HYDRATION OF CEMENT

It is the reaction (series of chemical reactions) of cement with water to form the binding material. In other words, in the presence of water, the silicates (C₃S and C₂S) and aluminates (C₃A and C₄AF) form products of hydration which in time produce a firm and hard mass - the hydrated cement paste.

There are two ways in which compounds of the type present in cement can react with water:

In the first, a direct addition of some molecules of water takes place, this being a true reaction of hydration.

The second type of reaction with water is hydrolysis, in which its nature can be illustrated using the C₃S hydration equation:

\[ 3\text{CaO} \cdot \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + x\text{CaO} \cdot y\text{SiO}_2 \cdot \text{aq.} \] (calcium silicate hydrate)

The reaction of C₃S with water continue even when the solution is saturated with lime and the resulted amounts of lime precipitate in crystals form Ca(OH)₂.

**Calcium silicate hydrate** → remains stable when it is in contact with the solution saturated with lime.

**Calcium silicate hydrate** → hydrolyzed when being in water - some of lime form, and the process continues until the water saturate with lime. If the calcium silicate hydrate remains in contact with water → it will leave the hardened compound only as hydrated silica due to the hydrolysis of all of the lime.

The rates of the chemical reactions of the main compounds are different:

**Aluminates**
- React with the water in the beginning
- Affect the route of the chemical reactions at early periods of hydration.

**Silicates** - Affect the later stage reactions.
The main hydrates of the hydration process are:

- **Calcium silicates hydrate**, including hydrated products of C₃S, and C₂S.

  \[ 2 \text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\ \text{Ca(OH)}_2 \]

  \[ 2 \text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{Ca(OH)}_2 \]

- **Tricalcium aluminate hydrate**.

  \[ \text{C}_3\text{A} + 6\text{H} \rightarrow \text{C}_3\text{AH}_6 \]

- **C₄AF** hydrates to tricalcium aluminate hydrate and calcium ferrite CaO·Fe₂O₃ in amorphous form.

Since calcium silicates (C₃S and C₂S) - are the main cement compounds (occupies about 75% of cement weight) - they are responsible for the final strength of the hardened cement paste.

With time:

- The rate of hydration decreases continuously.
- The size of unhydrated cement particles decrease. For instance, after 28 days in contact with water, grains of cement have been found to have hydrated to a depth of only 4 µm, and 8 µm after a year.

This is due to:

1) Accumulation of hydration products around the unhydrated cement grains which lead to prevent water from channeling to them.
2) Reduction of the amount of water either due to chemical reaction or evaporation.
3) Reduction of the amount of cement due to reaction.
The progress of hydration of cement can be determined by different means:

- The measurement of the amount of Ca(OH)$_2$ in the paste resulted from the hydration of the silicates.
- The heat evolved by hydration.
- The specific gravity of the paste.
- The amount of chemically combined water.
- The amount of unhydrated cement present (using X-ray quantitative analysis).
- Also indirectly from the strength of the hydrated paste.

**Tricalcium Aluminate Hydrate and the Action Of Gypsum**

The amount of C$_3$A present in most cements is comparatively small but its behavior and structural relationship with the other phases in cement make it of interest. The tricalcium aluminate hydrate forms a prismatic dark interstitial material in the form of flat plates individually surrounded by the calcium silicate hydrate.

The reaction of pure C$_3$A with water is very violent with evolution of large amount of heat, forming calcium aluminates hydrate in the form of leaf hexagonal crystals. In Portland cement, this reaction leads to immediate stiffening known as "flash setting".

Gypsum, added to the clinker through grinding process cause delaying the reaction of C$_3$A with water by its reaction with C$_3$A to form insoluble calcium sulfoaluminate (3CaO.A1$_2$O$_3$.3CaSO$_4$.30-32H$_2$O) - ettringite - around C$_3$A particles, which permits enough time for the hydration of C$_3$S that its reaction is slower than C$_3$A and permits the occurring of natural setting. But eventually tricalcium aluminate hydrate is formed, although this is preceded by a metastable 3CaO.A1$_2$O$_3$.CaSO$_4$.12H$_2$O, produced at the expense of the original high-sulfate calcium sulfoaluminate.

The reaction of gypsum with C$_3$A continues until one of them exhausted, while C$_3$S continue in hydration.
If $C_3A$ exhausted before gypsum

The surplus gypsum $\rightarrow$ expand $\rightarrow$ become an agent assist the disruption and deterioration of cement paste.

If gypsum exhausted before $C_3A$

The remaining $C_3A$ begins in hydration:

$$C_3A + 6H \rightarrow C_3AH_6$$

$C_3AH_6$ is stable - cubical crystals - with high sulfate resistance.

Calcium aluminate hydrate - Be at many forms before transforming to the stable state ($C_3AH_6$). It is probably forming hexagonal crystals ($C_4AH_8$, $C_4AH_{10}$, $C_4AH_{12}$) before the cubical crystals.

When the hexagonal crystals expose to sulfates (inside concrete from sand or external from soil or ground water) $\rightarrow$ react with it forming calcium sulfoaluminate $\rightarrow$ with increase in volume, depending on the amount of remaining aluminates and the concentration' of sulfates $\rightarrow$ crack and deteriorate of the hardened concrete.

