By: Dr. Shamshad Ahmad

LECTURE NO. 7 & 8

SETTING OF CEMENT AND MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Objectives:

- To explain the setting of a cement
- To explain the factors affecting setting of cement
- To explain the properties of the major hydration products
- To explain the different components of the microstructure of a hydrated cement paste
  - C-S-H
  - CH
  - Calcium sulfoaluminates
  - Minor components
  - Porosity

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SETTING OF CEMENT

- ***Setting* is the term used to describe the *stiffening of the cement paste***
- **Setting is also refereed as the *change of the cement paste from a fluid to a rigid state***
- **Although, during setting, the paste acquires some strength, for practical purposes it is important to *distinguish setting from hardening***
- ***Hardening* refers to the *gain of strength of a set cement paste***
- **Since the flash setting of C_3A is prevented by addition of gypsum, C_3S sets first**
- **Initial, final, and false settings of cement have already been defined in a previous lecture**

FACTORS AFFECTING SETTING OF CEMENT

Effect of cement composition:

- **Setting time is affected by the percentages of C_3S, C_3A, and gypsum in the cement**
- **In case of low or no gypsum, even a lower percentage of C_3A may cause flash set reducing setting time**
- **In case of adequate amount of gypsum, even a high percentage of C_3A may not cause flash set and thereby may not affect the setting time. In this case percentage of C_3S controls the setting time.**

FACTORS AFFECTING SETTING OF CEMENT

Effect of fineness of cement:

- **With increase in fineness the surface area per unit mass of cement increases.**
- **Since hydration starts at the surface of the particles, it is the total surface area of cement that affects the rate of hydration and therefore the setting time**
- **Therefore, the setting time decreases with increase in the fineness**
- **Since increase in the fineness increases reactivity of C_3A, the amount of gypsum is required to be increased for cements with higher fineness**

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FACTORS AFFECTING SETTING OF CEMENT

Effect of fineness of cement:

Following are the other properties of cement paste affected by the fineness of cement:

- **Increase in fineness helps in rapid development of strength and reducing bleeding**

- **Finer cement leads to a stronger reaction with alkali-reactive aggregate and increases the chances of shrinkage and cracking of the cement paste**

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FACTORS AFFECTING SETTING OF CEMENT

Effect of temperature:

- **Setting time is more at low temperatures**
- **Setting time decreases with a rise in temperature, but above about 30°C, a reverse effect may be observed**

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PROPERTIES OF THE HYDRATION PRODUCTS

Summary of Properties of the Hydration Products of Portland Cement Compounds

Compound	*Specific Gravity*	*Crystallinity*	*Morphology in Pastes*	*Typical Crystal Dimensions in Pastes*	*Resolved by*[a]
C–S–H	2.3–2.6[b]	Very poor	Spines; Unresolved morphology	1 × 0.1 μm (Less than 0.01 μm thick)	SEM, TEM
CH	2.24	Very good	Nonporous striated material	0.01–0.1 mm	OM, SEM
Ettringite	~1.75	Good	Long slender prismatic needles	10 × 0.5 μm	OM, SEM
Monosulfo-aluminate	1.95	Fair–good	Thin hexagonal plates; irregular "rosettes"	1 × 1 × 0.1 μm	SEM

[a]OM, optical microscopy; SEM, scanning electron microscopy; TEM, transmission electron microscopy.
[b]Depends on water content.

