Admixtures And Special Concretes

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Lecture 02

Overview of cement chemistry and concrete performance: Quality control and composition

Reactions in the Kiln:

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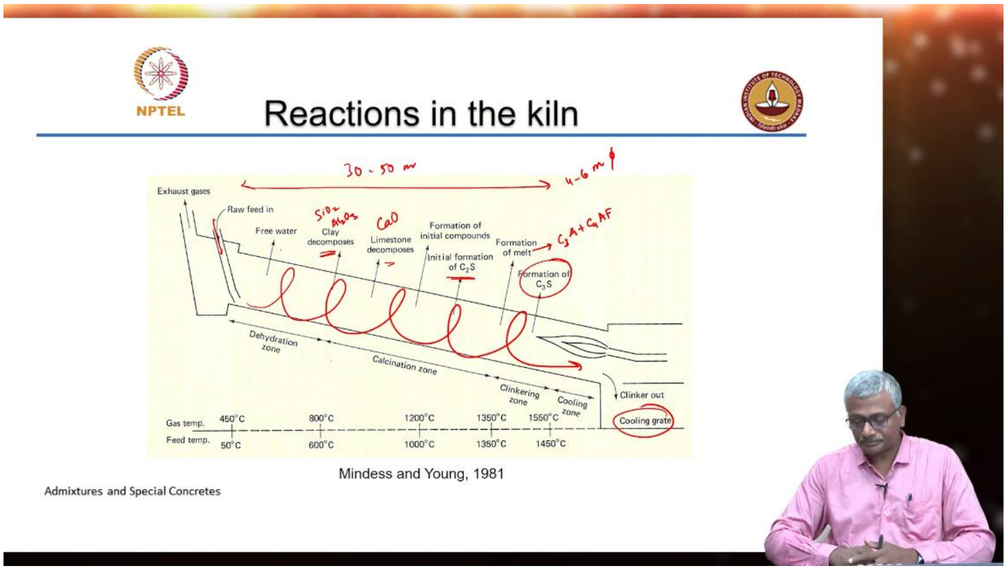

Reactions in the kiln

Mindess and Young, 1981

Admixtures and Special Concretes

Just to give you some basic idea about what happens in the kiln, as I said, the raw feed comes in at the top end of the kiln and, just goes by gravity to the other side. So, there is a slow process by which the material comes in and goes out to the other end. Mind you, this entire kiln can be as long as 30 to 50 meters. Most kilns are 30 to 40 meters, but in a wet process plant, the kiln can be as high as 80 to 100 meters because we need that extra bit of length for removing the water that is there in the process. But today most kilns will be about 30 to 50 meters and about 4 to 6 meters in diameter. That is a very large piece of capital equipment that you are putting in a cement plant.

So, the free water basically, goes out first. Of course, in our case, as I said earlier, the pre-heater itself will remove all the free water. The decomposition or activation of the clay can happen at around 600 degrees Celsius and then you have decomposition of limestone that happens typically around 700 to 900 degrees Celsius.

And then you start combining the silica and the alumina from the clay with the calcium oxide from the limestone. In various proportions, these combine and start forming compounds. One of the initial compounds that forms is C_2S and then you have the melt formation which is basically, C_3A and C_4AF. I will come to these compounds a little bit later. And then in the final stage, you have the formation of C_3S inside the kiln.

The clinker comes out and goes to the cooling process which maintains a certain structure of the C_3S and C_2S. Without this cooling process being optimal, you will have the wrong combination that you end up getting after the cooling happens.

Intergrinding with gypsum:

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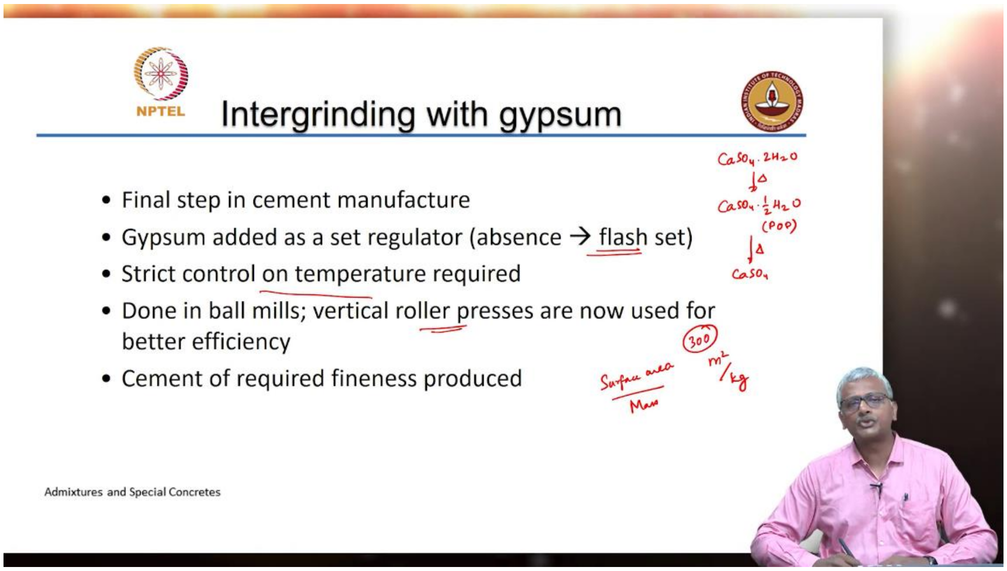

