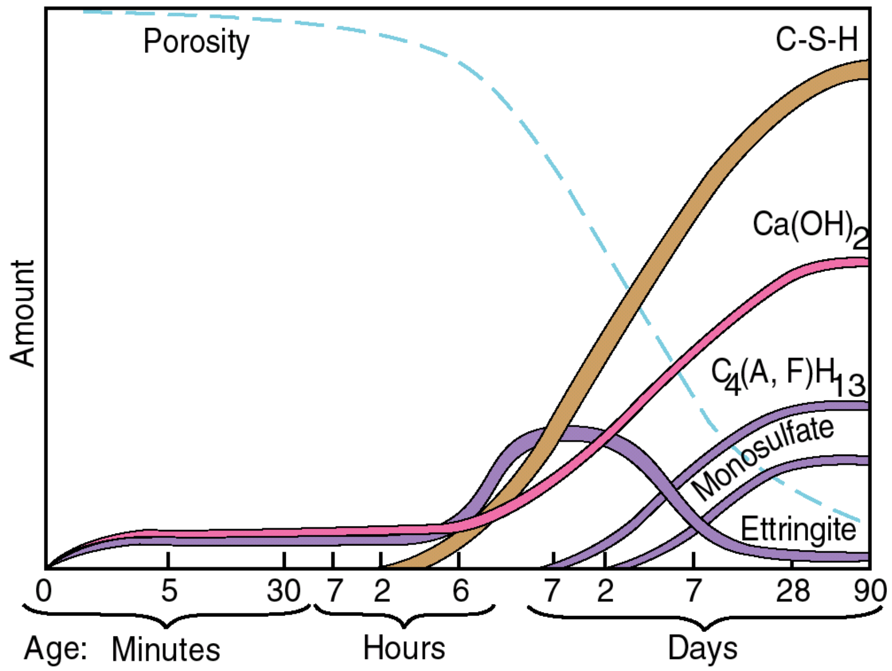



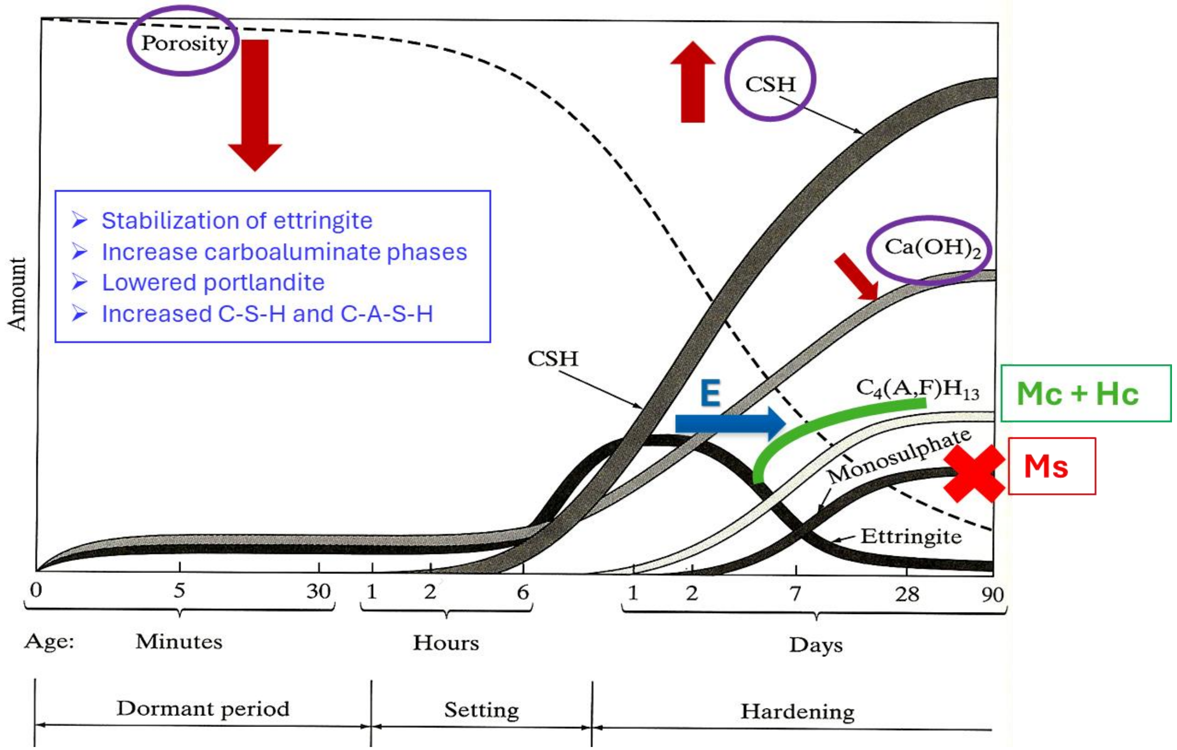




Fly ash concrete reduces early-age temperature rise, delays early strength but improves long-term strength and durability by lowering permeability.

Mustard, 1959

# Evolution of Phase Assemblage with OPC, Limestone and SCM




Young et al. 1998

# Benefits of Using Water-Reducing Admixtures

| Test series | Cement content (kg/m$^3$) | Water-cement ratio | Slump (mm) | Compressive strength (MPa) | |
|---|---|---|---|---|---|
| | | | | 7 days | 28 days |
| A—Reference concrete (no admixture) | 300 | 0.62 | 50 | 25 | 37 |
| Water-reducing admixture is added for the purpose of: | | | | | |
| B—Consistency increase | 300 | 0.62 | 100 | 26 | 38 |
| C—Strength increase | 300 | 0.56 | 50 | 34 | 46 |
| D—Cement saving | 270 | 0.62 | 50 | 25.5 | 37.5 |

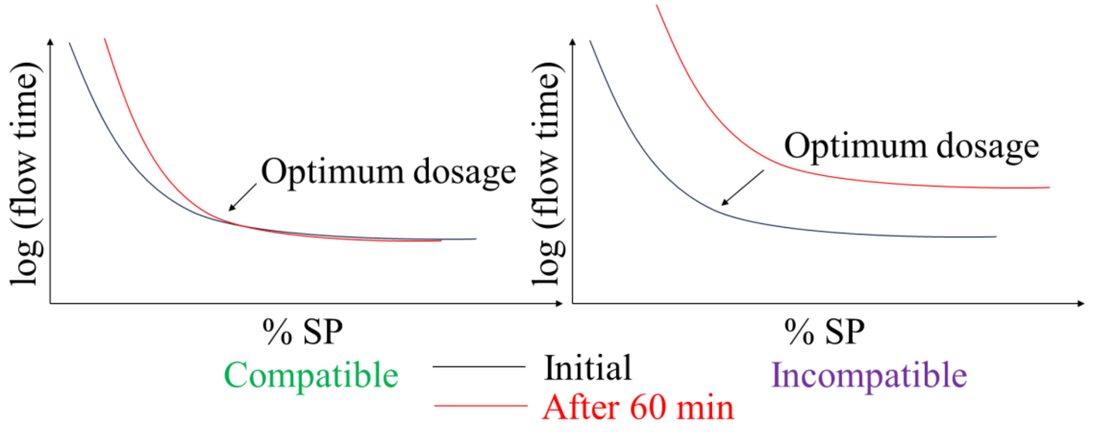
## High-Range Water Reducers

- 1st generation: **Lignosulphonates** (high dosages)
- 2nd generation: Polysulphonates (SNF &SMF)
- 3rd generation: Polycarboxylates,Polyacrylates,etc; Up to 40% water reduction

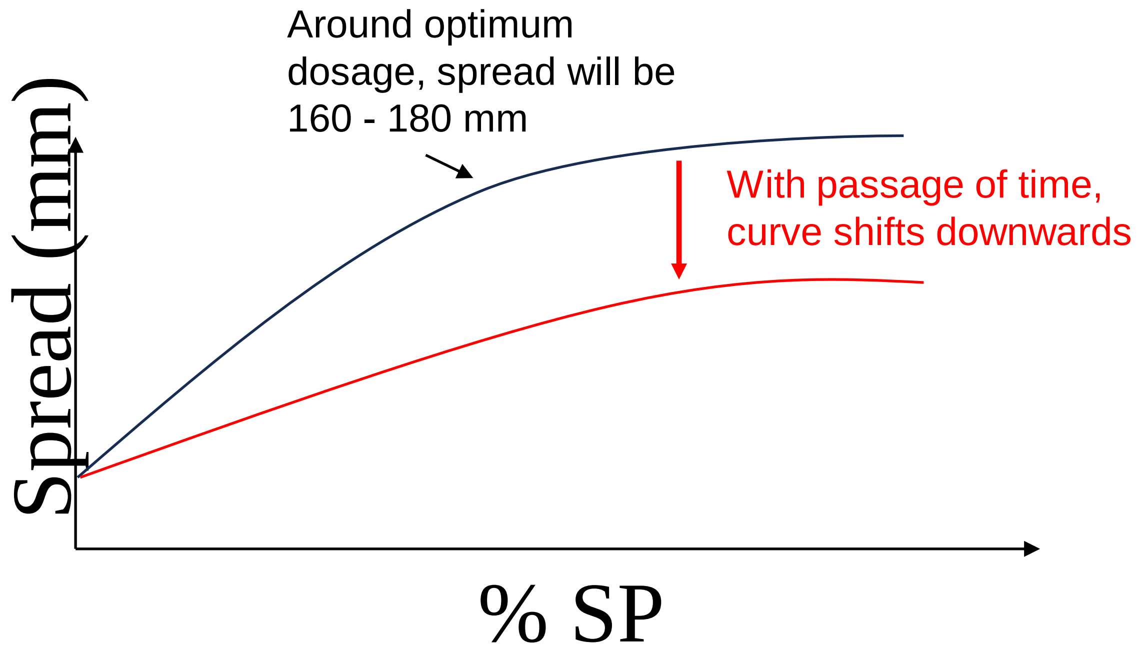
Superplasticizers typical dosage: 0.7 – 1.0% by weight of cement