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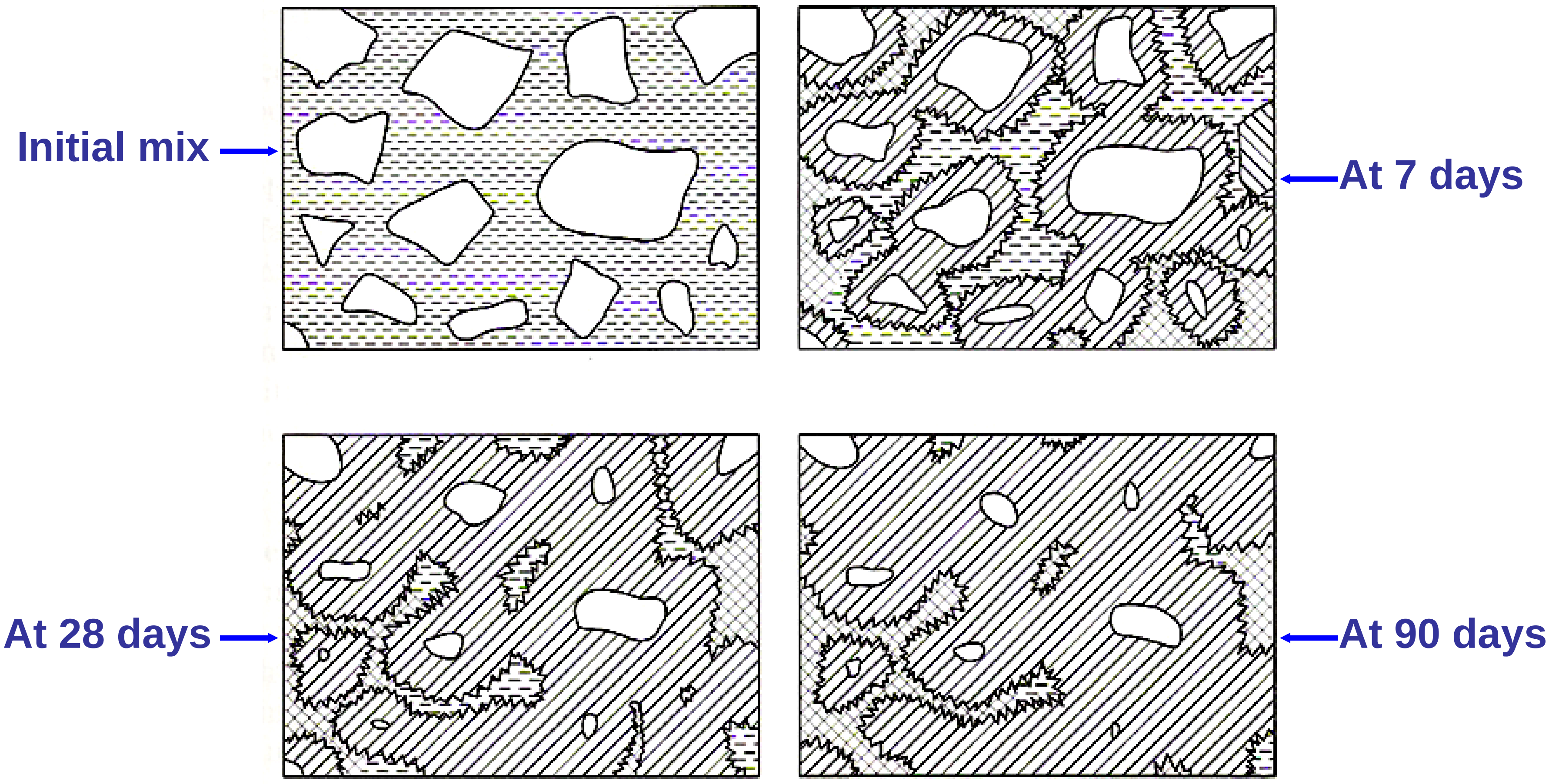
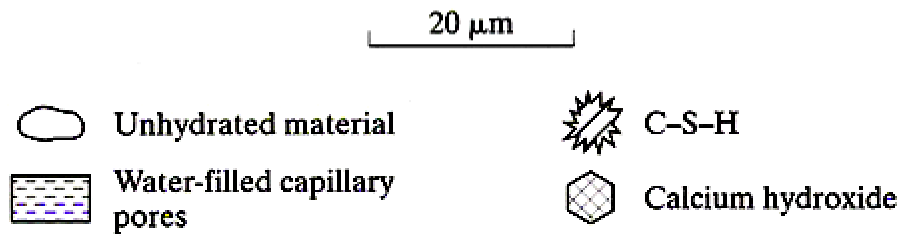
MICROSTRUCTURE OF HYDRATED CEMENT PASTES



Changes in microstructure of cement paste with progress of hydration



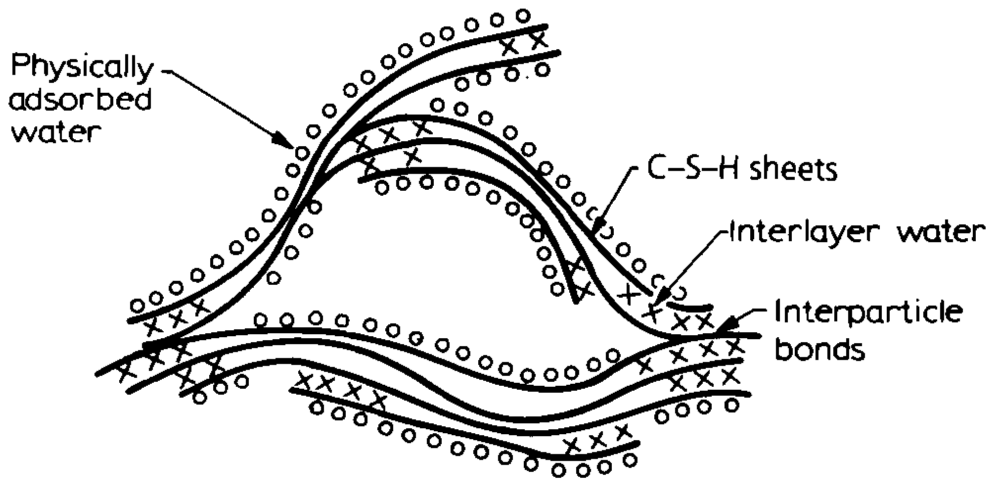
MICROSTRUCTURE OF HYDRATED CEMENT PASTES

- **As shown in the previous slide, *microstructure* of cement paste is formed in *sequence* as hydration proceeds**
- **The formation of microstructure involves the *replacement of water* confined between cement particles in the fluid paste *with solid hydration products* that form a continuous matrix and *bind the residual cement grains together* over a period of time**
- **The formation of the continuous solid matrix happens because the hydration products ($\rho \approx 2.3$) occupy a greater volume than the original cement compounds ($\rho = 3.2$)**

COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

C-S-H

- **C-S-H constitutes *about 50% to 67% of the volume of the hydrated paste* and must therefore dominate its behavior**
- **During early hydration, C-S-H grows out from the cement particle surface into surrounding water-filled space in the form of low-density arrangement of thin sheets (termed as early or "outer" product), as shown in below**

