LECTURE NO. 6

By: Dr. Shamshad Ahmad

HYDRATION OF INDIVIDUAL CEMENT COMPOUNDS

Objectives:

- **To explain the hydration of individual cement compounds: C_3S, C_2S, C_3A, and C_4AF**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT

- **Hydration is the collective term describing the chemical and physical processes that take place between cement and water**
- **It is assumed, although not completely valid, that the hydration of each of the four cement compounds takes place independently of the others**
- **Hydration of cement is very important as it is responsible for setting and hardening of concrete**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3S

The following chemical reaction takes place when C_3S comes in contact with water:

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

tri-calcium silicate	water	C-S-H	calcium hydroxide

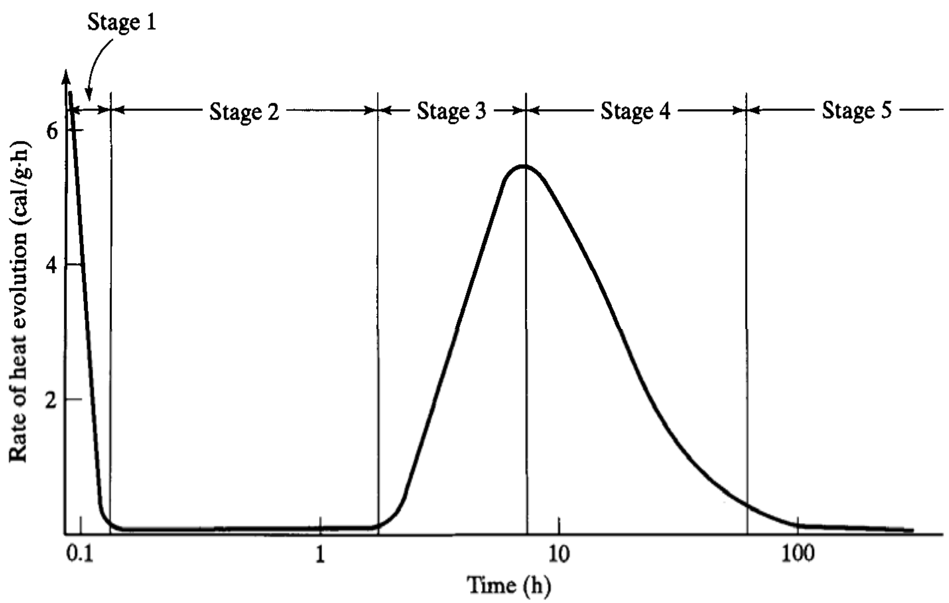
- **C-S-H (calcium-silicate-hydrate) is the principal hydration product**
- **The formula $C_3S_2H_3$ for C-S-H is only approximate because the composition of C-S-H is actually variable over a quite a wide range**
- **C-S-H is poorly crystalline material which forms extremely small particles in the size range of colloidal matter (< 1 μm)**
- **CH (calcium hydroxide) is the secondary hydration product**
- **Unlike the C-S-H, CH is a crystalline material with a fixed composition**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3S

Stages of hydration of C_3S

There are five important stages of the C_3S hydration, as described by the following calorimetric curve (i.e. time versus rate of heat evolution curve):



Rate of heat evolution during hydration of tricalcium silicate.