Mehta and Monteiro

# Tests on Superplasticizers

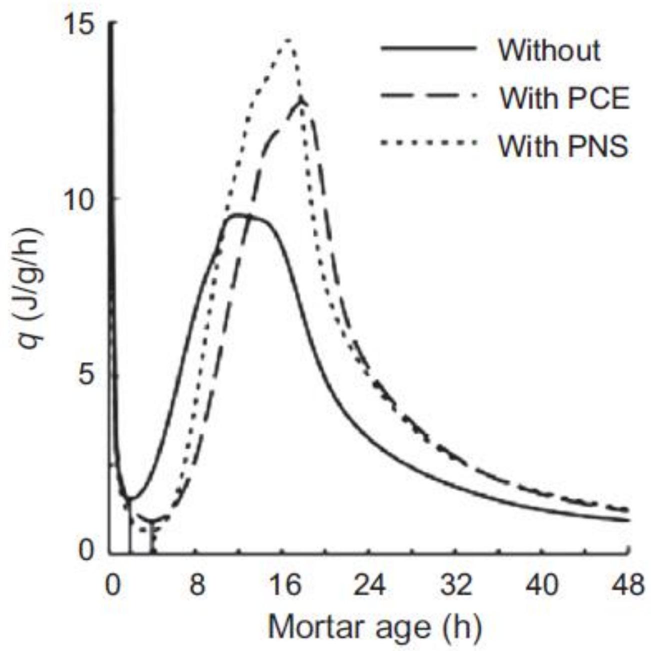


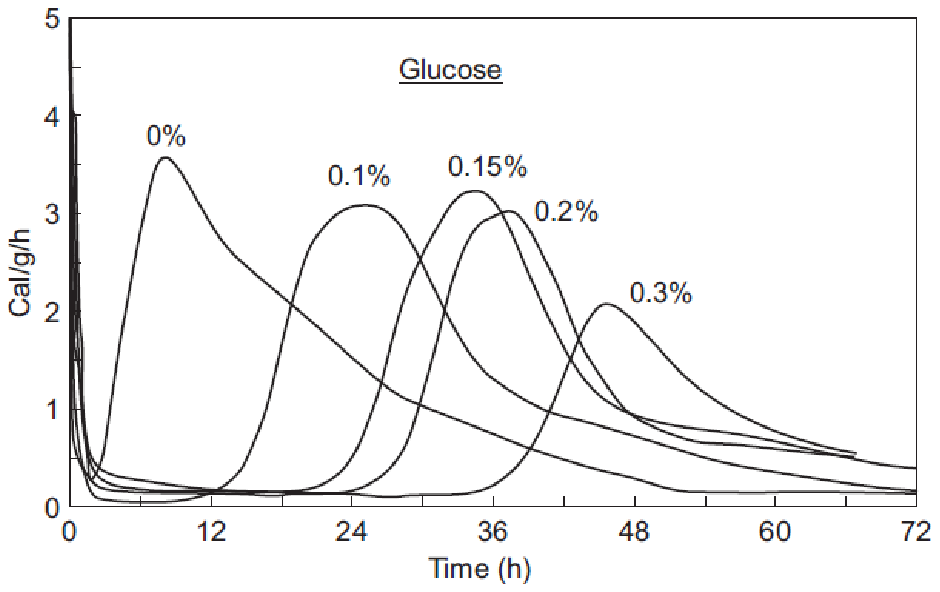

**Mini-Slump Test**




**Beyond optimum dosage, no significant change in spread. Bleeding can be seen at high dosages**

# Retardation of Cement Hydration



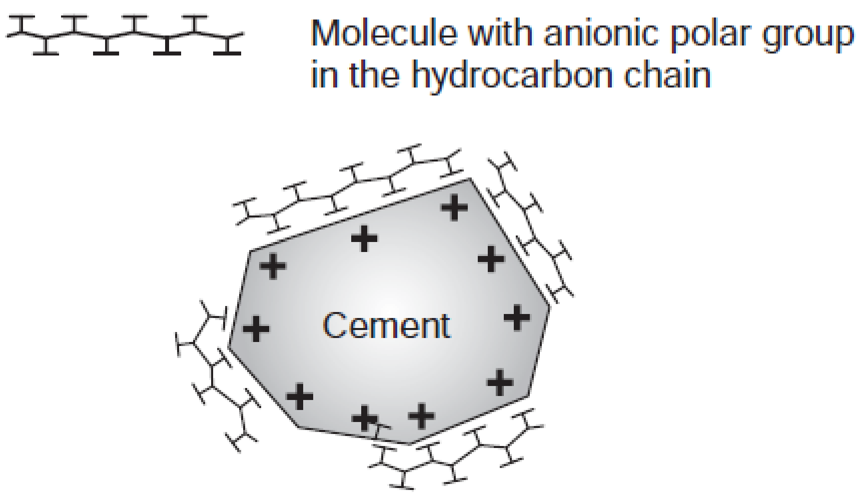



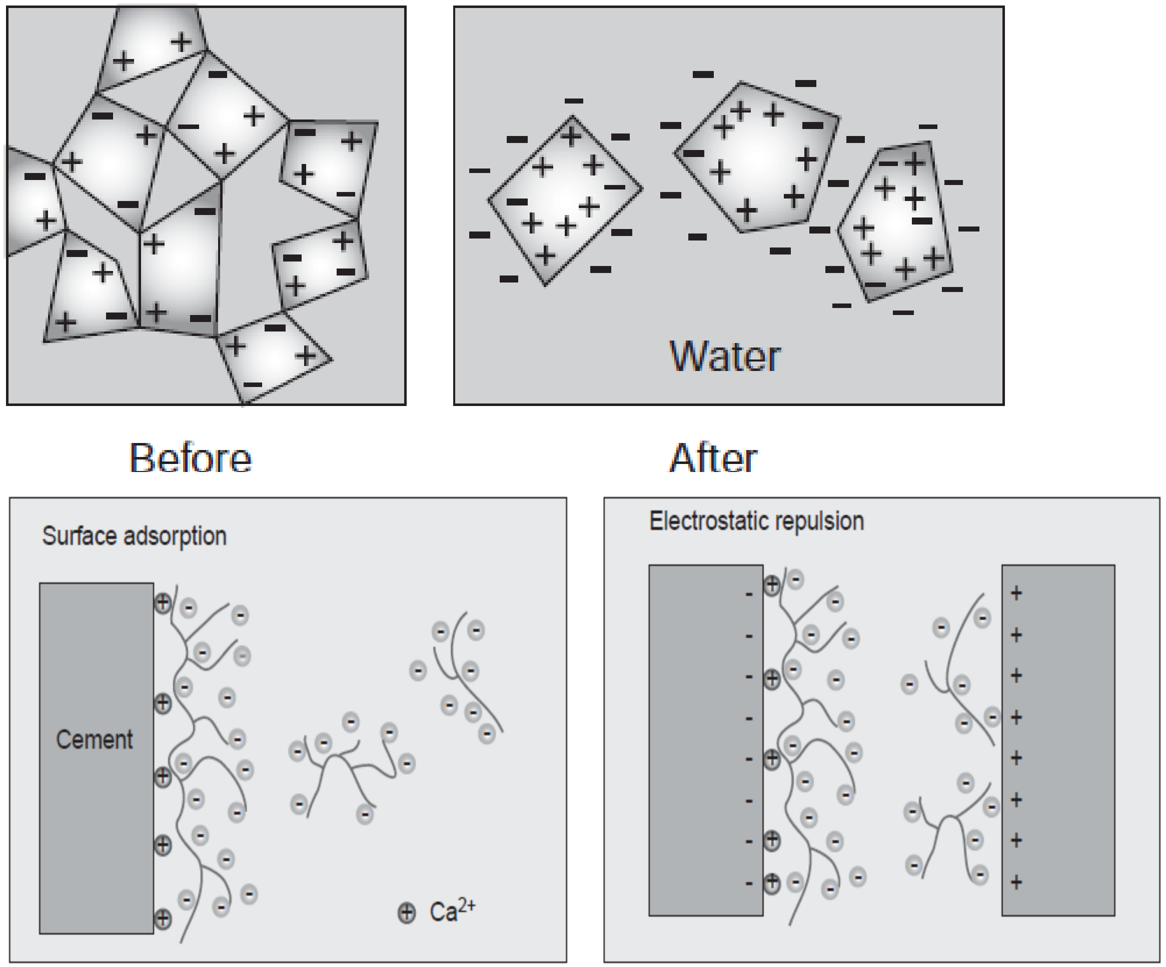

**Adsorption:**

- Inhibition of nucleation and/or growth of hydrates
- Poisoning of nuclei or prevention of growth
- Complexation

