Advanced Concrete Technology
Dr. Manu Santhanam
Department of Civil Engineering
Indian Institute of Technology, Madras

Lecture – 04
Cement Composition – Part 2

We already talked about what is the basis for understanding the formation of different forms of compounds of cement inside the rotary kiln, which happens because of the very high temperature clinkering reactions. These reactions lead to a formation of different stoichiometries of compounds which are not exact. They are just given these approximate nomenclatures like tri calcium silicate, di calcium silicate, tri calcium aluminate and tetra calcium aluminoferrite.

The important aspects include, first the combination of lime and silica to form C_2S and then later after the appearance of the molten phase as the aluminates, the conversion of C_2S into C_3S which takes care of the excess lime that is present in the system. At the end of the entire process there is very little free lime that is actually left in the system and that is of advantage because the lesser the free lime the lesser we can expect would be the problems, because of unsoundness of the cement, so for having the good cement, we need to have the free calcium oxide controlled as much as possible. One more thing I talked about earlier was the fact that free magnesia or magnesium oxide also needs to be controlled to an extent that does not cause any expansion problems during the time period of setting. We already talked about different compounds and different oxides that are actually present in the cement and what is the approximate composition. We saw that cement is primarily composed of C_3S these days because we want cements to gain strength at an early stage and C_3S is the one which really helps in improving the early age strengths okay? So most of modern cement chemistry is based on C_3S. We do not give that much importance to C_2S because C_2S the reactions are fairly delayed and the strength gains with C_2S happen very slowly.

Of course, when we look at curing for 28 days, we can be reasonably assured that some of the C_2S also has reacted. Amongst the aluminates, the C_3A is something that reacts very early in the process whereas, the C_4AF is something which may not react for a long period of time and possibly never at all and that is primarily because the iron in the C_4AF makes it highly insoluble.

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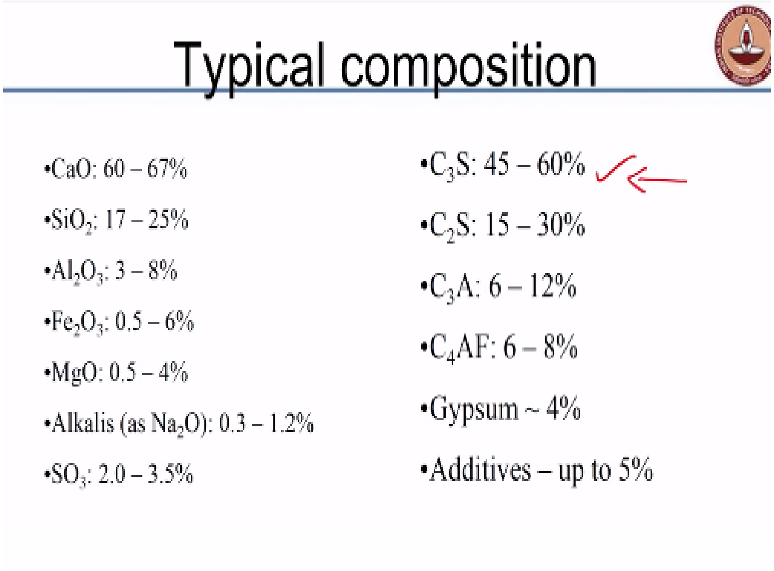

Typical composition

- CaO: 60 – 67%
- SiO_2: 17 – 25%
- Al_2O_3: 3 – 8%
- Fe_2O_3: 0.5 – 6%
- MgO: 0.5 – 4%
- Alkalis (as Na_2O): 0.3 – 1.2%
- SO_3: 2.0 – 3.5%

- C_3S: 45 – 60% ✓ ←
- C_2S: 15 – 30%
- C_3A: 6 – 12%
- C_4AF: 6 – 8%
- Gypsum ~ 4%
- Additives – up to 5%

Because of the insoluble nature of C_4AF, it does not initiate the reaction at all and for a long time, the C_4AF may just remain unreacted in the system. We saw earlier that we have nearly half of the cement is C_3S and probably about half of the C_3S quantity is what we have in terms of C_2S, okay, C_3A is about 6 to 12% and C_4AF is 6 to 8%.

The total silicate content, take any cement, would be around 80% and total aluminate content will be about 20% of the clinker. When we look at it in terms of the clinker, 80% would be silicates and 20% would be aluminates. Now, gypsum is about 4% and the additives that are added in the system as performance improvers like ground limestone of fly ash would amount about 5% of the overall mass of the cement.