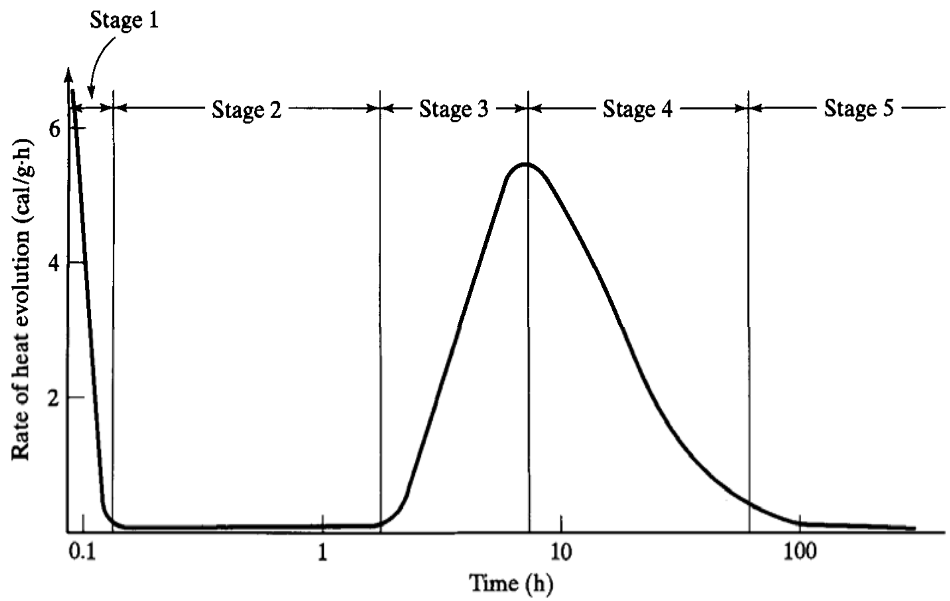
Stage-1 corresponds to a *period of rapid evolution of heat*, which ceases within about 15 min.

Stage-2 corresponds to a *dormant period* which lasts for several hours during which the hydration is almost at halt. This is the reason why the concrete remains in plastic state for several hours.

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3S

Stages of hydration of C_3S



Rate of heat evolution during hydration of tricalcium silicate.

Stage-3 corresponds to ***acceleration period*** **starting at the end of dormant period and lasting till the rate of heat evolution reaches a maximum value. By this time (4 to 8 h) final set has been passed and early hardening has begun**

Stage-4 corresponds to ***deceleration period*** **during which the rate of heat evolution reduces from its maximum value to a very low** ***steady state*** **rate (Stage-5)**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3S

Chemical and Physical Processes Controlling C_3S Hydration

Chemical control:

- **The *hydrolysis of the C_3S* (i.e., *the chemical reaction between C_3S and water*) which results into release of calcium ions and hydroxide ions from the surface of the C_3S grains, forming C-S-H and CH through crystallization of ions and increasing the pH to over 12 within a few minutes, is called as chemical control.**

- **The chemical control (i.e. the hydrolysis of C_3S) slows down quickly but continues throughout the dormant period.**

- **During the dormant period, the increase in Ca^{++} and OH^- concentrations continues slowly.**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3S

Chemical and Physical Processes Controlling C_3S Hydration

Nucleation control:

- **When the Ca^{++} and OH^- concentrations reach a critical value, the hydration products (C-S-H and CH) start to crystallize from solution and the hydrolysis of C_3S again proceeds rapidly.**
- **This whole process of attenuation of critical concentrations of Ca^{++} and OH^- corresponding to which the nuclei of the C-S-H and CH crystals starts forming giving way to the further hydrolysis of C_3S is termed as nucleation control.**

Diffusion control:

- **The hydration process is said to be under diffusion control when the coating over the C_3S grains, formed by layers of C-S-H, put a barrier through which water must flow to reach the un-hydrated C_3S for its hydrolysis and through which ions must diffuse to reach the growing crystals.**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3S

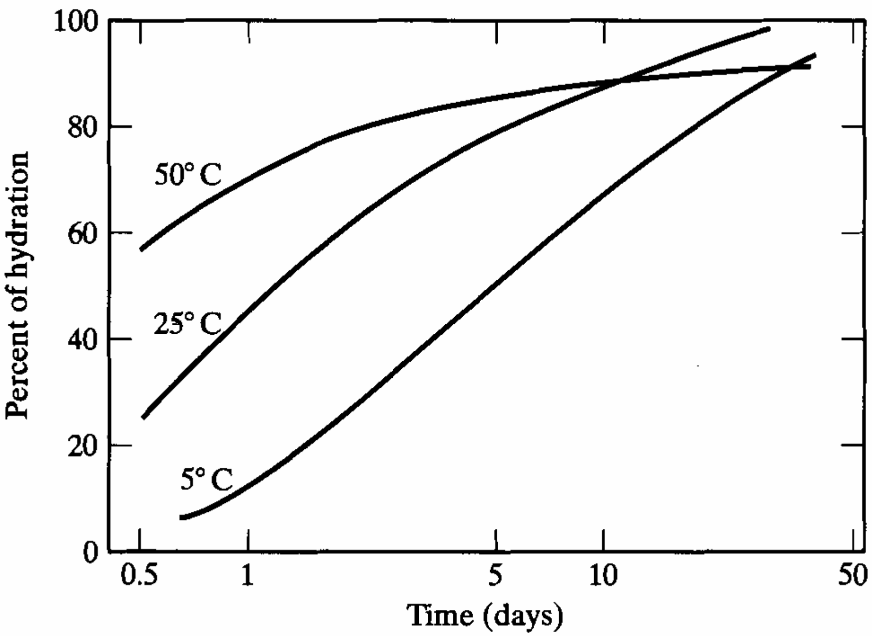
Sequence of Hydration of the Calcium Silicates