Science and Technology of Concrete Admixtures,

# Dispersion Mechanism: Electrostatic Repulsion



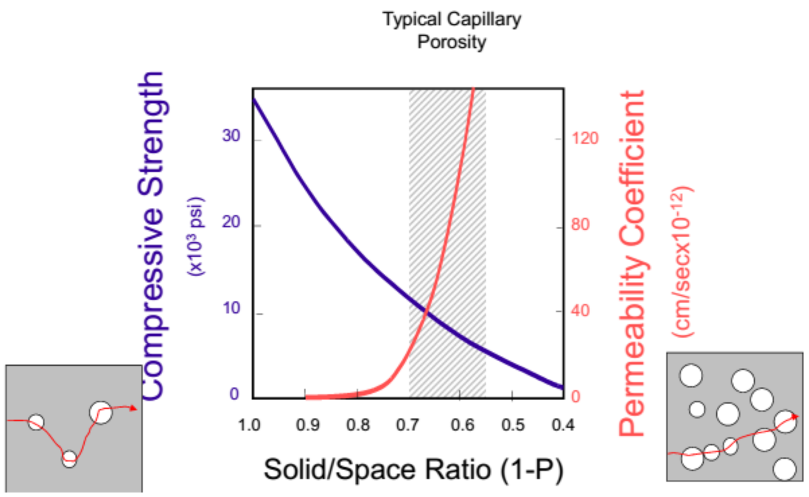




Mehta and Monteiro

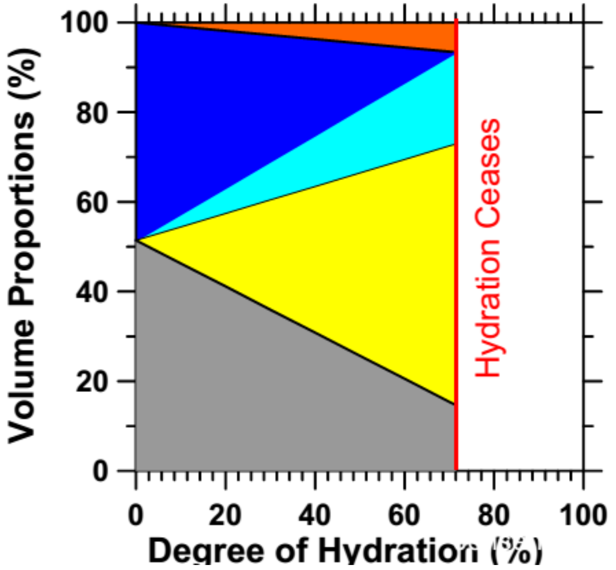
# Porosity, Gel Space, Strength and Permeability

**Porosity, Gel Space, Strength and Permeability**

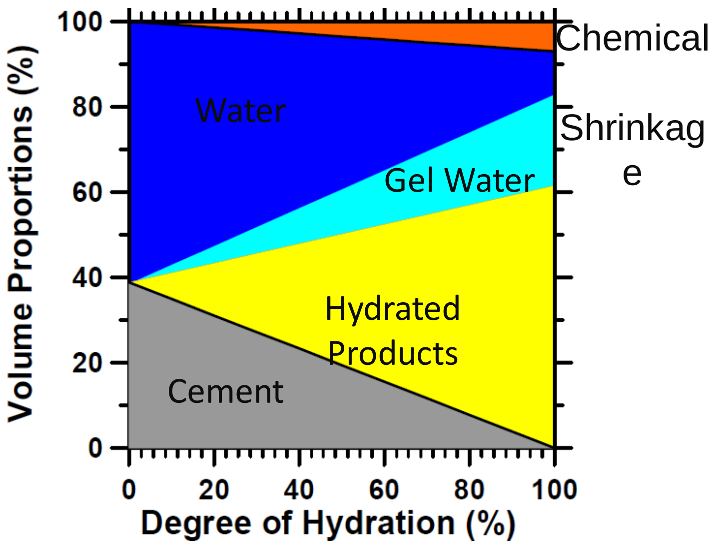
## Powers' Model




**w/c – 0.3**



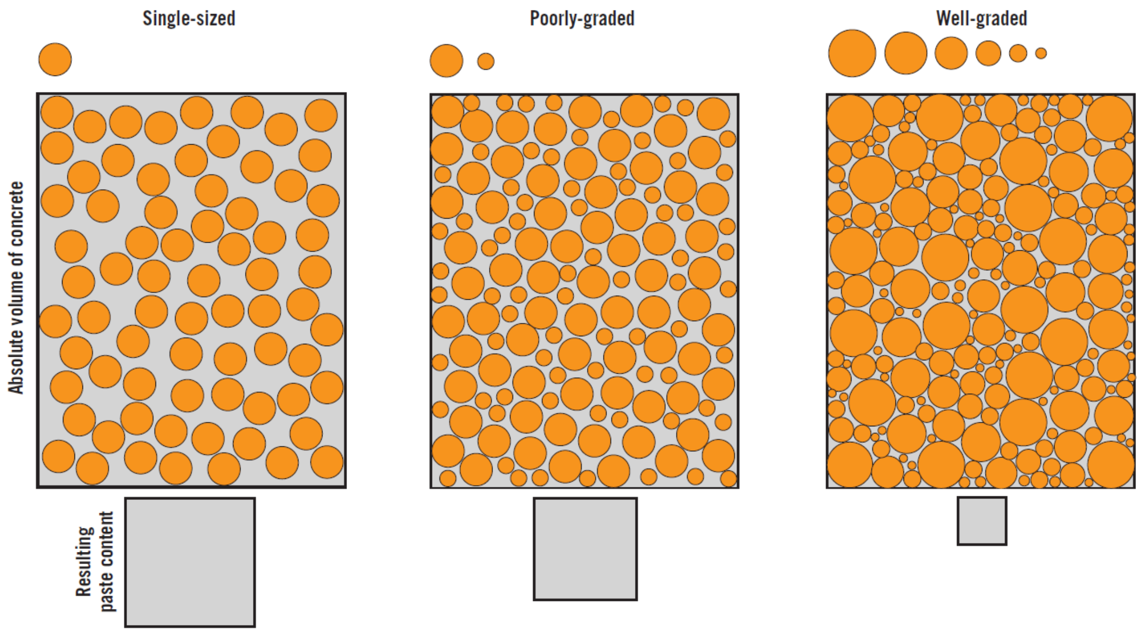

**w/c – 0.5**



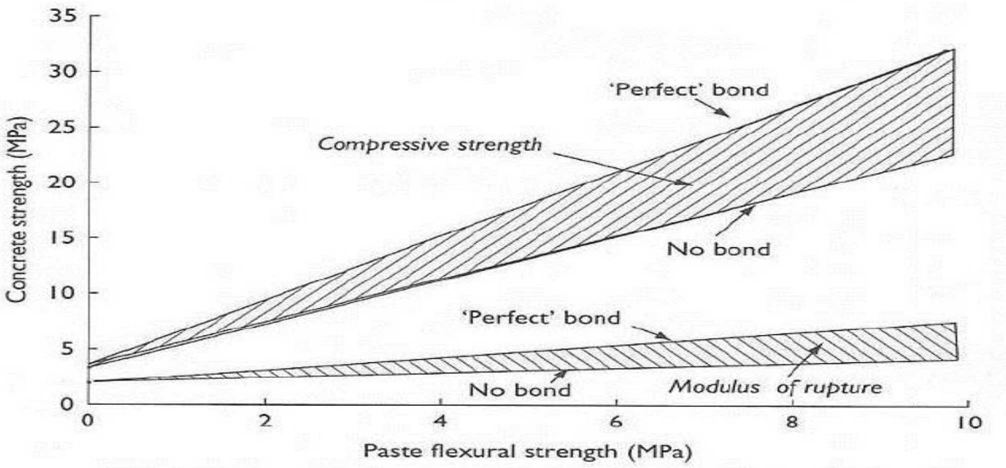

- 1 cm³ of cement ~ 2.14 cm³ of hydration product
- w/c < 0.36, complete hydration not possible