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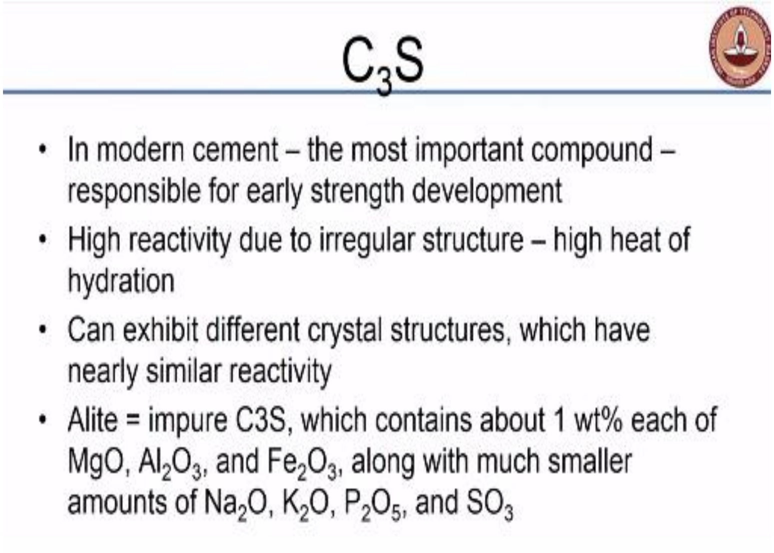

C_3S

- In modern cement – the most important compound – responsible for early strength development
- High reactivity due to irregular structure – high heat of hydration
- Can exhibit different crystal structures, which have nearly similar reactivity
- Alite = impure C3S, which contains about 1 wt% each of MgO, Al_2O_3, and Fe_2O_3, along with much smaller amounts of Na_2O, K_2O, P_2O_5, and SO_3

Now let us look at the structures of these different compounds and what causes them to have differences in their reactivity. C_3S is probably the most important compound in modern cement because it is related to the early strength development that we desire in the cements and we saw earlier, the irregular structure of the C_3S crystals. This irregular structure is what causes C_3S to have a high reactivity. The high reactivity also implies a high heat of hydration, that means when C_3S reacts it liberates a lot of heat and that is one of the problems in modern cement that modern cements release tremendous amount of heats upon hydration.

Now it is not easy to understand the crystal structure of C_3S because there is no one crystal structure that it exhibits. Depending upon the impurities that are present in the system and the kind of heating processes that occur in the kiln followed by the cooling process, you can actually get multiple polymorphs of the C_3S. Remember from your basic chemistry, polymorphs indicate different crystal forms of the same compound. For example, calcium carbonate is present as calcite or as baterite or as aragonite all of them are calcium carbonate. But all these 3 have different crystal forms. So those are polymorphs of calcium carbonate. Similar to that C_3S has various polymorphs. The issue with the polymorphs is that the reactivity does not differ as much as far as C_3S is concerned. So we do not really need to worry too much about controlling it.

Alite; is the name given to impure C_3S which contains about 1% by weight, each of magnesium oxide, aluminium oxide and iron oxide along with smaller quantities but very important quantities of the alkalis and sulphates. Primarily, the alkali sulphates are the ones which have attached themselves to the surface of the clinker particles and these alkali sulphates are the ones which lead to a high degree of reactivity with the Alite. So you have sodium, potassium, phosphorus oxide, sometimes and then you have sulphur trioxide which could be present in various quantities on the surface of the clinker particles. So, its these impurities which lend C_3S to have its unique structure as well as high levels of reactivity are also because of the presence of these impurities.

C_2S on the other hand have a much more regular or rounded structure but these structures also showed those very characteristic striations on the surface as seen in the micrographs.

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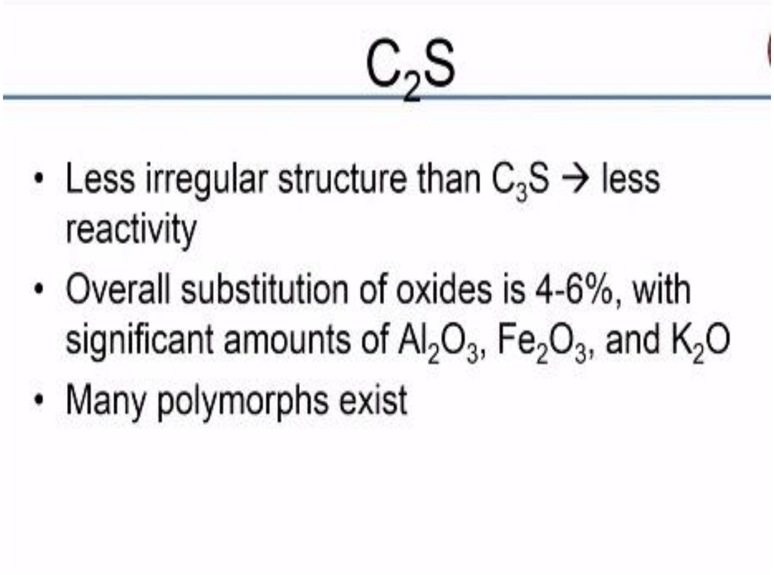
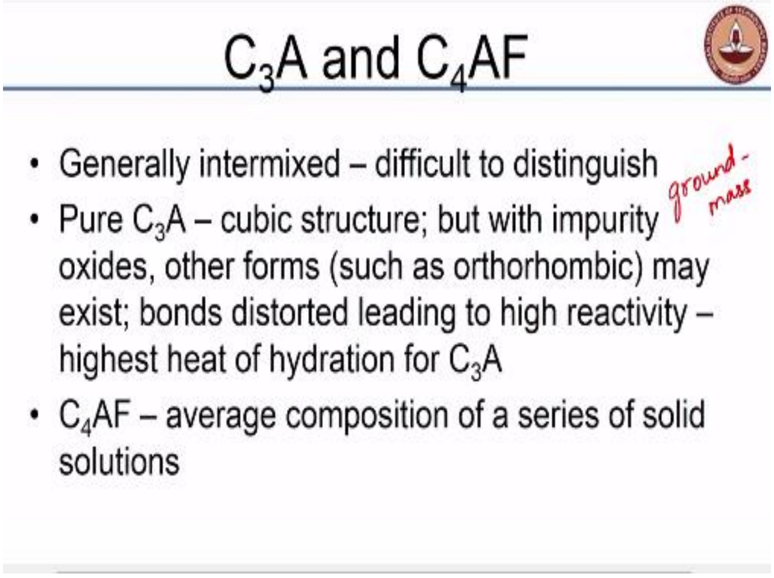