The transformation of calcium aluminates hydrate from the metastable exagonal form to the stable cubical form is accompanied with - change in the density and size of the crystals - leading to decrease in the late ages strength of the cement paste due to:

- lose the adhesion and cohesion in the microstructure
- increase the porosity of the hardened cement paste.

The presence of $C_3A$ in cement is undesirable: it contributes little to the strength of cement except at early ages (1-3 days) and, when hardened cement paste is attacked by sulfates, expansion due to the formation of calcium sulfoaluminate from $C_3A$ may result in a disruption of the hardened paste.

But it is useful in the cement industry - work as flux material - reduce the temperature needed to form the clinker. Also it facilitates the combination of lime with silica.
**C₄AF compound**

Gypsum reacts with C₄AF to form calcium sulfoaluminates and calcium sulfoferrite.

C₄AF - work as flux material and also it accelerates the hydration of silicates.

**Using The Optimum Percentage of Gypsum is Very Important Because:**

- It regulates the speed of the chemical reactions in the early ages.
- Prevent the local concentration of the hydration products.

The necessary gypsum content increase with the increase of:

- C₃A content in the cement.
- Alkalis content in the cement.
- Fineness of cement.

Iraqi specification No.5 limits the maximum gypsum content (expressed as the mass of SO₃ present) to be not more than 2.5% when C₃A ≤5% and 2.8% when C₃A >5 % for ordinary cement ,for sulfate resistance cement, SO₃ ≤2.5%.

**Calcium Silicates Hydrate**

C₃S

C₃S+ water $\rightarrow$

- lime and silica ions in the solution with molecular weight of 3: 1
- Ca(OH)₂ crystals
- Calcium silicate hydrate gel *(tobermorite)*

Hydration of C₃S - take about one year or more

This initial gel form an external layer over C₃S causing the delay of the reaction. After few hours, this initial C-S-H undergo hydrolysis to form the second product of the gel CSH. The full hydration of C₃S can be expressed approximately following equation

$$2 (3\text{CaO}.\text{SiO}_2) + 6\text{H}_2\text{O} \rightarrow 3\text{CaO}.2\text{SiO}_2.3\text{H}_2\text{O} + 3 \text{Ca(OH)}_2$$
C₂S

There are three main crystal forms of C₂S (α, β, γ) but the β-form is the only one occurred in the Portland cement and it react slowly with water.

- its reaction is slower than C₃S
- The amount of Ca(OH)₂ from its hydration is less.

Its formed gel is similar to that produced from C₃S, but there is difference in the route of the chemical reactions between the two components - the lime: silica during the hydration of C₂S differs than that formed during the hydration of C₃S. Hydration of C₂S - take more than 4 years.

The gel formed after the completion of hydration of the two components is → C₃S₂H₃ - Tobermorite.

C₃S and C₂S - require approximately the same amount of water for hydration, but C₃S produces more than twice as much Ca(OH)₂ as is formed by the hydration of C₂S, as shown in the equations below:

For C₃S hydration
2 C₃S + 6H → C₃S₂H₃ + 3 Ca(OH)₂
the corresponding masses involved are:
100 + 24 → 75+49

For C₂S hydration
2 C₂S + 4H → C₃S₂H₃ + Ca(OH)₂
the corresponding masses involved are:
100 + 24 → 99+22
Influence of the Compound Composition on Properties of Cement

Main Compounds

$\text{C}_3\text{S}$ and $\text{C}_2\text{S}$ - are the most important compounds - responsible for strength.

$\text{C}_3\text{S}$ - contributes most to the strength development during the first four weeks.

$\text{C}_2\text{S}$ - influences the gain in strength from 4 weeks onwards. At the age of about one year, the two compounds, contribute approximately equally to ultimate strength.

$\text{C}_3\text{A}$ contributes to the strength of the cement paste at one to three days, and possibly longer, but causes retrogression at an advanced age, particularly in cements with a high $\text{C}_3\text{A}$ or $(\text{C}_3\text{A}+\text{C}_4\text{AF})$ content. The role of $\text{C}_4\text{AF}$ in the development of strength of cement is not clear till now, but there certainly is no appreciable positive contribution.
Hydration of Cement can be presented by following schematic diagram

Basic elements of cement

| Ca | O₂ | Si | Al | Fe |

↓

Oxides of Elements

| CaO | SiO₂ | Al₂O₃ | Fe₂O₃ |

↓

Cement Compounds

| C₃S | C₂S | C₃A | C₄AF |

↓

Reaction of cement with water

| C-S-H gel | Ca(OH)₂ | Heat |
Optimum Gypsum Content O.G.C

Optimum Gypsum Content O.G.C is a percentage of gypsum that give higher compressive strength, low drying shrinkage and no excessive expansion in concrete volume when immersed in water, as shown in Figures below.
Factors affecting on O.G.C.

1. C₃A content: Increase C₃A content need to increase O.G.C because higher percentage will react in short time.

2. cement fineness: Increase in cement fineness promote to increase O.G.C.

3. Alkali content: Increase in alkali content means increase reaction of gypsum that leads to increase O.G.C.

4. Curing temperature: Increase in temperature of curing cause increase the reaction of C₃A with gypsum that means increase O.G.C.

5. Curing time: Increase in curing time promote to increase O.G.C because of (Autogenously Healing).

6. Free CaO and MgO: Increase of these oxides lead to decrease in O.G.C.

7. Clorides: Increase of clorides lead to decrease in O.G.C