Slide: J. Weiss

# Significance of Grading of Aggregates




## Influence of Paste-Aggregate Bond




Alexander and Mindess

Well-graded aggregates reduce voids and require less paste
Strong aggregate-paste bonding enhances both compressive and flexural strength

Portland Cement Association

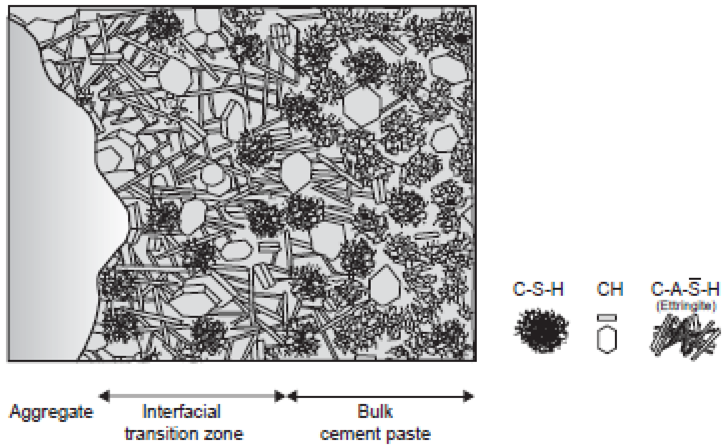
# Harmful Materials in Aggregates

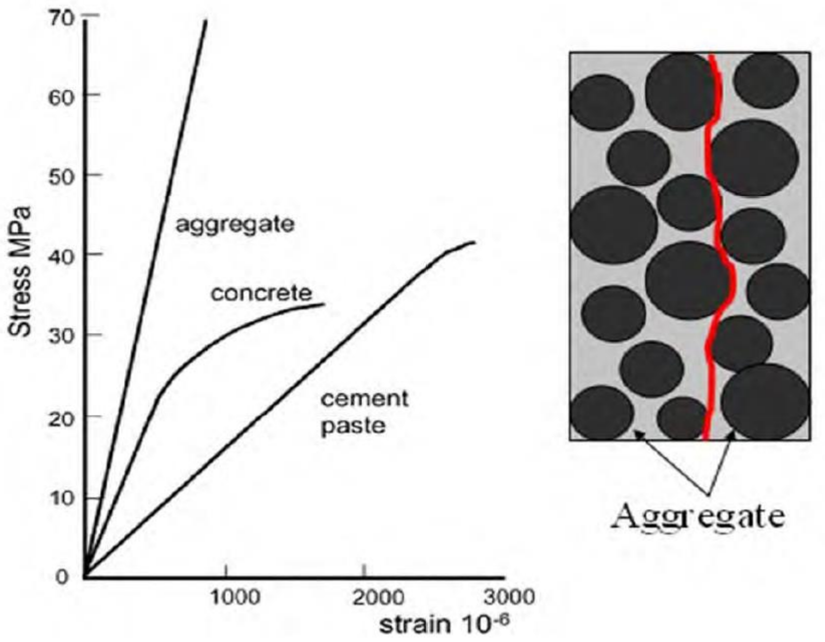
| Substances | Effect on Concrete |
| --- | --- |
| Organic impurities | Affects setting and hardening, may cause deterioration |
| Materials finer than the No. 200 (75 µm) sieve | Affects bond, increase water requirement |
| Coal, lignite, or other lightweight materials | Affects durability, may cause stains and popouts |
| Clay lumps and friable particles | Affects workability and durability, may cause popouts |
| Alkali-reactive aggregates | Causes abnormal expansion, map cracking, and popouts |

# Ponder Over why!

- Concrete components elastic individually, inelastic as concrete
- Concrete:
  - Brittle in tension, tough in compression
  - Higher compressive than tensile strength
- Mortar > Concrete strength
- Concrete is more permeable than cement paste

# Interfacial Transition Zone



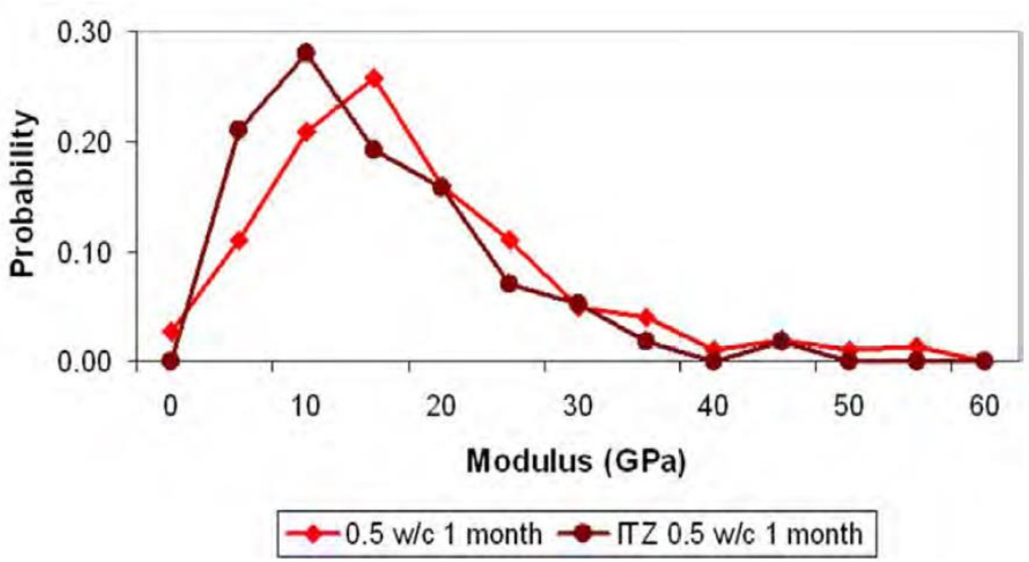




- High w/c closer to the aggregate
- Results in larger **CH, Ettringite crystals**
- Larger **porosity** closer to the aggregates
- Later, **CSH and ettringite** crystals fill voids.