Intergrinding with gypsum

- Final step in cement manufacture
- Gypsum added as a set regulator (absence → flash set)
- Strict control on temperature required
- Done in ball mills; vertical roller presses are now used for better efficiency
- Cement of required fineness produced

$CaSO_4 \cdot 2H_2O$

$\downarrow \Delta$

$CaSO_4 \cdot \frac{1}{2}H_2O$ (POP)

$\downarrow \Delta$

$CaSO_4$

$\boxed{300}$ m^2/kg

$\frac{\text{Surface area}}{\text{Mass}}$

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As I said, it is very important to intergrind the cement with the gypsum in the end because gypsum has to be present as a set regulator. In the absence of gypsum, we get a flash set. The aluminates that are present in the system can immediately react with water, give off a lot of heat, and that will lead to the flash setting of the cement.

During this process of ball milling or intergrinding, you need to have strict control over temperature. Why? Because if you can imagine, gypsum is basically, calcium sulphate dihydrate. If you heat it, it transforms into calcium sulphate hemihydrate or which we also call as plaster of Paris, POP, basically, half a molecule of water is present. You further heat it; it becomes anhydrous calcium sulphate. You lose all the water.

Now later when we talk about the cement chemical admixture compatibility, you will see that the form in which you have these sulphates available in your system can go a long way in dictating what happens in the early stages, when you add an admixture into the concrete. So, for that, you need to ensure that when you have a strict control over temperature, you can control or regulate this transformation of the gypsum between anhydrite or hemihydrate. All this is happening while the material is getting ground in a ball mill or today as I said, you have much more sophisticated roller presses that do a better job and produce more efficient ground cement systems. The result of this process is, you end up producing cement of the required fineness.

Typically, we express the fineness of the cement in surface area per unit mass or meter square per kilogram. That means if I take 1 kilogram of the cement and lay it out on a large sheet of paper and I can somehow compute the entire surface area of the cement, that is what the value will be. For most cement, this is around 300 square meters per kilogram, mostly true for India. But if you travel to Europe or the US, the cement fineness is typically of the order of 350 or even more in square meters per kilogram.

Quality control:

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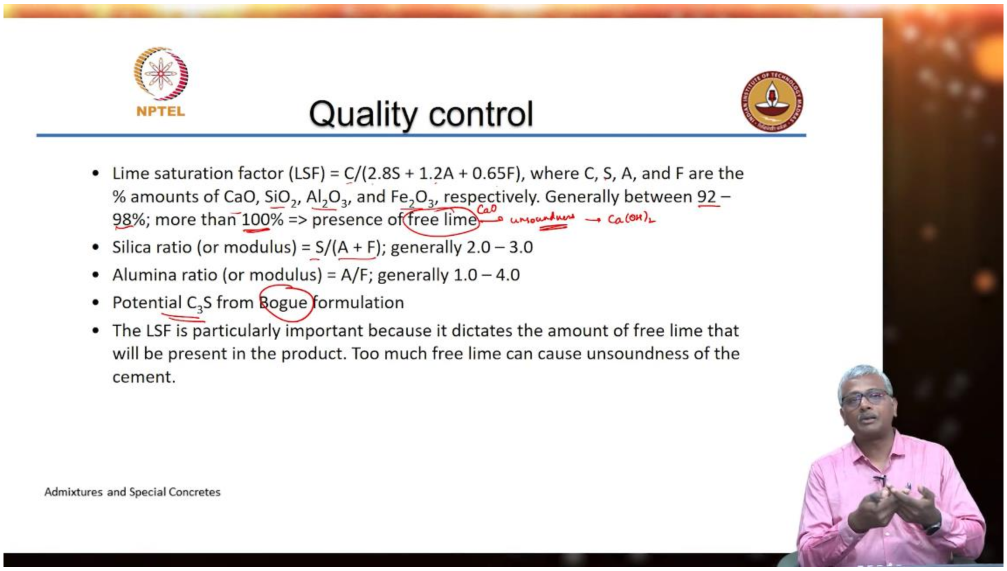