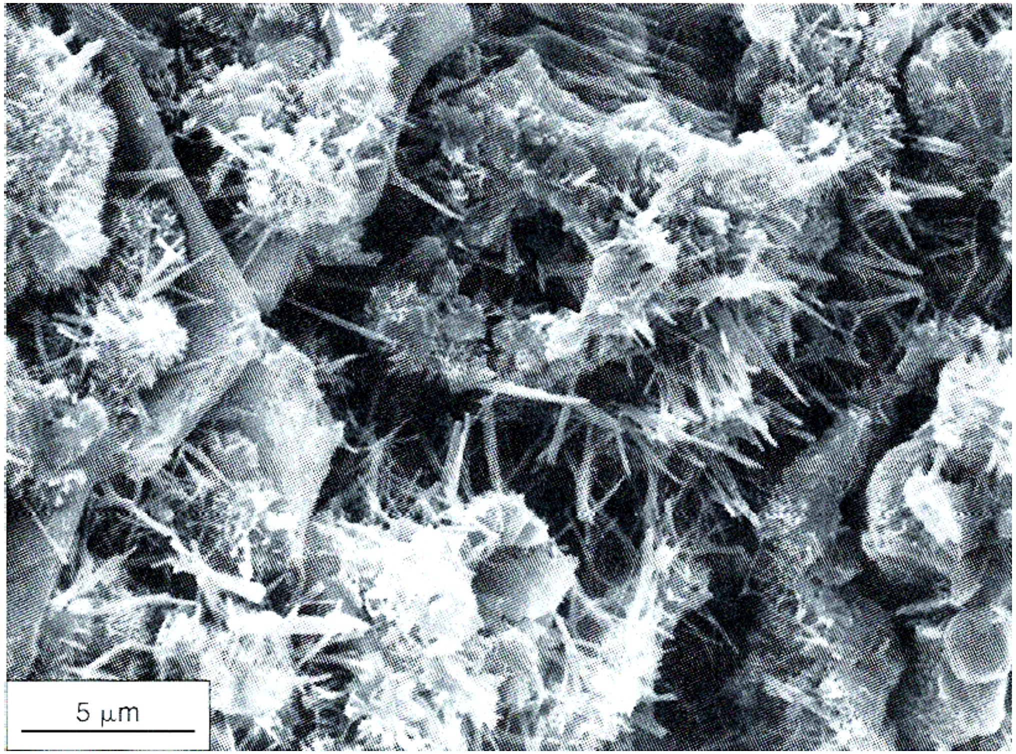


Probable structure of hydrated silicates

COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

C-S-H

- **The *morphology (i.e., forms and structures) of C-S-H* product obtained during early hydration (termed as early or "outer product) is shown in the following figure:**



SEM micrograph showing morphology of C-S-H formed during early hydration

- **As shown, this form of early or outer C-S-H product has a higher microporosity and on drying rearranges to a variety of morphological forms and coarser porosity**
- **This C-S-H also contains a high level of impurities (aluminum, sulfate, alkalis)**

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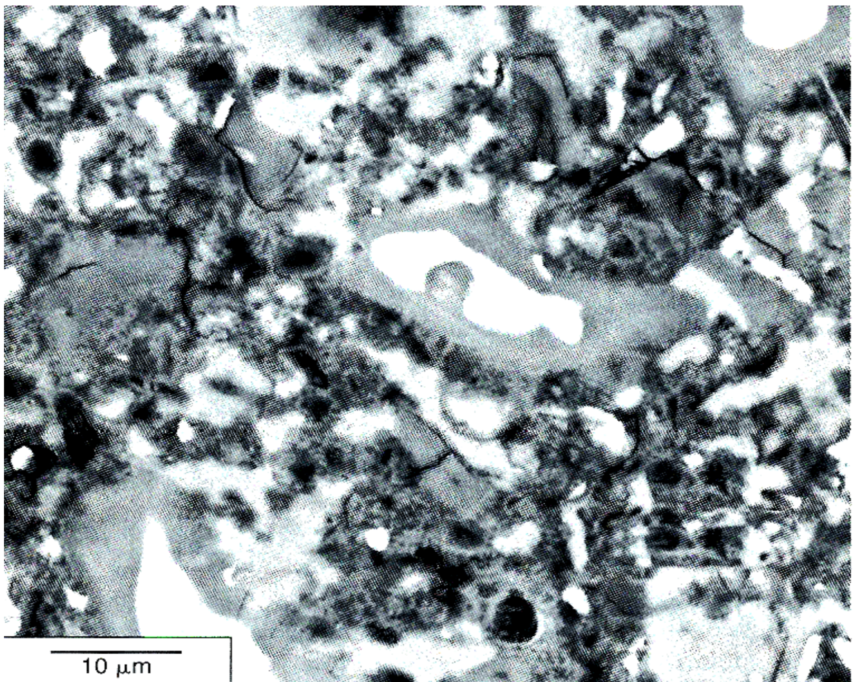
COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

C-S-H

- **Once hydration has become diffusion controlled, C-S-H forms primarily as a denser coating around the hydrating cement grains, termed as late or "inner" product**
- **The *morphology (i.e., forms and structures) of C-S-H* product obtained during late hydration is shown in the following figure:**



SEM micrograph showing morphology of C-S-H formed during late hydration

- **As shown, coatings of cement grains by late or outer C-S-H product form the diffusion barrier and thicken with time, growing inwards as well as outwards**
- **The coatings maintain the shape of the original grains and surround unhydrated residues**

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COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

CH

- **CH crystals *occupy about 20 to 25% of the hydrated paste volume***
- **CH only *grows where free space* is available**
- **CH *morphology may vary*, being found as small equidimensional crystals; large flat, platy crystals, large thin, elongated crystals; and all variations in between**
- **CH morphology is particularly affected by admixtures and by the temperature of hydration**
- **The *morphologies(i.e. forms and structures) of CH* are shown in the following figures**