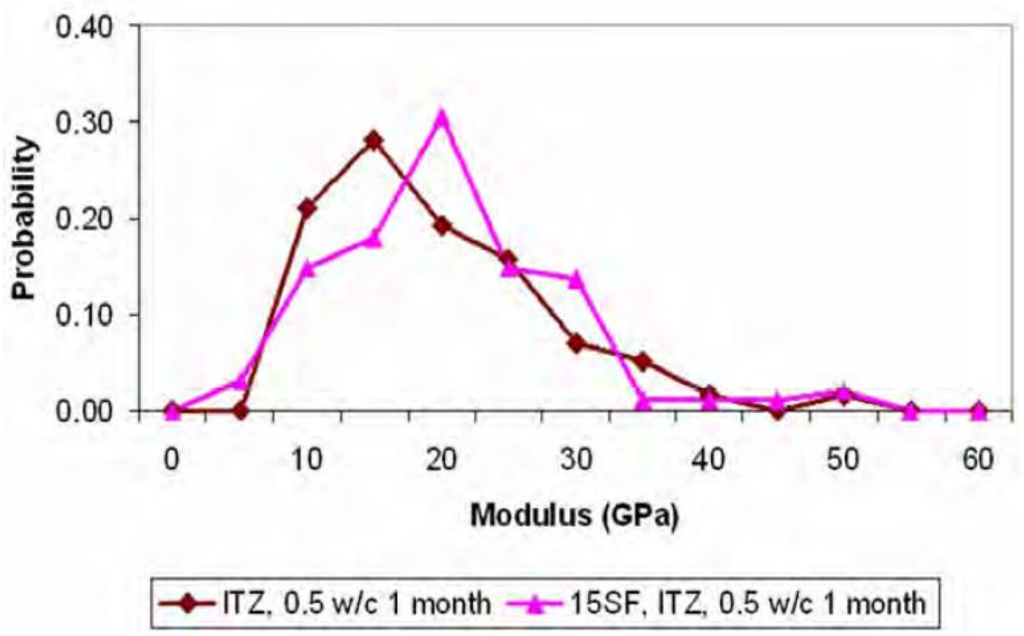
Mehta and Monteiro

# Modulus of ITZ

Lower modulus value of ITZ



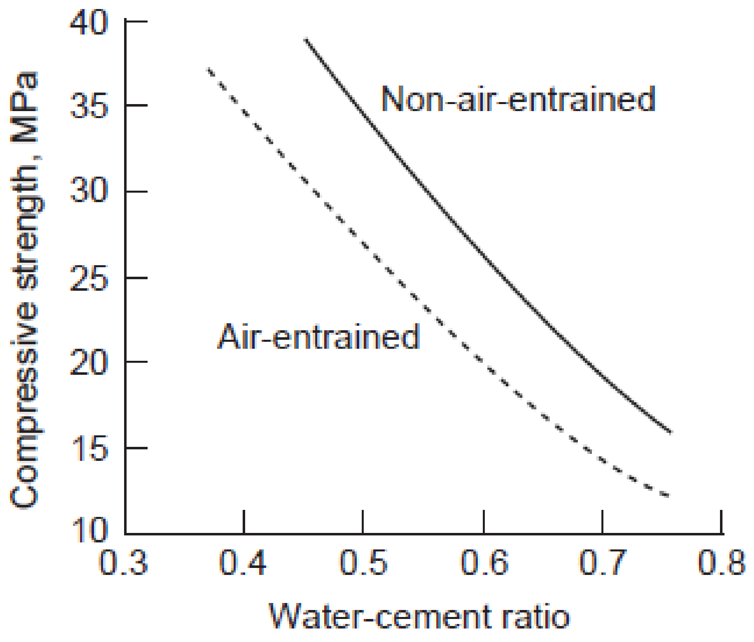

Increased ITZ modulus in presence of SF



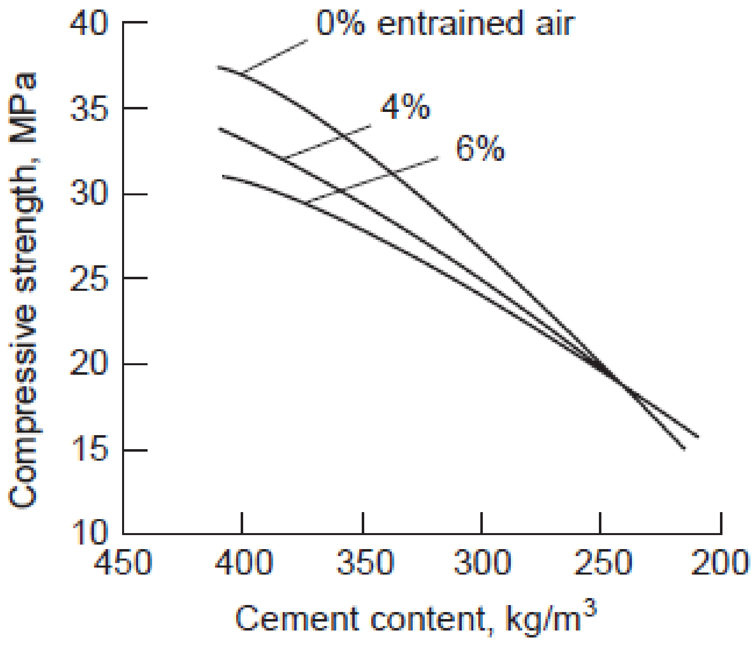

**ITZ can be enhanced with the use of silica fume and other SCMs**

# Factors Affecting Strength of Concrete

**w/c Ratio**




**Cement Content**



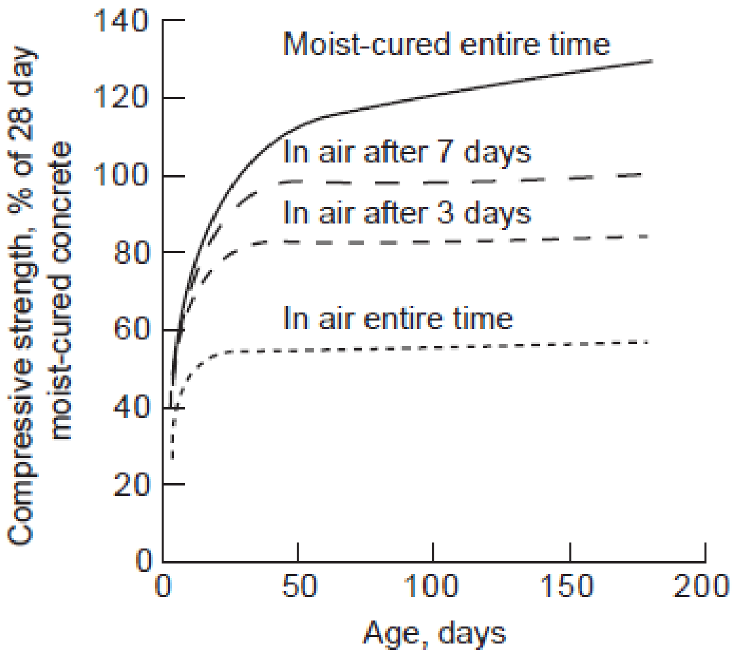

Compressive strength increases as the w/c ratio decreases.

Higher cement content improves compressive strength, while increased air content reduces it.

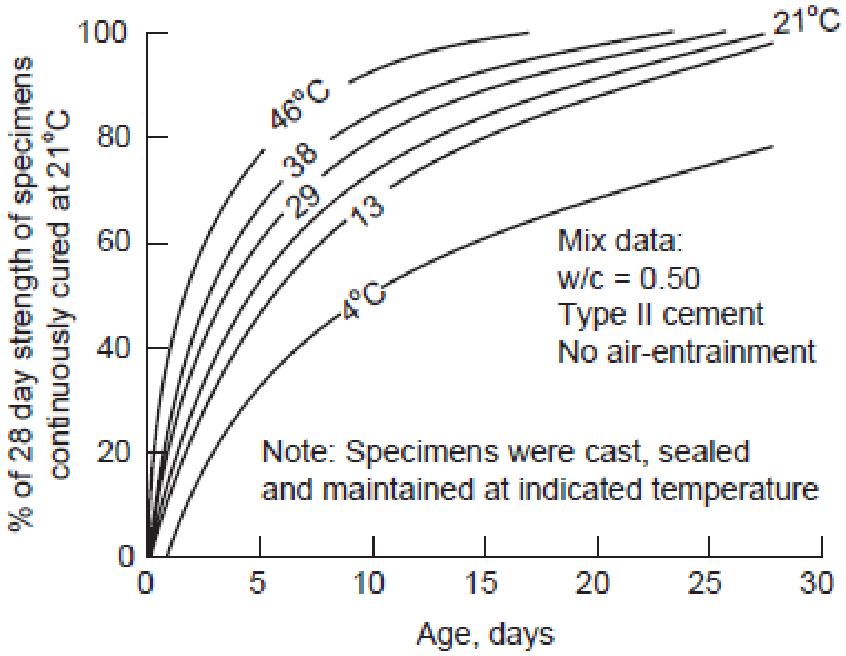
Mehta and Monteiro

# Factors Affecting Strength of Concrete

## Curing



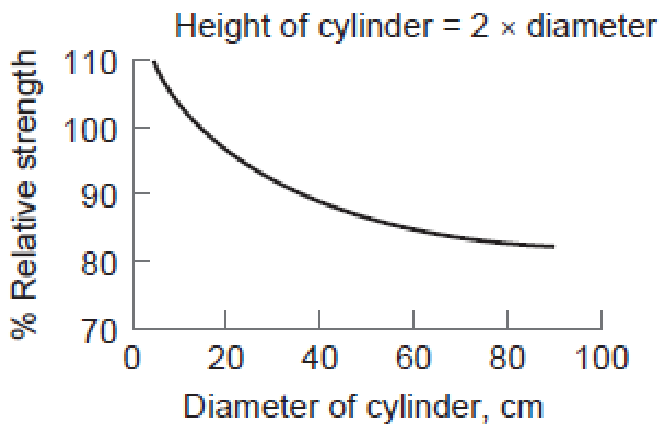

## Temperature

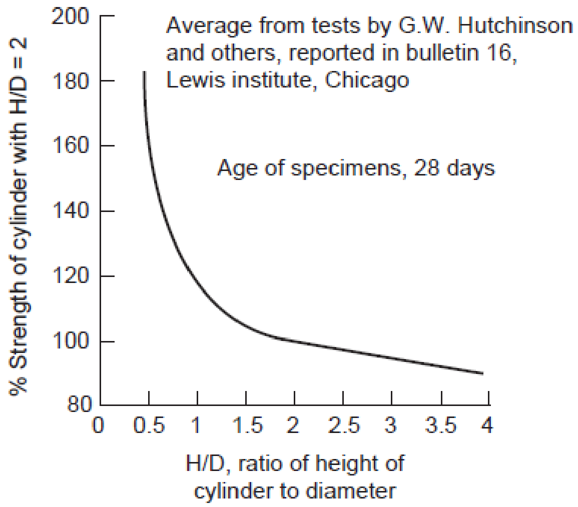


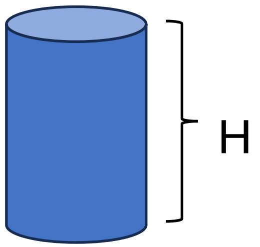

**Moist curing** is critical: Ensures strong and durable concrete. Avoid air curing.

Higher curing temperatures enhances compressive strength initially, however later strength is more or less equal