Quality control

- Lime saturation factor (LSF) = C/(2.8S + 1.2A + 0.65F), where C, S, A, and F are the % amounts of CaO, SiO_2, Al_2O_3, and Fe_2O_3, respectively. Generally between 92 – 98%; more than 100% => presence of free lime $\overset{CaO}{\rightarrow}$ unsoundness → $Ca(OH)_2$
- Silica ratio (or modulus) = S/(A + F); generally 2.0 – 3.0
- Alumina ratio (or modulus) = A/F; generally 1.0 – 4.0
- Potential C_3S from Bogue formulation
- The LSF is particularly important because it dictates the amount of free lime that will be present in the product. Too much free lime can cause unsoundness of the cement.

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Now as I said, you need to do a very strict quality control of the entire process. Otherwise, you are going to be producing cement that is highly variable and you can only imagine, if you are producing cement and transporting it to the job site for a project that happens over several years and if the cement is continuously going to be variable then you have a problem. Concrete quality will not be maintained, the concrete characteristics will not be predictable and you will end up producing concrete, which is not up to the mark if your cement is not properly controlled.

So, for that, several factors are carefully chosen and ensured that you are maintaining your cement composition within those limits. One important factor is the lime saturation factor. The lime saturation factor looks at what is the content of the lime that can properly combine with the silica, alumina, and iron oxide to produce the cementitious compound. So here lime saturation factor is given as

$$Lime\ Saturation\ Factor\ (LSF) = C/(2.8S + 1.2A + 0.65F)$$

where C, S, A, F, again cement chemistry we are a little bit different in terms of the notations that we used as compared to the actual chemists. C here is not carbon, C is calcium oxide, S is silicon dioxide, A is Al_2O_3 and F is Fe_2O_3. So, all these oxides are given these short notations so that we have some comfort while writing the equations. We do not want to be lost while writing these equations.

So, we want the lime saturation factor to be generally as close to 1 as possible. That means almost all the calcium oxide is present in a bound form. Generally, between 92 and 98 percent is generally preferable. If you have more than 100 percent that means there is an excess of lime available and that is what we call as free lime. This free lime is not good for the cement because it leads to unsoundness. Unsoundness means at the time of setting the cement paste experiences an increase in its volume and that happens because of the transformation of free lime, that is calcium oxide to calcium hydroxide. When it reacts with water, it transforms to calcium hydroxide and there is a change in volume of the cement paste which is not considered to be a good thing. That is why we want to restrict the free lime to as low as possible.

Now the silica ratio is another factor that is controlled or silica modulus sometimes it is called, is the silica to the sum of the alumina and the iron oxide that is present in the system.

$$Silica\ ratio\ (or\ modulus) = S/(A + F)$$

It is generally maintained between 2 and 3.

The alumina ratio or modulus A by F is generally about 1 to 4.

$$Alumina\ ratio\ (or\ modulus) = A/F$$

Of course, this is a very large value that I am giving you here but then, more or less it is closer to about 1 to 2, is what would be the correct level of alumina modulus that is present. The other factor that needs to be controlled is the potential C_3S from Bogue formulation. Now, Bogue was another cement scientist who did a lot of basic understanding of cement chemistry and he proposed that based on the way that cement forms in the kiln or based on the way that the oxides combine in the kiln from a starting mixture of calcium oxide, silicon dioxide, aluminum oxide and iron oxide, you can then predict the potential quantities of the compounds that are ending up forming. Compounds like C_3S, C_2S, C_3A and C_4AF.

So, the lime saturation factor as I said again is very important. We do not want excess free lime in your system that leads to the unsoundness of the cement paste.