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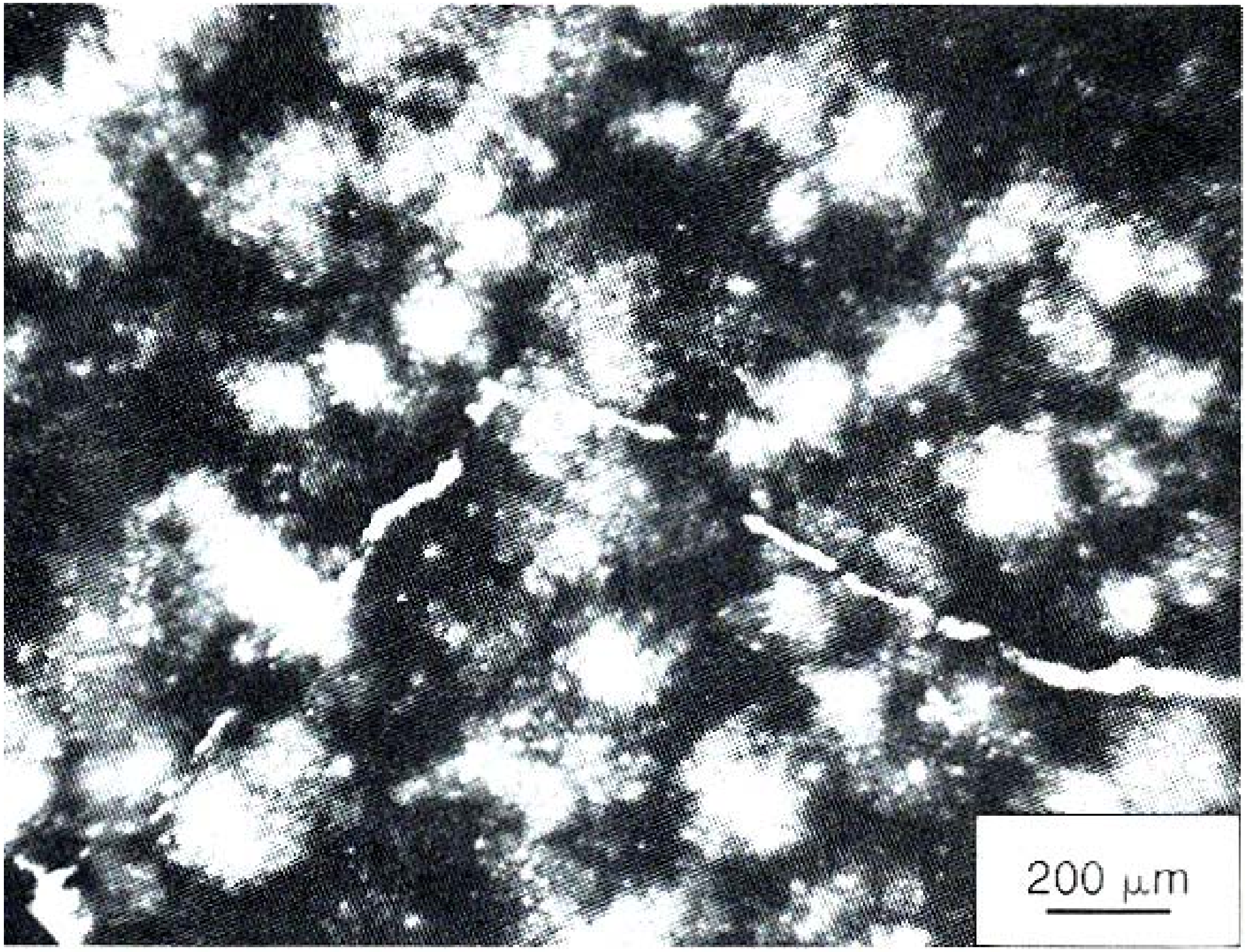
COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