C_2S

- Less irregular structure than C_3S → less reactivity
- Overall substitution of oxides is 4-6%, with significant amounts of Al_2O_3, Fe_2O_3, and K_2O
- Many polymorphs exist

And the regular structure implies a lower reactivity and overall substitution of oxides in this case also is about 4 to 6% with significant amounts of alumina, iron oxide and potassium oxide. So again you have minority oxides that are present in the surface of the clinker grains but the reactivity is not as high primarily because of the regular structure of C_2S. Again, similar to C_3S, there are several polymorphs that may exist depending upon the kind of heating and cooling processes right.

And the kind of impurities that are actually present in the system and these polymorphs are usually named as alpha, beta, gamma, etc. and mostly what we are concerned with in modern cement is beta C_2S or Belite and that is what we are commonly finding in modern cements and these details about polymorphs are beyond the scope of the syllabus. It is advised to refer more about crystal structures as this has indeed a large influence on the heat of hydration and also on the reactivity that you see from these cementitious materials.



C_3A and C_4AF

- Generally intermixed – difficult to distinguish
- Pure C_3A – cubic structure; but with impurity oxides, other forms (such as orthorhombic) may exist; bonds distorted leading to high reactivity – highest heat of hydration for C_3A
- C_4AF – average composition of a series of solid solutions

ground-mass

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We have the aluminates next, which are forming the minority constituent in the cement clinker compounds. As shown in the micrographs, the C_3A and C_4AF are difficult to distinguish because they are intermixed and because the sizes of these crystals are so small, in other words, they called micro crystalline compounds because their formation happens very quickly when the molten state converts to solid, when we cooled the molten mixture that comes out with the clinker at 1450°C. When we cool it rapidly into 1200°C, we form the aluminate compounds, which we had earlier termed as the ground mass compounds. Because of the fine crystal sizes and the fact that they intermixed, it is not easy to distinguish them, but if we employ a technique like x-ray diffraction, we can actually decipher the kind of structures of these compounds also.

Pure C_3A has a cubic structure and cubic is something that you associate with a very high ordered material and very high order implies obviously, a controlled reactivity. But with the impurity oxides that are present with C_3A, just like with C_3S or C_2S, you can have other forms of C_3A also like orthorhombic. When you have the other forms there could be some distortion in your bonds that leads to high reactivity in the system.

In crystals, the more ordered the crystal the lesser will be the reactivity and the more disordered the higher will be the reactivity. So highest heat of hydration among cementitious compounds is for C_3A. It has got a highly ordered structure, and also has a highest rate of reactivity if you leave it to react on its own, and it has got the highest heat of hydration. Why do you think that happens?

It is an ordered structure but still it is highly reactive because one of the aspects that controls the rate at which the reaction progresses is how fast your aluminates or calcium from the C_3A can come into solution to start reaction, and C_3A turns out to be quite highly soluble because the crystal sizes are very small. So solubility is high, because of which the reactivity is also high, in spite of the ordered structure of C_3A. C_4AF on the other hand is not as reactive as C_3A. It has got a structure that is also highly ordered and because of the very low solubility of the iron and very low mobility of the iron in a solution, you will have very limited reactivity of C_4AF. It has got much lower heat of hydration as compared to C_3A.

As mentioned earlier when talked about the formation of C_4AF from the CAF ternary phase diagram, we said that it is going to be a mixture of different solid solutions. That means, it does not have a definite composition but an average composition is C_4AF. It is actually a mixture of different solid solutions. Going beyond these details would mean that we are getting into a completely different realm of studies and probably, if we keep ourselves more focused towards how cement actually interacts with the other ingredients in the concrete system that will help our cause more than trying to decide for the intricacies of what cement compounds are like as that becomes a very highly sophisticated and specialized subject.