Reaction Stage	*Kinetics of Reaction*	*Chemical Processes*	*Relevance to Concrete Properties*
1 Initial hydrolysis	Chemical control; rapid	Initial hydrolysis; dissolution of ions	
2 Induction period	Nucleation control; slow	Continued dissolution of ions	Determines initial set
3 Acceleration	Chemical control; rapid	Initial formation of hydration products	Determines final set and rate of initial hardening
4 Deceleration	Chemical and diffusion control; slow	Continued formation of hydration products	Determines rate of early strength gain
5 Steady state	Diffusion control; slow	Slow formation of hydration products	Determines rate of later strength gain

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3S

Effect of Temperature on C_3S Hydration



Effect of temperature on the hydration of tricalcium silicate.

- The hydration of C_3S is sensitive to temperature (i.e. there is increase in the rate of hydration with increase in temperature) ***but*** only when the reaction is chemically controlled (e.g. stage 3)
- Once hydration is completely diffusion-controlled in stage 5, it is much less temperature-sensitive, although the diffusion coefficient of the hydrate barrier varies with temperature.
- The overall effect of temperature on the hydration of C_3S is shown in the figure.

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_2S

- C_2S hydrates in a similar manner as that of C_3S:

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

dicalcium silicate	water	C-S-H	calcium hydroxide

- But the hydration of C_2S is much slower than C_3S because it is a less reactive compound than C_3S. This is the reason why C_2S does not contribute to initial strength.

- Due to very low amount of heat liberated on the hydration of C_2S, it is not easy to measure the low heat experimentally and therefore calorimetric curve for C_2S hydration is hardly plotted

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3A

In Portland cement the hydration of C_3A involves *reactions mostly with sulfate ions* which are supplied by the dissolution of gypsum added during the manufacturing of cement

Reactions involved in the hydration of C_3A:

1. The primary initial reaction of C_3A, when ample amount of gypsum is present, is as follows:

C_3A	+	$3C\bar{S}H_2$	+	$26H$	$\rightarrow$	$C_6A\bar{S}_3H_{32}$
tri-calcium aluminate		gypsum		water		ettringite

- **The above reaction is exothermic**
- **Ettringite (i.e. "calcium sulfoaluminate hydrate") is the name given to a naturally occurring mineral of the same composition**
- **Ettringite is a stable hydration product *only while* there is an ample supply of sulfate available**
- **The formation of ettringite slows down the hydration of C_3A by creating a diffusion barrier around unhydrated C_3A particles, analogous to the behavior of C-S-H during the hydration of silicates**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3A

Reactions involved in the hydration of C_3A:

1. **If all the sulfate is consumed before the C_3A has completely hydrated, then ettringite becomes unstable and transforms to another calcium sulfoaluminate hydreate containing less sulfate through following reaction:**

$$C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12}$$

- **The second product $3C_4A\bar{S}H_{12}$ is simply called as "monosulfoaluminate"**
- **Monosulfoaluminate may sometimes form before ettringite if C_3A reacts more rapidly with the sulfate ions than they can be supplied by the gypsum to the mix water**
- **The diffusion barrier, created by the formation of ettringite, is broken down during the conversion of ettringite into monosulfoaluminate and C_3A is allowed to react rapidly again**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3A

Reactions involved in the hydration of C_3A:

3. **When monosulfoaluminate is brought into contact with a new source of sulfate ions (e.g. external source of sulfate ions), then ettringite can be reformed, as fllows:**

$$C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16H \rightarrow C_6A\bar{S}_3H_{32}$$

This potential for reforming ettringite is the *basis for sulfate attack* of Portland cements when exposed to an external supply of sulfate ions.