CH



Optical micrograph of CH after 7 days hydration

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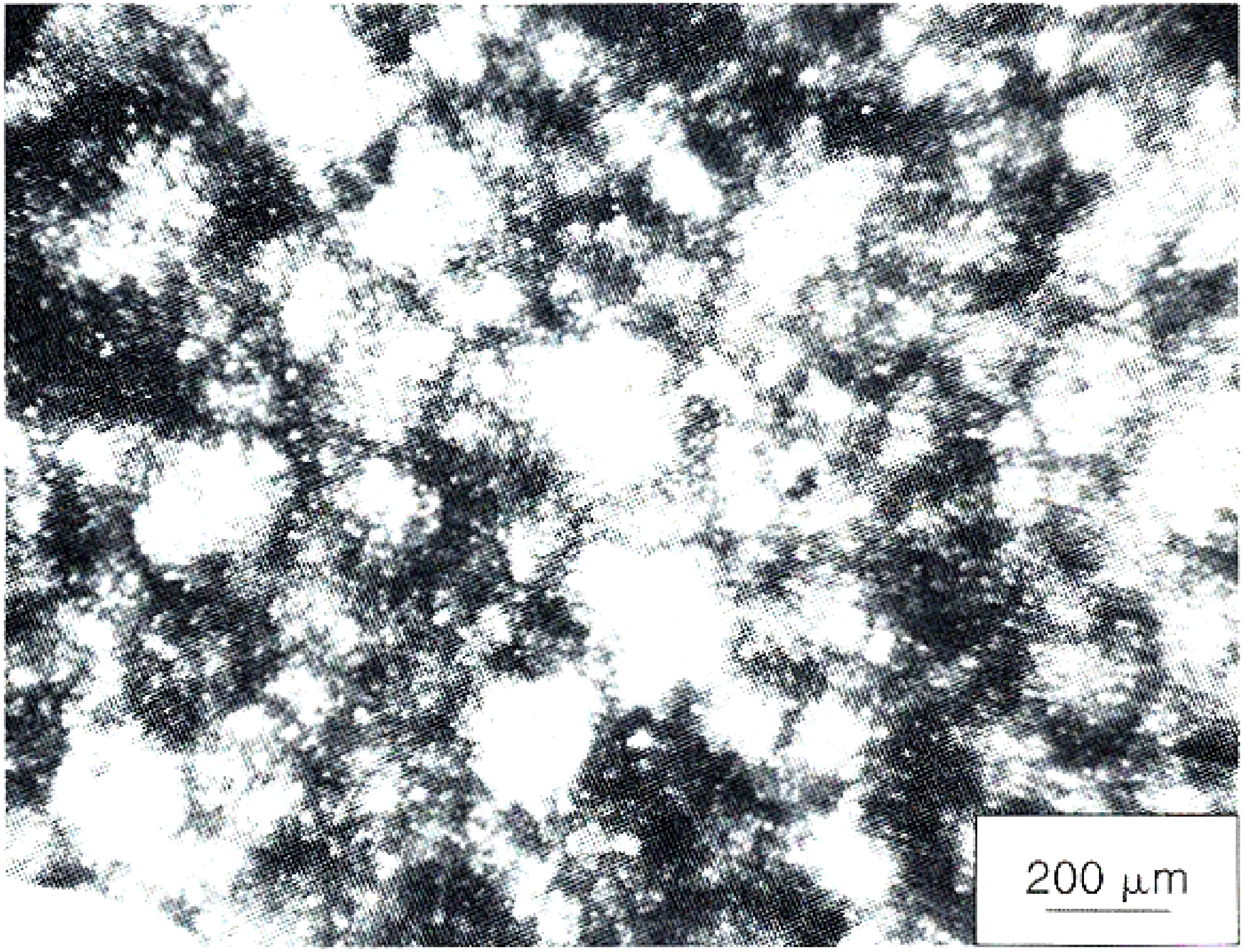
COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

CH



Optical micrograph of CH after 15 days hydration

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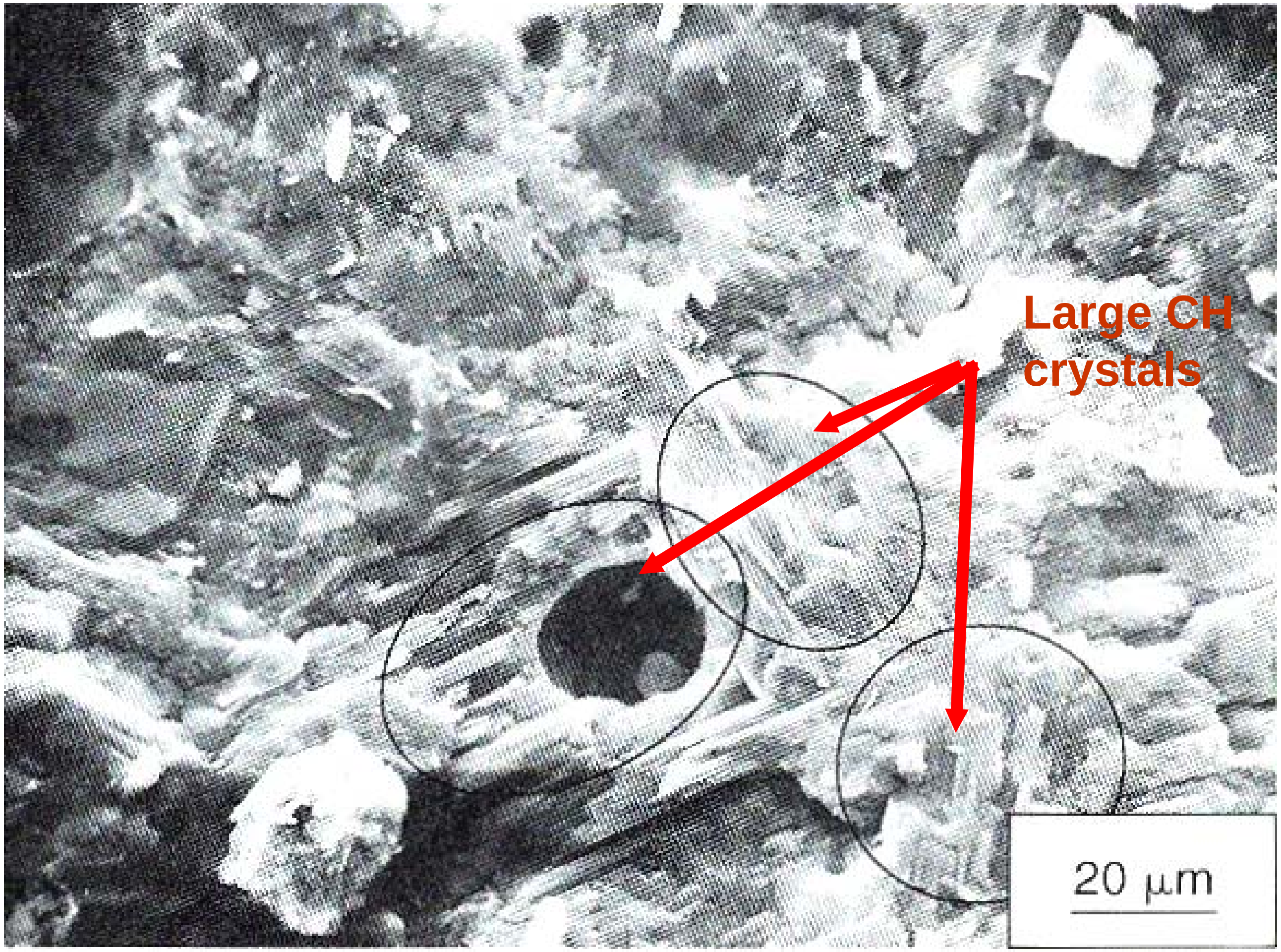
COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

