LECTURE NO. 6
HYDRATION OF INDIVIDUAL CEMENT COMPOUNDS

Objectives:

- To explain the hydration of individual cement compounds: $\text{C}_3\text{S}$, $\text{C}_2\text{S}$, $\text{C}_3\text{A}$, and $\text{C}_4\text{AF}$
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.
HYDRATION OF CEMENT: Hydration of C$_3$S

The following chemical reaction takes place when C$_3$S comes in contact with water:

$$2\text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{CH}$$

- C-S-H (calcium-silicate-hydrate) is the principal hydration product
- The formula C$_3$S$_2$H$_3$ 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 $\text{C}_3\text{S}$

Stages of hydration of $\text{C}_3\text{S}$

There are five important stages of the $\text{C}_3\text{S}$ hydration, as described by the following calorimetric curve (i.e. time versus rate of heat evolution curve):

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.
HYDRATION OF CEMENT: Hydration of C₃S

Stages of hydration of C₃S

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).
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.
HYDRATION OF CEMENT: Hydration of C₃S

Chemical and Physical Processes Controlling C₃S Hydration

**Nucleation control:**

• When the Ca²⁺ and OH⁻ concentrations reach a critical value, the hydration products (C-S-H and CH) start to crystallize from solution and the hydrolysis of C₃S again proceeds rapidly.

• This whole process of attenuation of critical concentrations of Ca²⁺ and OH⁻ corresponding to which the nuclei of the C-S-H and CH crystals starts forming giving way to the further hydrolysis of C₃S is termed as nucleation control.

**Diffusion control:**

• The hydration process is said to be under diffusion control when the coating over the C₃S grains, formed by layers of C-S-H, put a barrier through which water must flow to reach the un-hydrated C₃S for its hydrolysis and through which ions must diffuse to reach the growing crystals.
## HYDRATION OF CEMENT: Hydration of C₃S

### Sequence of Hydration of the Calcium Silicates

<table>
<thead>
<tr>
<th>Reaction Stage</th>
<th>Kinetics of Reaction</th>
<th>Chemical Processes</th>
<th>Relevance to Concrete Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Initial hydrolysis</td>
<td>Chemical control; rapid</td>
<td>Initial hydrolysis; dissolution of ions</td>
<td>Determines initial set</td>
</tr>
<tr>
<td>2 Induction period</td>
<td>Nucleation control; slow</td>
<td>Continued dissolution of ions</td>
<td>Determines final set and rate of initial hardening</td>
</tr>
<tr>
<td>3 Acceleration</td>
<td>Chemical control; rapid</td>
<td>Initial formation of hydration products</td>
<td></td>
</tr>
<tr>
<td>4 Deceleration</td>
<td>Chemical and diffusion control; slow</td>
<td>Continued formation of hydration products</td>
<td>Determines rate of early strength gain</td>
</tr>
<tr>
<td>5 Steady state</td>
<td>Diffusion control; slow</td>
<td>Slow formation of hydration products</td>
<td>Determines rate of later strength gain</td>
</tr>
</tbody>
</table>
**HYDRATION OF CEMENT: Hydration of C₃S**

**Effect of Temperature on C₃S Hydration**

- The hydration of C₃S 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 C₃S is shown in the figure.

*By: Dr. Shamshad Ahmad*
HYDRATION OF CEMENT: Hydration of C$_2$S

- C$_2$S hydrates in a similar manner as that of C$_3$S:

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

- But the hydration of C$_2$S is much slower than C$_3$S because it is a less reactive compound than C$_3$S. This is the reason why C$_2$S does not contribute to initial strength.