4. **If gypsum is not added in the cement, the hydration of C_3A can lead to flash set due to the rapid formation of calcium aluminate hydrates (C-A-H):**

$$C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$$

These hydrates (C_4AH_{13} + C_2AH_8) are not stable and later convert to C_3AH_6 (hydrogarnet)

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

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3A

Reactions involved in the hydration of C_3A:

5. **When quite a small amounts of gypsum are present, there may still be unhydrated C_3A present when all of the ettringite has been converted to monosulfoaluminate.**

In such cases, the monosulfoaluminate reacts with the unhydrated C_3A forming the monosulfoaluminate solid solution $[C_3A(C\bar{S}CH)H_{12}]$

$$C_4A\bar{S}H_{12} + C_3A + CH + 12H \rightarrow C_3A(C\bar{S}CH)H_{12}$$

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3A

Formation of hydration products from C_3A:

Formation of the hydration products from C_3A, depending upon the sulfate/C_3A molar ratio, is presented in the following table:

Formation of Hydration Products from C_3A

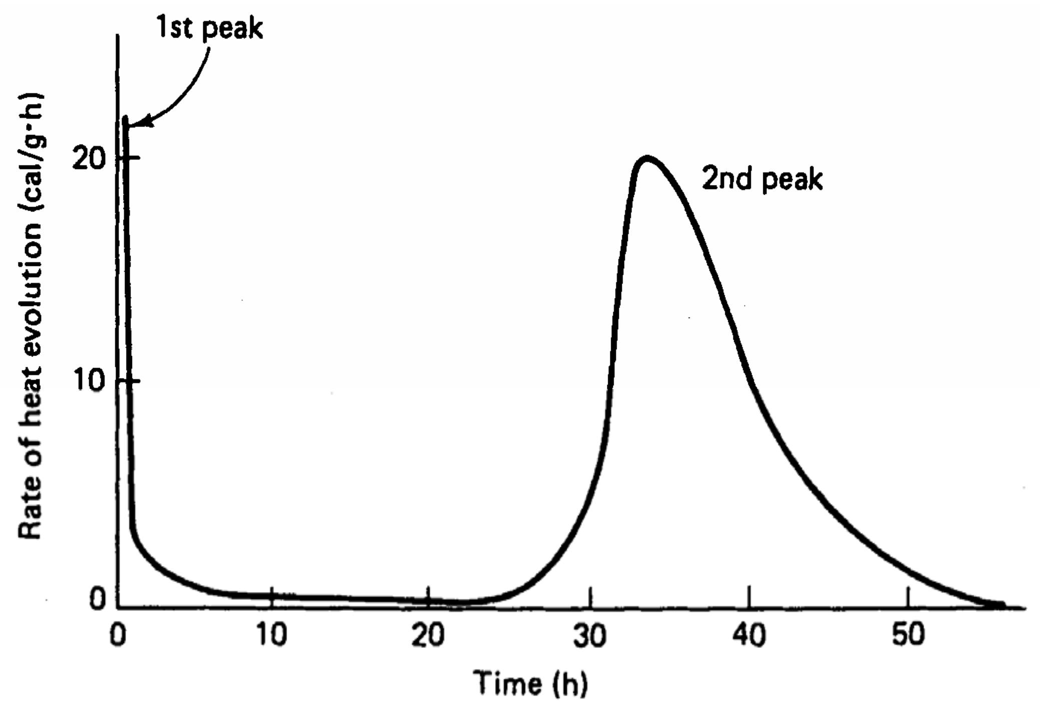
$C\bar{S}H_2/C_3A$ Molar Ratio	Hydration Products Formed
3.0	Ettringite
3.0–1.0	Ettringite + monosulfoaluminate
1.0	Monosulfoaluminate
<1.0	Monosulfoaluminate solid solution
0	Hydrogarnet

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3A

Hydration curve for C_3A:

The calorimetric for hydrating C_3A, which looks qualitatively much like the curve for C_3S, is shown below:



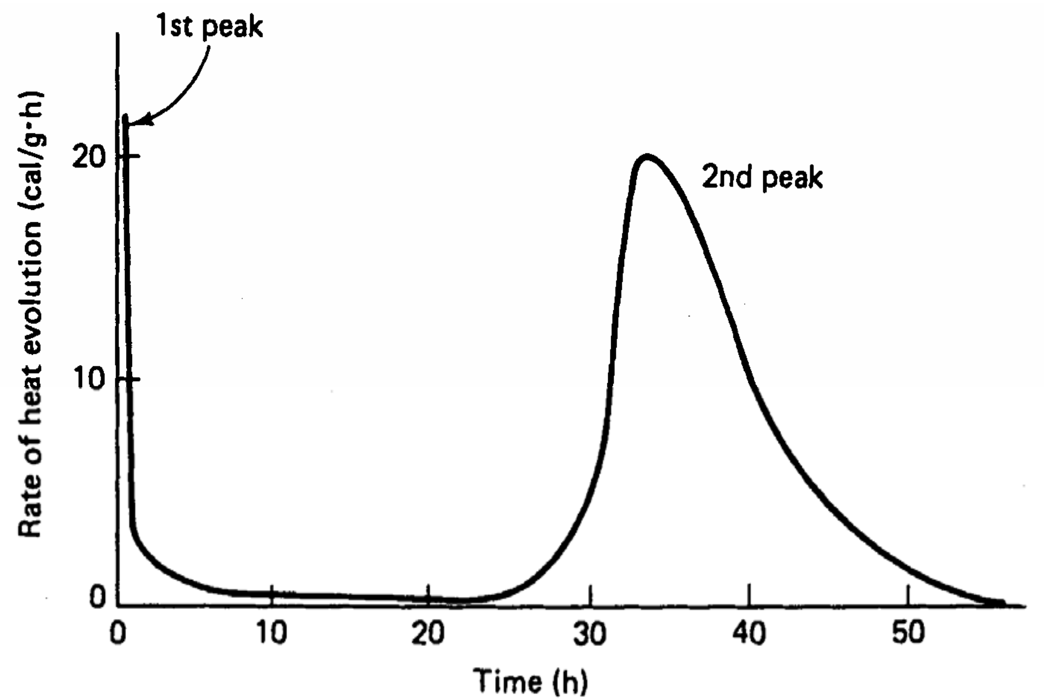
Rate of heat evolution during hydration of tricalcium aluminate with gypsum.

- **The first heat peak is completed in 10 to 15 min and then the rate of heat evolution has been reduced to a very lower value due to the formation of the ettringite barrier**
- **The heat of hydration remains at low value till the ettringite barrier is broken by transformation of ettringite to mono-sulfo-aluminate after all the gypsum has been used to form the ettringite**

By: Dr. Shamshad Ahmad

HYDRATION OF CEMENT: Hydration of C_3A

Hydration curve for C_3A:



Rate of heat evolution during hydration of tricalcium aluminate with gypsum.

- The more gypsum there is in cement, the longer the ettringite will remain stable
- In most cements ettringite remains in stable condition for a period of 12 to 36 hours.
- The rate of heat evolution starts increasing with start of ettringite conversion to mono-sulfo-aluminate and reaches to the second heat peak and then again starts decreasing approaching to a steady-state condition

HYDRATION OF CEMENT: Hydration of C_4AF

- **C_4AF forms the same sequence of hydration products as does C_3A, with or without gypsum**

$$C_4AF + 3C\bar{S}H_2 + 21H \rightarrow C_6(A, F)\bar{S}_3H_{32} + (A, F)H_3$$

$$C_4AF + C_6(A, F)\bar{S}_3H_{32} + 7H \rightarrow 3C_4(A, F)\bar{S}H_{12} + (A, F)H_3$$

- **The reactions are slower and involve less heat**
- **C_4AF never hydrates rapidly enough to cause flash set, and gypsum retards C_4AF hydration even more drastically than it does C_3A**
- **With increase in iron content in C_4AF, hydration of C_4AF becomes slower**
- **Practical experience has shown that cements low in C_3A and high in C_4AF are resistant to sulfate attack**
- **This means that the formation of ettringite from mono-sulfo-aluminate does not occur in case of C_4AF due to presence of iron in it.**