Hydration of cement

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

The two calcium silicates are the main cementitious compounds in cement and C3S hydrate more rapidly than C2S. Since calcium silicates (C3S and C2S) - are the main cement compounds (occupies about 75% of cement weight) - they are responsible for the strength of the hardened cement paste.

These silicates contain impurities which have strong effect on the properties of cement. sometimes C3S with impurities called alite and C2S with impurities called belite.

The products of hydration of C3S and C2S are the calcium silicate hydrate C3S2H3 and Ca(OH)2

Calcium silicate hydrate (or C-S-H) is the main product of the hydration of Portland cement and is primarily responsible for the strength in cement.

For C_3S hydration

$2\ C_3S + 6H \longrightarrow C_3S_2H_3 + 3Ca(OH)_2$

The corresponding masses involved are:

$100 + 24 \longrightarrow 75 + 49$

For C_2S hydration

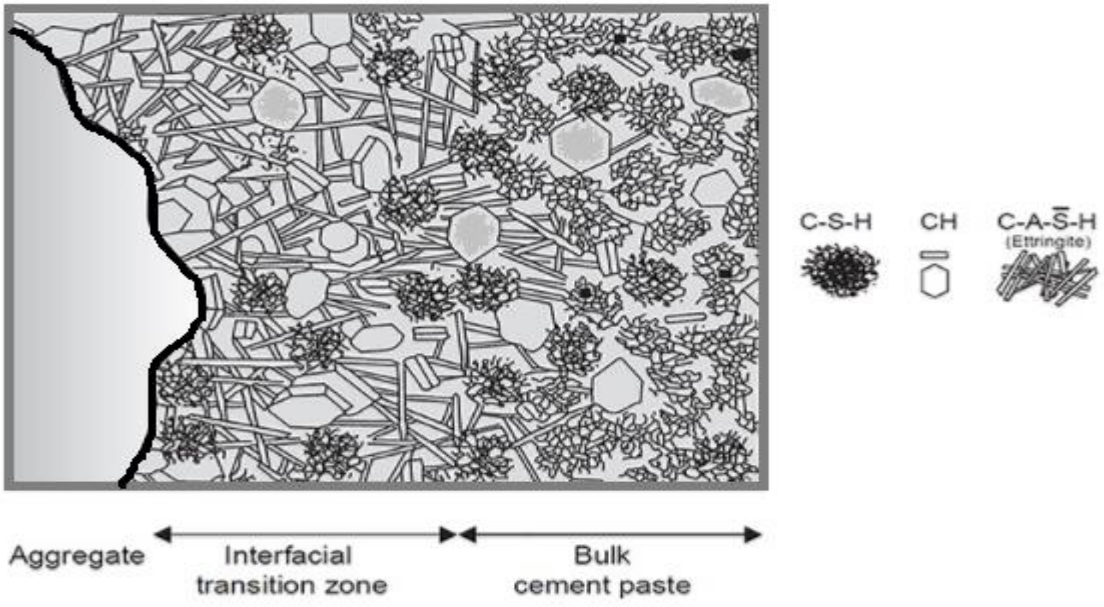
$2\ C_2S + 4H \longrightarrow C_3S_2H_3 + Ca(OH)_2$

The corresponding masses involved are:

$100 + 21 \longrightarrow 99 + 22$

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

C3S and C2S - require approximately the same amount of water for hydration, but C3S produces more than twice Ca(OH)2 than the amount formed by the hydration of C2S



With time the rate of hydration decreases continuously and the size of un-hydrated cement particles decrease this is due to:

1) Accumulation of hydration products around the unhydrated cement grains which lead to prevent water from reaching to the unhydrated cement.

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 hydration of C3A results in tricalcium aluminate hydrate forms a cubic crystals surrounded by the calcium silicate hydrate.

The reaction C3A with water is accommodated with evolution of large amount of heat, forming calcium aluminates hydrate. 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 C3A with water which permits enough time for the hydration of C3S to the occurring of natural setting.

$$C_3A + 6H \longrightarrow C_3AH_6$$

C3AH6 is stable -cubical crystals- Calcium aluminate hydrate - Be at many forms before transforming to the stable state (C3AH6). It is probably forming hexagonal crystals (C4AH8, C4AH10, C4AH12) before the cubical crystals. When the hexagonal crystals expose to sulfates (inside concrete from sand **or** external from soil or ground water) react with it forming

calcium sulfoaluminate with increase in volume, depending on the amount of remaining aluminates and the concentration of sulfates — crack and deteriorate of the hardened concrete.