CH



SEM micrograph of CH after 64 days hydration

COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Calcium Sulfoaluminates

- **As mentioned earlier,**
  - **the primary calcium sulfoaluminate (simply called as ettringite) is formed as a result of reaction between C_3A and sulfate ions supplied by dissolution of gypsum**
  - **The secondary calcium sulfoaluminate (simply called as monosulfoaluminate) is formed as a result of reaction between C_3A and ettringite after sulfate is all consumed**
- **The calcium sulfoaluminates are *a relatively minor constituent* of a mature paste, making up about *10 to 15% by volume***
- **Because of their *less amount they play minor role* in the microstructure of the hydrated cement paste and are therefore omitted from figure showing the microstructure**
- **SEM micrographs of calcium sulfoaluminates are shown as follows:**

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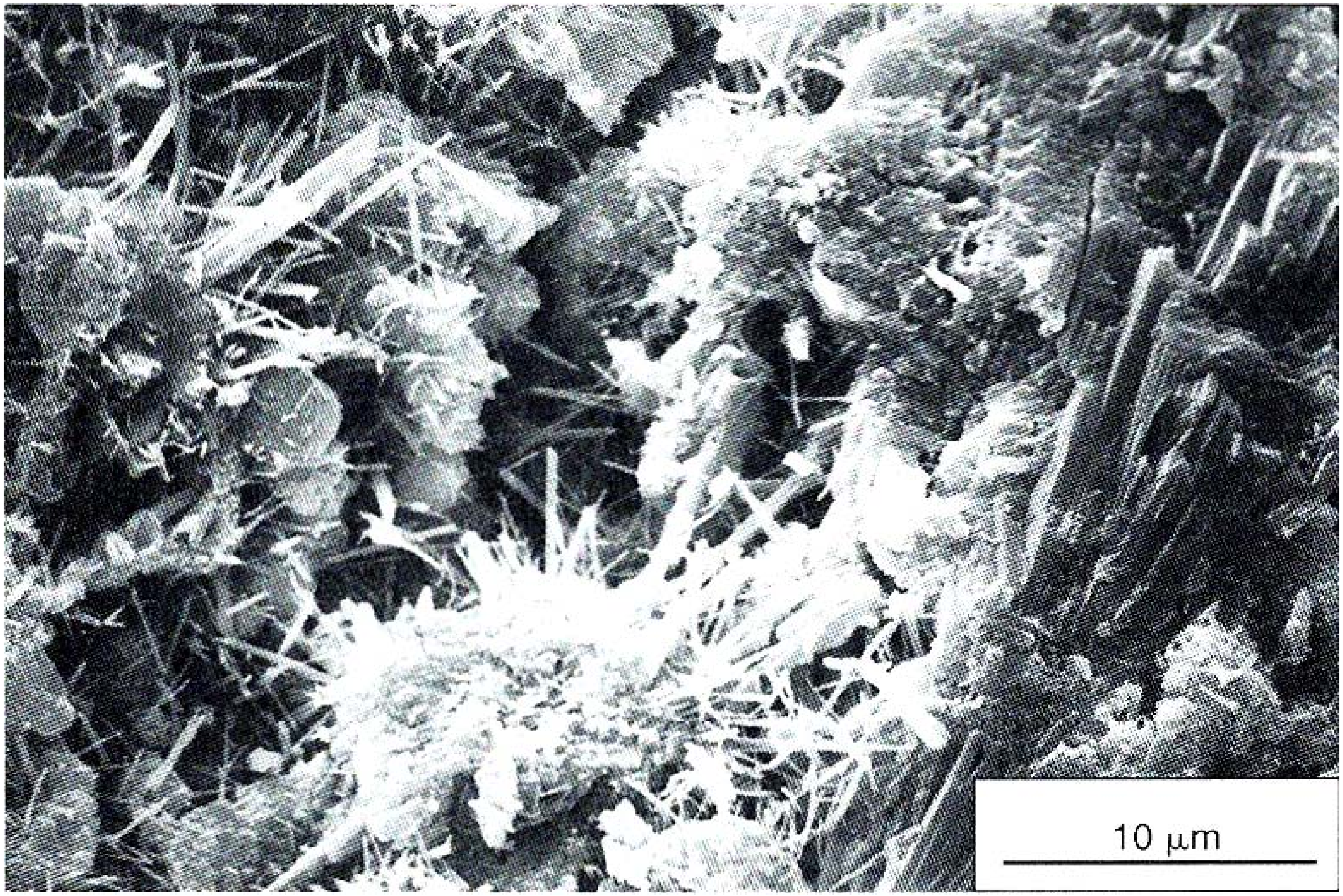
COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Calcium Sulfoaluminates