# Effect of Geometry on Strength



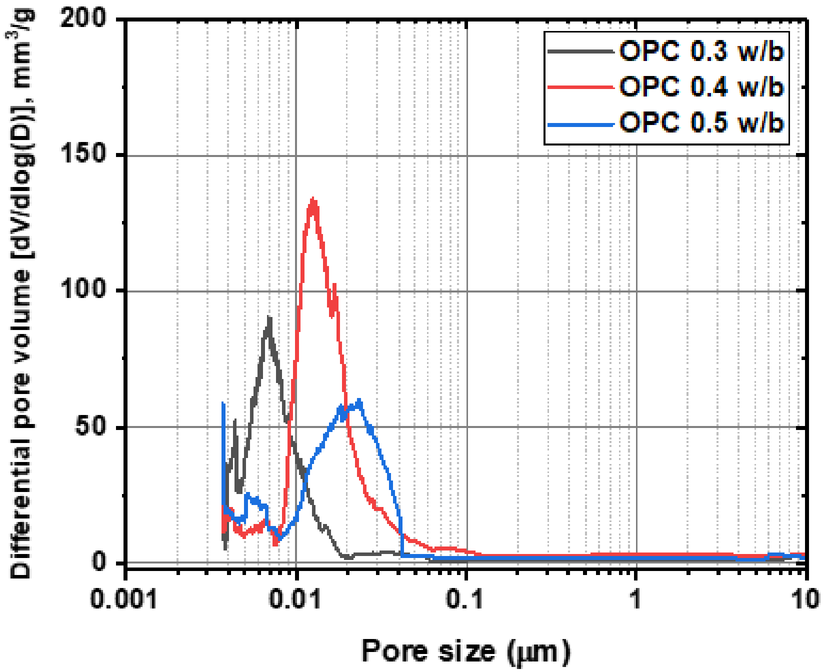




**Specimen geometry significantly influences strength values.**

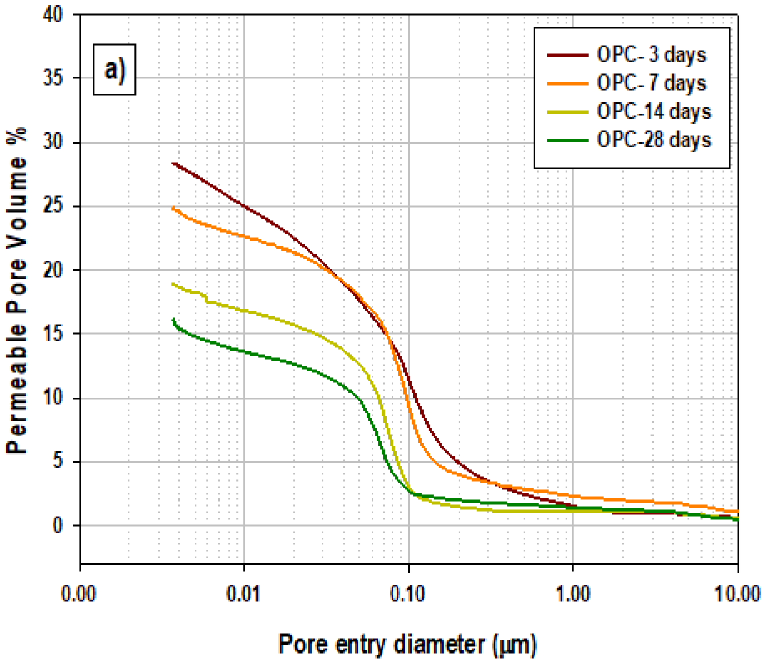
Mehta and Monteiro

# Effect of water-binder ratio and curing period

Effect of water-binder ratio




Effect of curing period

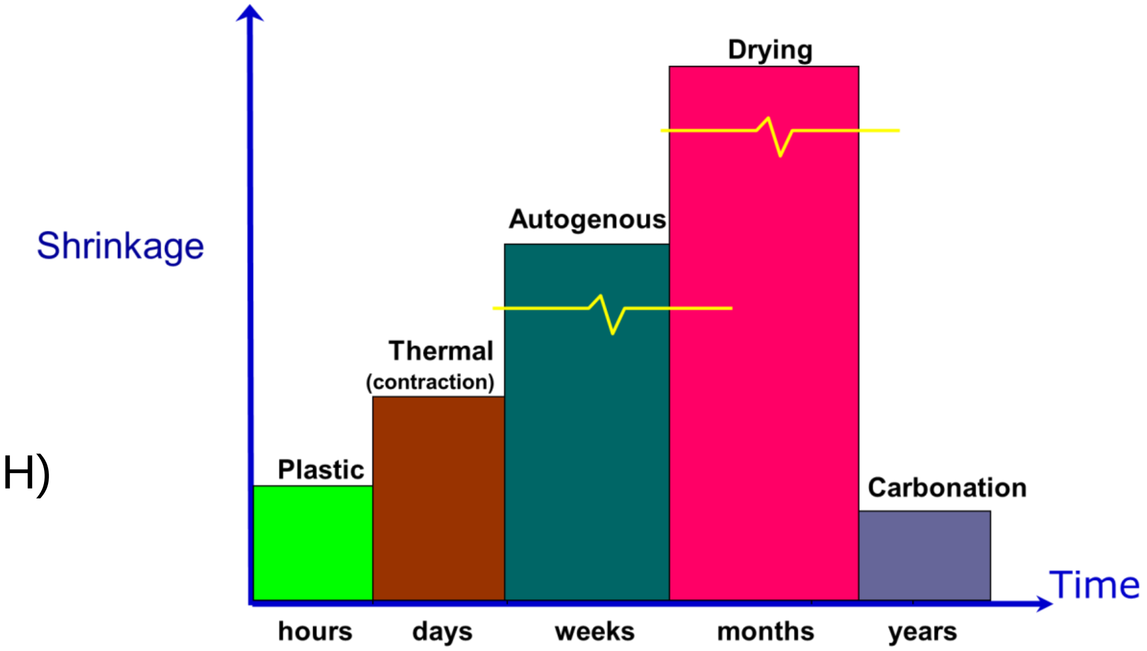



Lower w/b ratio reduces pore size
Increased curing decreases pore volume

Santhanam et al. (ACF, Thailand, 2017), Dhandapani and Santhanam (2017)

# Different Types of Shrinkage on Concrete

- Plastic shrinkage: in fresh concrete while the concrete is plastic
- Autogenous shrinkage: chemical and self-desiccation shrinkage during hydration
- Drying shrinkage in hardened concrete
- Thermal shrinkage: Due to temperature change
- Carbonation shrinkage: When hydrated cement paste (CH) reacts with $CO_2$ to form $CaCO_3$



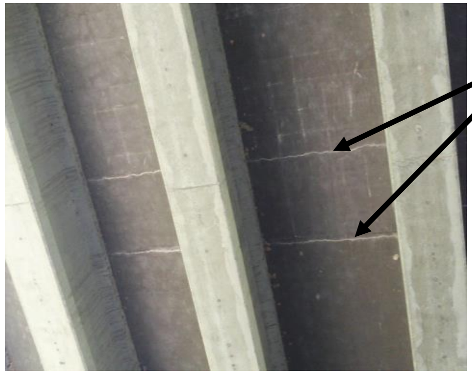
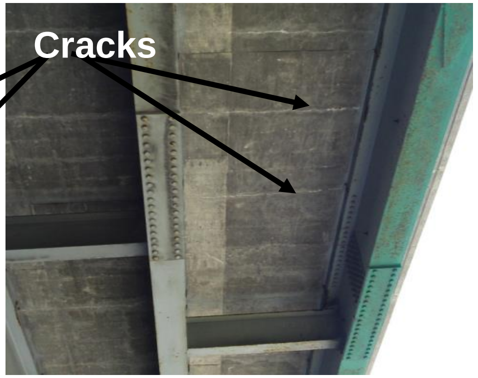

To reduce shrinkage:

- Use of pozzolanic materials and mineral admixtures
- Moisten aggregates
- Curing
- Shrinkage reducing admixtures (SRAs)
- Addition of fibers

# Examples of Shrinkage Cracking



Chennai metro decks (Plastic shrinkage)


Concrete Society, UK

# Types of chemical attack

- Sulphate attack
- Alkali Silica Reaction(ASR)
- Chloride attack
- Carbonation


Hooton, 2009

Mechanism of **sulphate attack**:

$SO_4^{2-}$ (external)→ $SO_4^{2-}$ (internal)

$Ca(OH)_2 + SO_4^{2-} \rightarrow CaSO_4.2H_2O$ (gypsum)

AFm+ $CaSO4.2H_2O \rightarrow$ AFt (Ettringite) expansive

Protection against sulphate attack

- Use of low $C_3A$ cements
- Use of high alumina cement
- Use of supersulphated cement
- Use of pozzolanic materials and mineral admixtures
- Low w/c and good impermeability

Photos courtesy Prof. P. Paramasivam

# Carbonation

- **$CO_2$ Diffusion** in Concrete: Reacts with calcium hydroxide, reducing pH
- **pH Reduction**: **Destroys** the protective **passivity** of reinforcing steel.