- Due to very low amount of heat liberated on the hydration of C$_2$S, it is not easy to measure the low heat experimentally and therefore calorimetric curve for C$_2$S hydration is hardly plotted.
HYDRATION OF CEMENT: Hydration of C₃A

In Portland cement the hydration of C₃A 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 C₃A:

1. The primary initial reaction of C₃A, when ample amount of gypsum is present, is as follows:

   \[
   \text{C}_3\text{A} + 3\text{CaSO}_4 \cdot \text{H}_2 \cdot \text{H}_2\text{O} + 26\text{H}_2\text{O} \rightarrow \text{C}_6\text{A}_3\text{S}_3\text{H}_32
   \]

   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 C₃A by creating a diffusion barrier around unhydrated C₃A particles, analogous to the behavior of C-S-H during the hydration of silicates
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:

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

- The second product $3C_4A\overline{S}H_{12}$ 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

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HYDRATION OF CEMENT: Hydration of C₃A

Reactions involved in the hydration of C₃A:

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 follows:

\[
C_4A\overline{S}H_{12} + 2C\overline{S}H_2 + 16H \rightarrow C_6A\overline{S}_3H_{32}
\]

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 C₃A 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 (C₄AH₁₃ + C₂AH₈) are not stable and later convert to C₃AH₆ (hydrogarnet)

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

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HYDRATION OF CEMENT: Hydration of C$_3$A

Reactions involved in the hydration of C$_3$A:

5. When quite a small amounts of gypsum are present, there may still be unhydrated C$_3$A present when all of the ettringite has been converted to monosulfoaluminate.

In such cases, the monosulfoaluminate reacts with the unhydrated C$_3$A forming the monosulfoaluminate solid solution [C$_3$A(C$\bar{S}$CH)H$_{12}$]

\[ C_4A\bar{S}H_{12} + C_3A + CH + 12H \rightarrow C_3A(C\bar{S}CH)H_{12} \]
**HYDRATION OF CEMENT: Hydration of C₃A**

**Formation of hydration products from C₃A:**

Formation of the hydration products from C₃A, depending upon the sulfate/C₃A molar ratio, is presented in the following table:

<table>
<thead>
<tr>
<th>$\text{CSH}_2/\text{C}_3\text{A}$ Molar Ratio</th>
<th>Hydration Products Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>Ettringite</td>
</tr>
<tr>
<td>3.0–1.0</td>
<td>Ettringite + monosulfoaluminate</td>
</tr>
<tr>
<td>1.0</td>
<td>Monosulfoaluminate</td>
</tr>
<tr>
<td>&lt;1.0</td>
<td>Monosulfoaluminate solid solution</td>
</tr>
<tr>
<td>0</td>
<td>Hydrogarnet</td>
</tr>
</tbody>
</table>

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HYDRATION OF CEMENT: Hydration of C₃A

Hydration curve for C₃A:

The calorimetric for hydrating C₃A, which looks qualitatively much like the curve for C₃S, is shown below:

- 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.

Rate of heat evolution during hydration of tricalcium aluminate with gypsum.
HYDRATION OF CEMENT: Hydration of $C_3A$

**Hydration curve for $C_3A$:**

- 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 $\text{C}_4\text{AF}$

- $\text{C}_4\text{AF}$ forms the same sequence of hydration products as does $\text{C}_3\text{A}$, with or without gypsum

$$\text{C}_4\text{AF} + 3\text{S}_2\text{H}_2 + 21\text{H} \rightarrow \text{C}_6(\text{A, F}) \text{ S}_3\text{H}_{32} + (\text{A, F})\text{H}_3$$
$$\text{C}_4\text{AF} + \text{C}_6(\text{A, F}) \text{ S}_3\text{H}_{32} + 7\text{H} \rightarrow 3\text{C}_4(\text{A, F}) \text{ S}_1\text{H}_{12} + (\text{A, F})\text{H}_3$$

- The reactions are slower and involve less heat

- $\text{C}_4\text{AF}$ never hydrates rapidly enough to cause flash set, and gypsum retards $\text{C}_4\text{AF}$ hydration even more drastically than it does $\text{C}_3\text{A}$

- With increase in iron content in $\text{C}_4\text{AF}$, hydration of $\text{C}_4\text{AF}$ becomes slower

- Practical experience has shown that cements low in $\text{C}_3\text{A}$ and high in $\text{C}_4\text{AF}$ are resistant to sulfate attack

- This means that the formation of ettringite from mono-sulfo-aluminate does not occur in case of $\text{C}_4\text{AF}$ due to presence of iron in it.

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