Oxide Composition:

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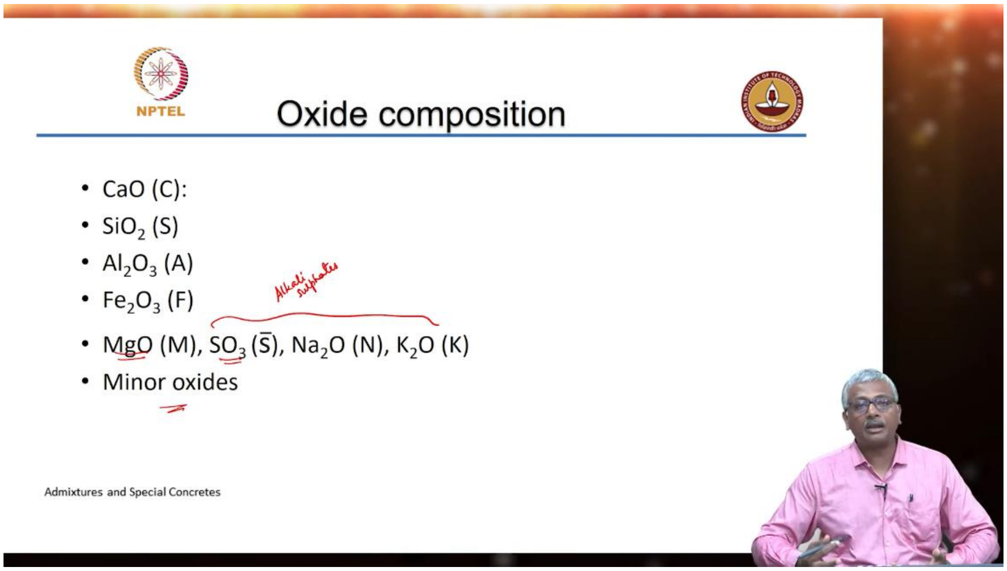

Oxide composition

- CaO (C):
- SiO_2 (S)
- Al_2O_3 (A)
- Fe_2O_3 (F)
- MgO (M), SO_3 ($\bar{S}$), Na_2O (N), K_2O (K)
- Minor oxides

Alkali sulphates

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So, in terms of oxide composition, you have calcium oxide which is written as C, silicon dioxide S, aluminum oxide A, and Fe_2O_3 as F and you may also have other minor oxides that are present but which have a large role to play in how the cement performs. Magnesium oxide could be from the magnesium-bearing impurities present in the limestone. You have sulphur trioxide SO_3 which is coming from the gypsum obviously and some amount of alkaline sulphates could also be present. Your alkali oxides, as well as the sulphur trioxide, could also be from alkali sulphates. The alkali sulphates are impurities that are present along with the clinker sometimes. There are other minor oxides which are not having a very large bearing on the way that cement reacts with water.

Towards compound composition:

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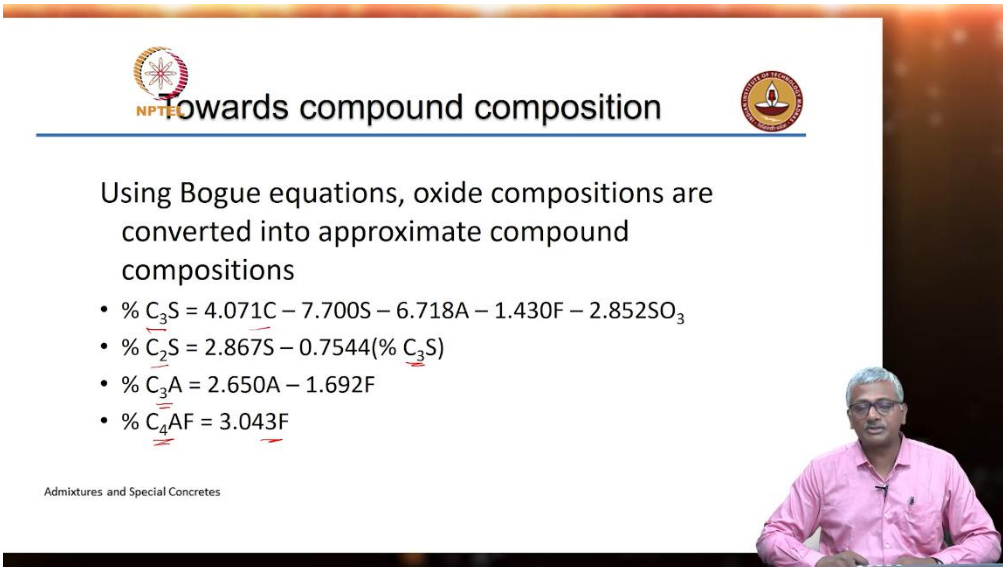

Towards compound composition

Using Bogue equations, oxide compositions are converted into approximate compound compositions

- % C_3S = 4.071C – 7.700S – 6.718A – 1.430F – 2.852SO_3
- % C_2S = 2.867S – 0.7544(% C_3S)
- % C_3A = 2.650A – 1.692F
- % C_4AF = 3.043F