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

For Carbonation to take place:

**40–80% RH**

**Moisture**

# Alkali-Silica Reaction (ASR)

Alkalis
+
Reactive Silica
+
Moisture

⇨ ASR Gel which expands ⇨ Concrete cracking

AASHTO Innovative Highway Technologies

Concrete Pavement

Bridge element

**To mitigate ASR**

- Use of **low alkali cement** (< 0.6% equivalent $Na_2O$)
- Preventing **access of moisture**
- Use of **mineral admixtures** such as silica fume

# Limestone Clacined Clay Cement (LC3)

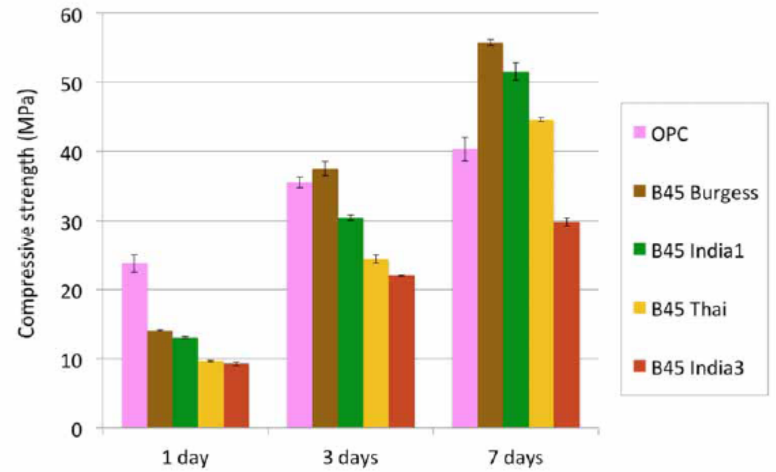
Metakaolin "MK" plus limestone

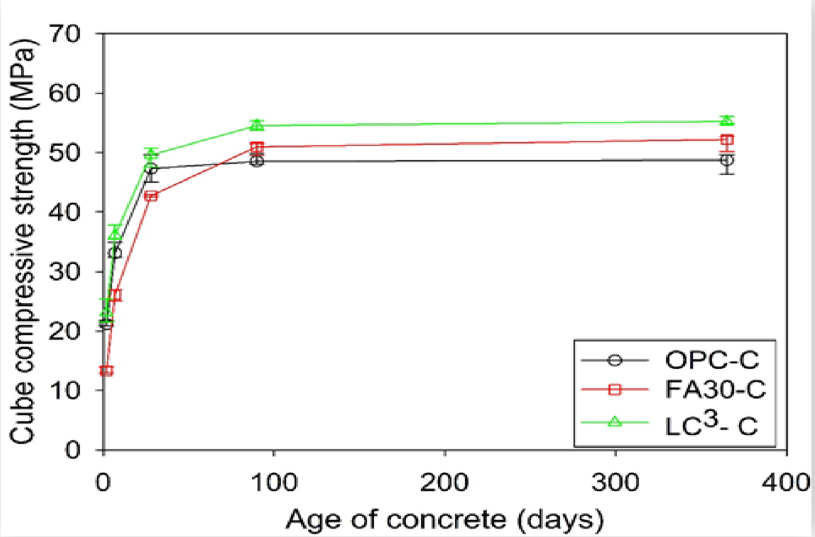
- $(Al_2O_3) : 2{\cdot}(SiO_2)$ + $CaCO_3$

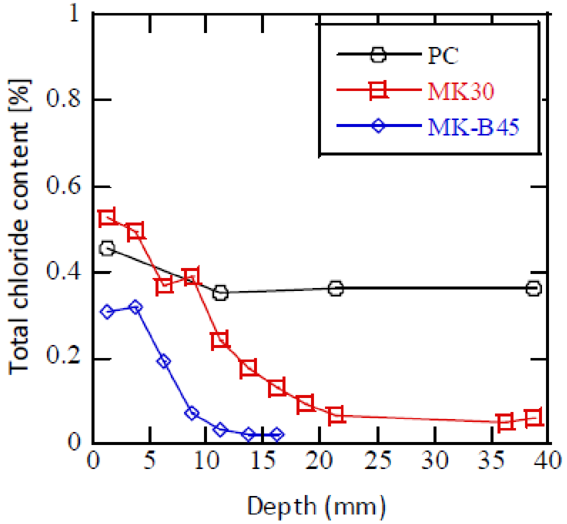
Formation of monocarbo aluminate "Mc" (AFm)

- $Al_2O_3 + CaCO_3 + Ca^{2+} + OH^{-} \Rightarrow C_4A\underline{C}H_{11}$

| | Burgess | India1 | Thai | India3 |
|---|---|---|---|---|
| Kaolinite content (%) | 95 | 80 | 50 | 20 |