SEM micrograph of primary calcium sulfoaluminate (ettringite)

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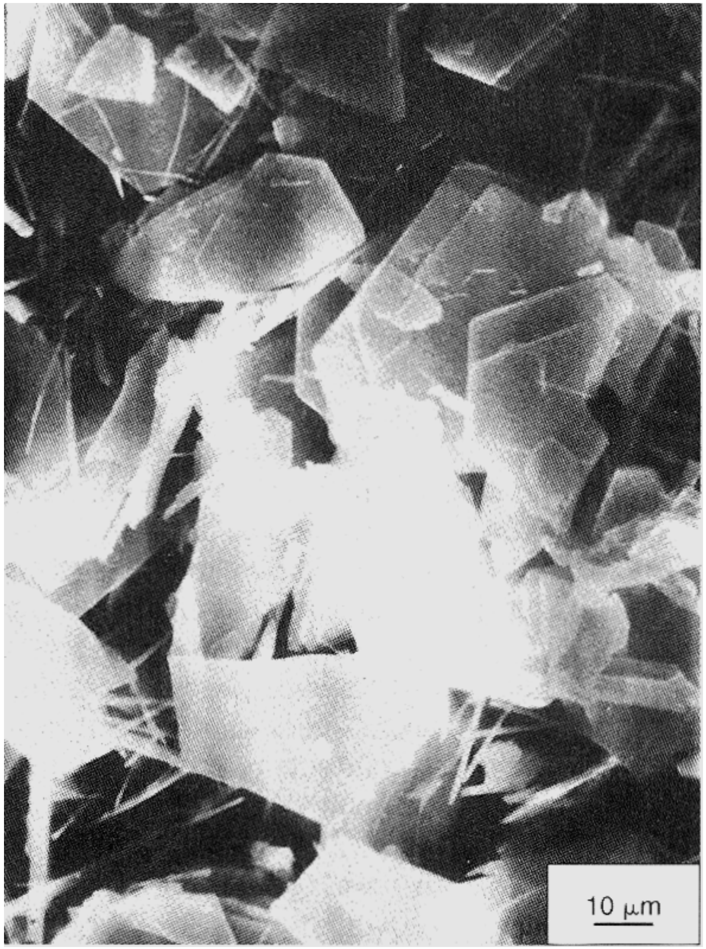
COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Calcium Sulfoaluminates



SEM micrograph of secondary calcium sulfoaluminate (monosulfoaluminate)

COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Minor Compounds

- ***Unhydrated residues*** **of the cement grains and *small amounts of magnesium hydroxide* are the minor components of the microstructure of a hydrated paste**

- **These components are *not likely to amount more than 5% by volume* in mature pates**

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COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Porosity

- **Porosity is the *another major component* of the microstructure**
- **Porosity (pores and their-size distribution) of the microstructure of a hydrated cement paste is *found to significantly affect the physical properties of paste***
- **Pores in a hydrated paste are classified into following two types:**
  i. ***Capillary pores* are the *remnants of water-filled space* that exists between the partially hydrated cement grains**
  ii. ***Gel pores* can be regarded as a *part of the C-S-H.* Gel pores are included in the volume occupied by C-S-H**

Capillary pores and gel pores are shown in the next slide

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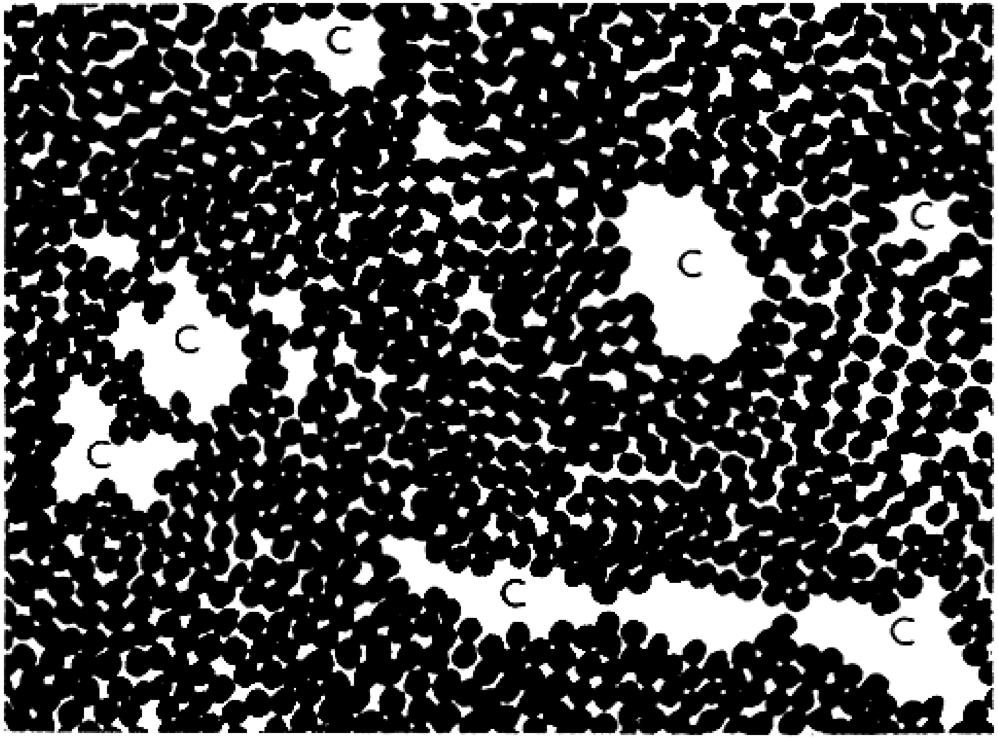
COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Porosity



Simplified model of paste structure.