The transformation of calcium aluminates hydrate from the metastable hexagonal 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 C3A in cement is undesirable: it contributes little to the strength of cement except at early ages (1-3 days) but it facilitates the combination of lime with silica.

Gypsum reacts with C4AF to form calcium sulfoaluminates and calcium sulfoferrite. C4AF accelerates the hydration of silicates.

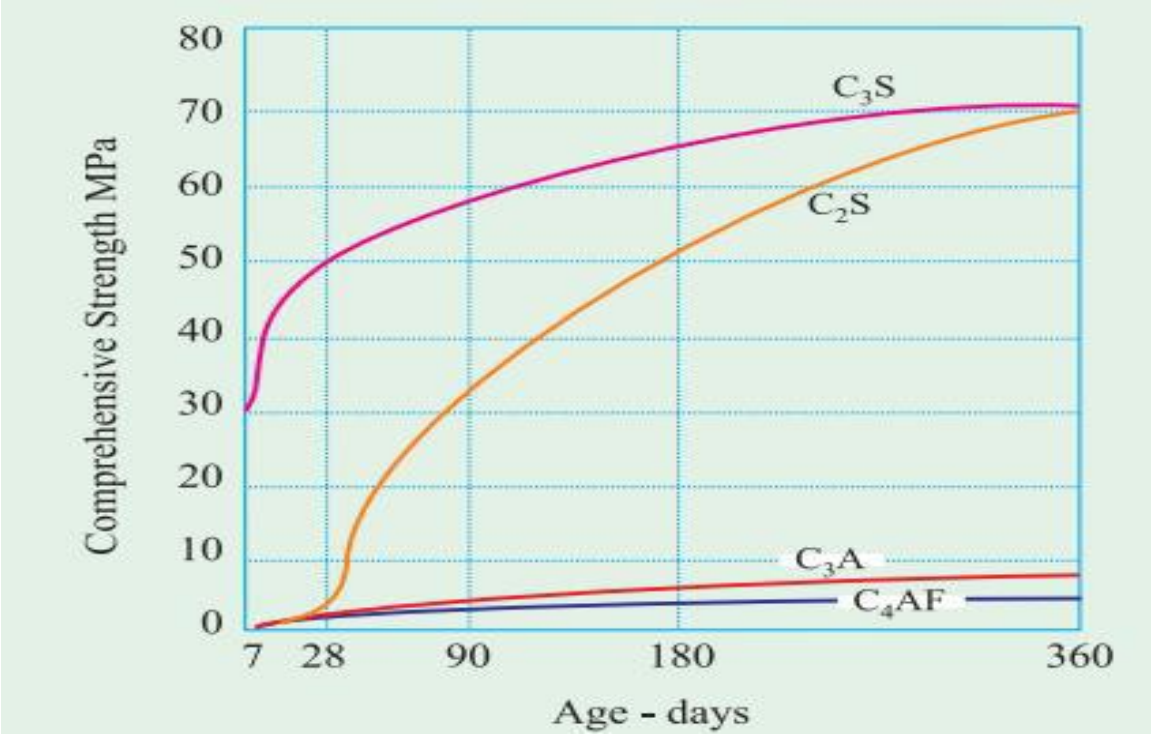
Using the optimum percentage of gypsum is very important because:
- It regulates the speed of the chemical reactions in the early ages.
- Prevent the local concentration of the hydration products.
The necessary gypsum content increase with the increase of:
- C3A content in the cement.
- Alkalis content in the cement.
- Fineness of cement.

Iraqi specification No. 5 limits the maximum gypsum content to be not more than 2.5% when C3A < 7% and 3% when C3A >7%.

The reaction of gypsum with C3A continues until one of them exhausted, while C3S continue in hydration.

- If C3A exhausted before gypsum The surplus gypsum expand become an agent assist the disruption and deterioration of cement paste.

-If gypsum exhausted before C3A The remaining C3A begins in hydration:



Development of Strength of cement Compounds