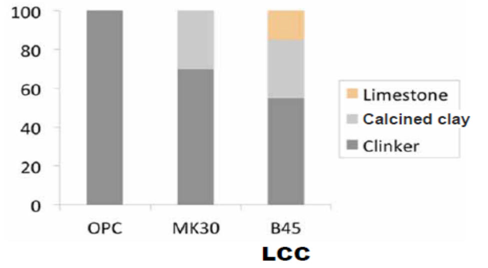



LC3 – Strength performance

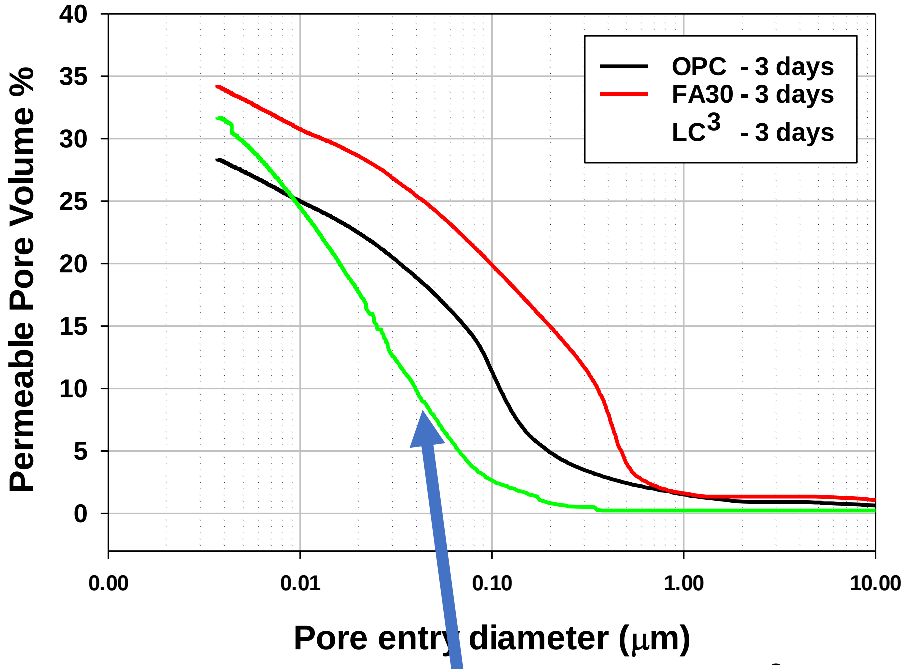
LC3 – Durability performance

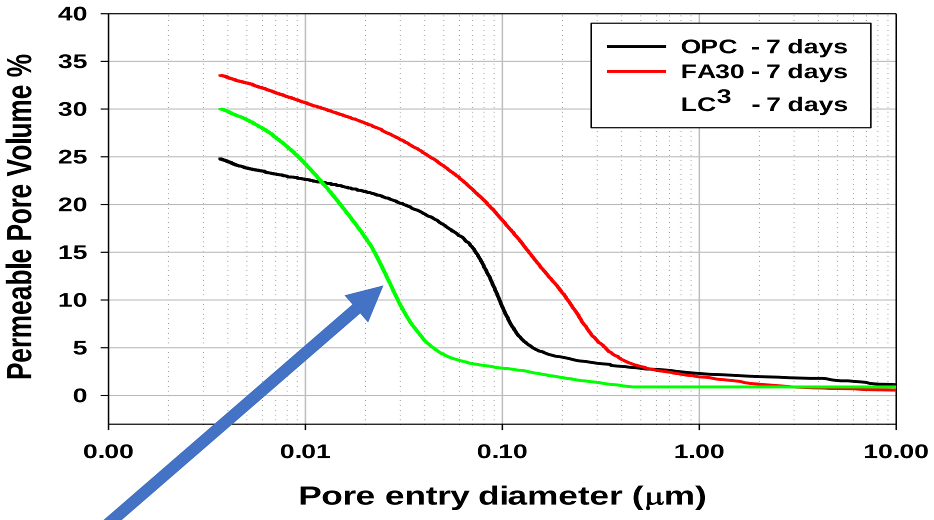


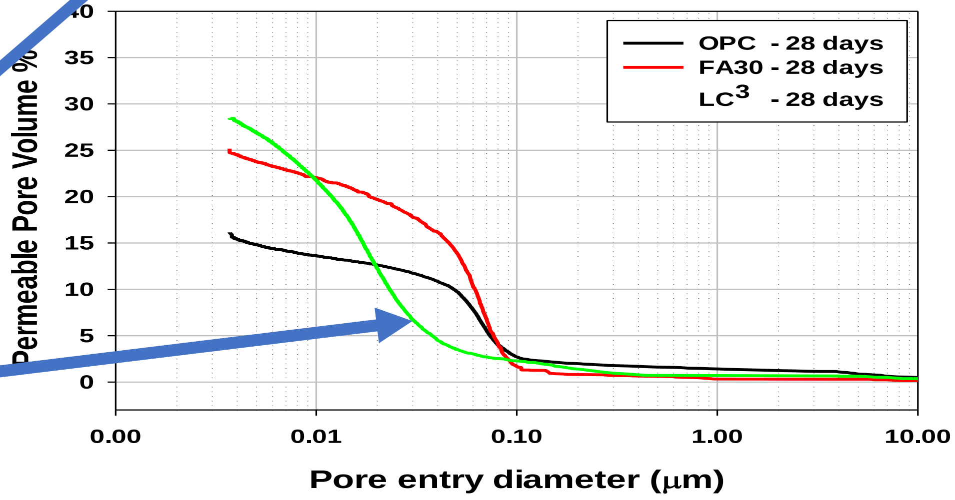

LC3 concrete shows better strength development than OPC and FA30

Research results from EPFL Switzerland and UCLV Cuba

# Refinement of pore structure in LC3

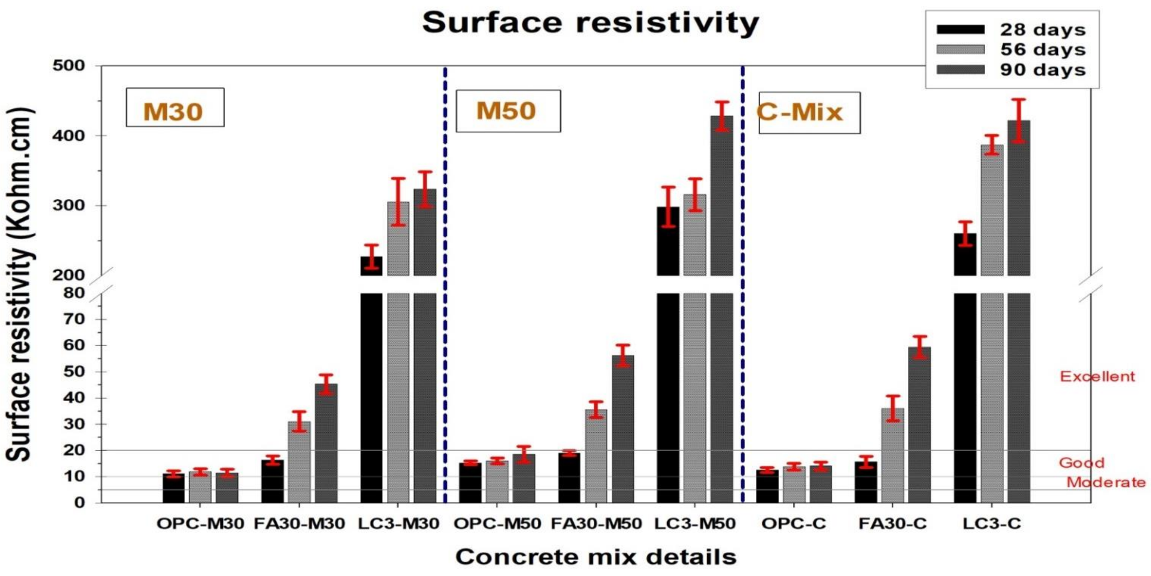


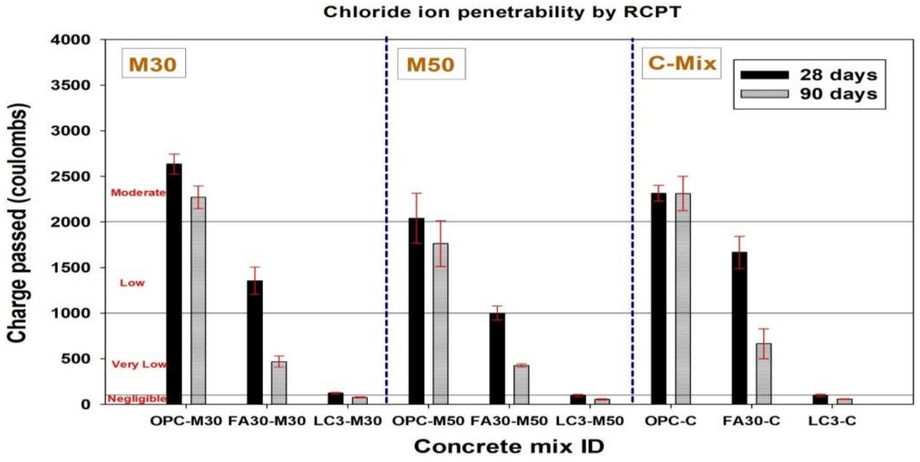



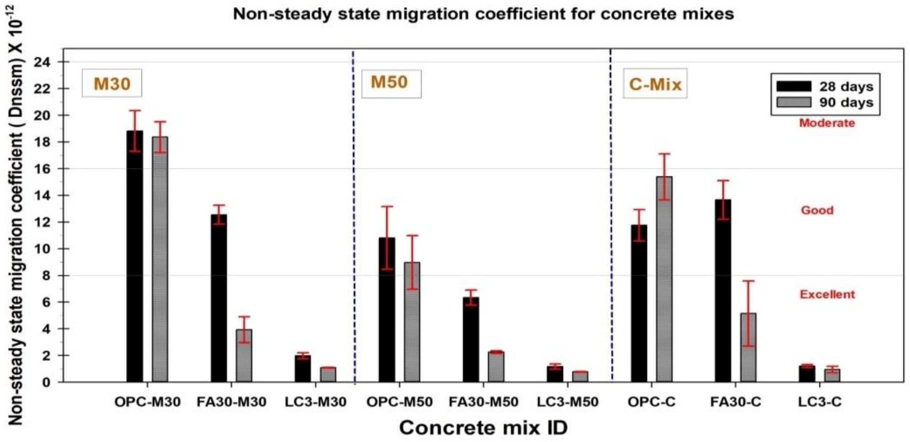




- Highly refined pore structure early up.
- Fly ash blend accelerates by 28 days

# Durability performance




- Measured on saturated Cylindrical sample of 100 mm dia and 200 mm height
- Very high resistivity value in all the LC3 mixes – potentially better resistance to corrosion propagation
- Excellent resistance to chloride penetration by combined transport mechanisms

# Performance vs Prescriptive Specifications

**Performance:**

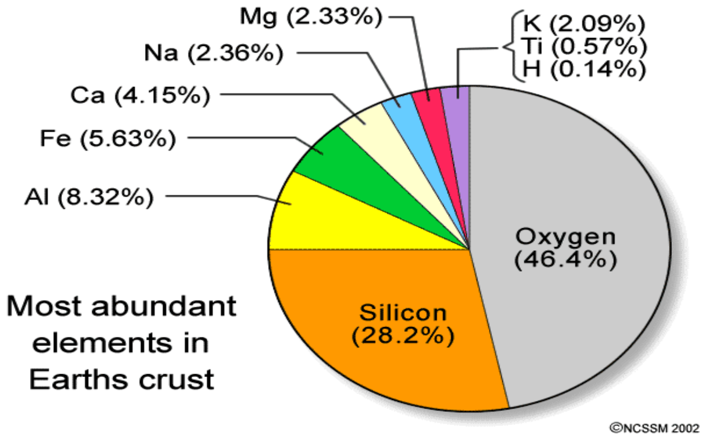
- Compressive or tensile strength
- Cover depth
- Max. shrinkage
- Permeability

**Prescriptive:**

- Curing duration and method
- Minimum cement content
- Binder type
- Max. w/c ratio

# Conclusions – is there a future without cement?

- Very few alternatives – none of them have long term potential
- Cement – possibly optimized combination of elements on the earth's crust
- Way forward – maximize the **use of blended cements**; improve concreting practices; adopt performance-based specifications
- Use of **SCMs**
- **Chemical admixtures** incorporation
- **Reduce w/c ratio** for better strength and durability
- Proper **Curing**



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