- Solid dots represent gel particles;
- Interstitial spaces are gel pores;
- Spaces such as those marked C are capillary pores.

Size of gel pores is exaggerated

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COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Porosity

Classification of Pore Sizes in Hydrated Cement Pastes

Designation	Diameter	Description	Role of Water	Paste Properties Affected
Capillary pores	10–0.05 μm (50 nm)	Large capillaries	Behaves as bulk water	Strength; permeability
	50 ~10 nm	Medium capillaries	Moderate surface tension forces generated	Strength; permeability; shrinkage at high humidities
Gel pores	10–2.5 nm	Small (gel) capillaries	Strong surface tension forces generated	Shrinkage to 50% RH
	2.5~0.5 nm	Micropores	Strongly adsorbed water; no menisci form	Shrinkage; creep
	<~0.5 nm	Micropores "interlayer"	Structural water involved in bonding	Shrinkage; creep

COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Porosity

There are two main *methods* that are used *to measure the pore-size distribution* of hardened cement paste:

a. Mercury intrusion porosimetry, MIP, *(gives a better measure of capillary porosity)*

b. Physical adsorption of gases *(gives a better measure of gel porosity)*

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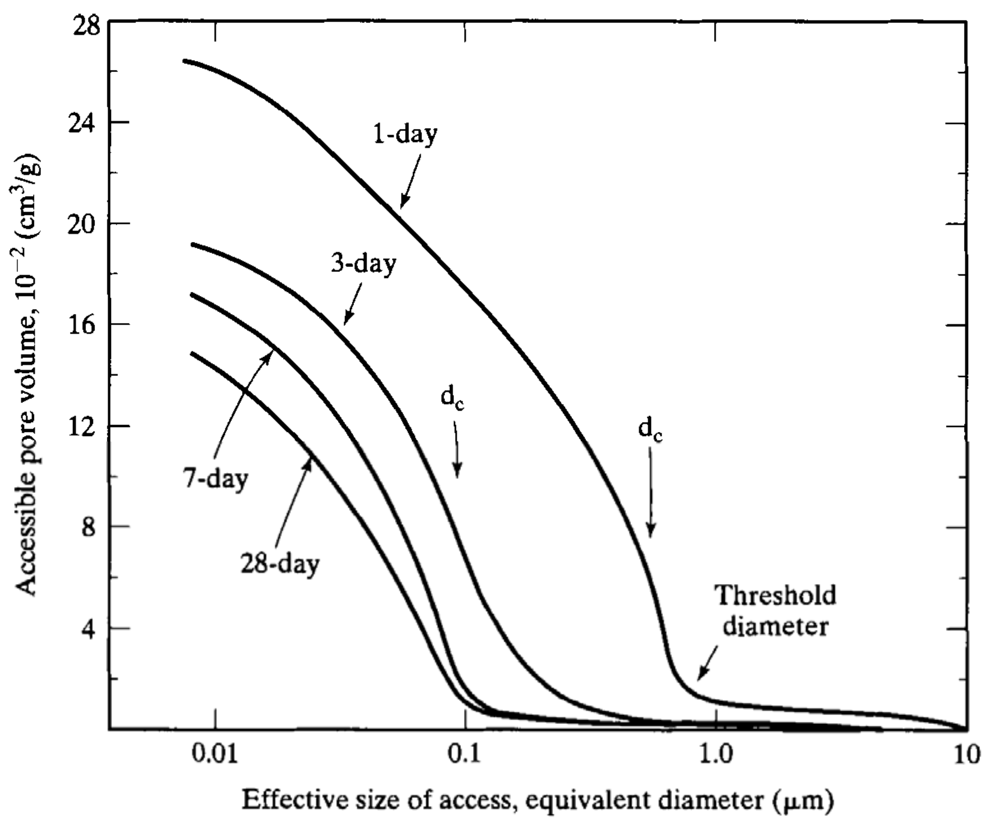
COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Porosity

MIP:

- MIP involves forcing mercury into the pore system of the paste by the application of external pressure.
- The pressure required is inversely proportional to the pore radius
- MIP curves, as shown in the following figure, may be obtained for hydrated cement pastes



Mercury intrusion porosimetry curves for portland cement pastes.

The above MIP curves are very useful for permeability and shrinkage at high humidities

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COMPONENTS OF THE MICROSTRUCTURE OF HYDRATED CEMENT PASTE

Self -desiccation

- Because most of the products of hydration are colloidal during hydration, the surface area of the solid phase increases enormously, and a large amount of free water becomes adsorbed on this surface
- If no water movement to or from the cement paste is permitted, the reactions of hydration use up the water until too little is left to saturate the solid surfaces, and the relative humidity within the paste decreases
- The above phenomenon is known as *"self-desiccation"*
- At lower w/c ratios, self-desiccation leads to a lower hydration (because of the shortage of water) compared with a moist-cured paste
- However, at w/c ratios $>$ 0.5, the hydration remains unaffected by self-desiccation