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So, as I said from the oxide composition you can apply the approximate equations, which we know as Bogue equations, to convert the oxide compositions into compound compositions. So, percentage C_3S is given as,

$$\%\ C_3S = 4.071C - 7.700S - 6.718A - 1.430F - 2.852SO_3$$

percentage C2S is calculated after you determine C3S, and is given as

$$\%\ C_2S = 2.867S - 0.7544(\%C_3S)$$

percentage C4AF, is based on the assumption that all the iron combines to form C4AF and is given as

$$\%\ C_3A = 2.650A - 1.692F$$

and then you can calculate percentage C3A and is given as

$$\%\ C_4AF = 3.043F$$

So, all of these compounds can be approximately calculated but this is not the way to actually get the true mixture of the compounds that are present in cement.

You have much more sophisticated methods than this to get a quantitative estimate of the amount of these compounds present in the cement. Usually, we do it by a quantitative X-ray diffraction analysis but that is not a focus of this course so I am not going to get there in detail. But for approximate understanding of the compound composition, you can apply the Bogue equations.

Appearance of clinker:

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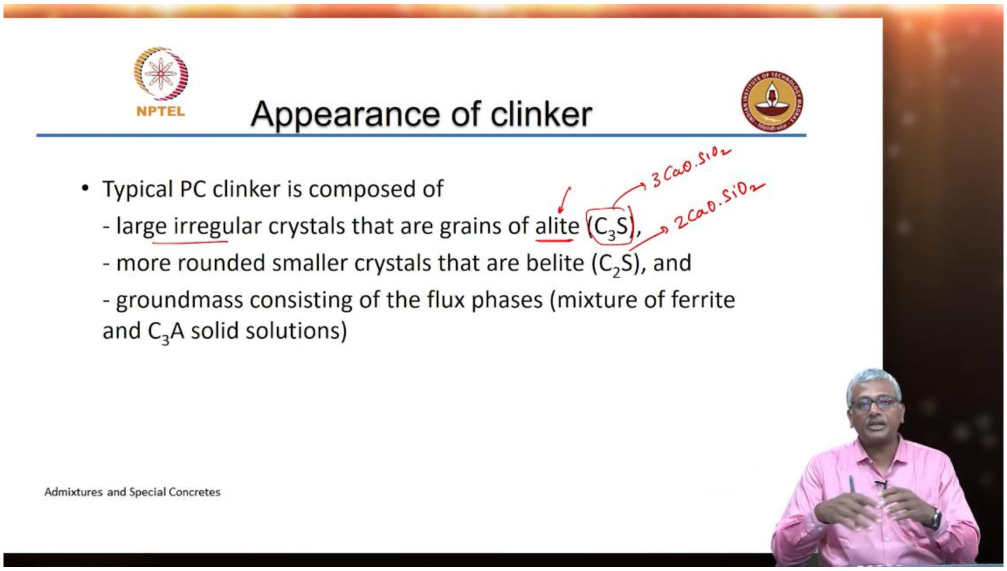

Appearance of clinker

- Typical PC clinker is composed of
  - large irregular crystals that are grains of alite (C_3S), $\rightarrow 3CaO.SiO_2$
  - more rounded smaller crystals that are belite (C_2S), and $\rightarrow 2CaO.SiO_2$
  - groundmass consisting of the flux phases (mixture of ferrite and C_3A solid solutions)

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So once the cement forms and if you look under the microscope, you will see a mixture of different types of grains that are present in the system. You will get the primary grains of calcium silicates or which are C_3S and C_2S and you will then get a fairly inconsistent or unrecognizable, with a high degree of clarity, an unrecognizable mass of products that are basically your aluminates that are forming in your system.

So, you have large irregular crystals of C_3S, which we otherwise call as alite. Alite is an impure form of C_3S as a compound. C_3S is 3 $CaO.SiO_2$ and C_2S is 2 CaO.SiO2. That means 3 parts of calcium oxide is combining with one part of silica. We do not really know this product as a mineral on its own or naturally occurring mineral because most naturally occurring minerals will be named it with a 'ite' at the end.

That is why cement scientists chose to name C_3S as alite. C_3S, which is not pure as I said, has alkaline sulphates, it may have other oxides that are present as impurities, and because of that, it is known as alite. Similarly, C2S is transformed into the name belite, just to make it look like a mineral. Most minerals have that kind of a nomenclature, mostly the names ending with 'ite.' And then the ground mass, which I said is not very consistent, are not able to recognize each of these phases individually. The groundmass consists of the flux phases which are basically, aluminates - C_3A and C_4AF.

Examples of clinker:

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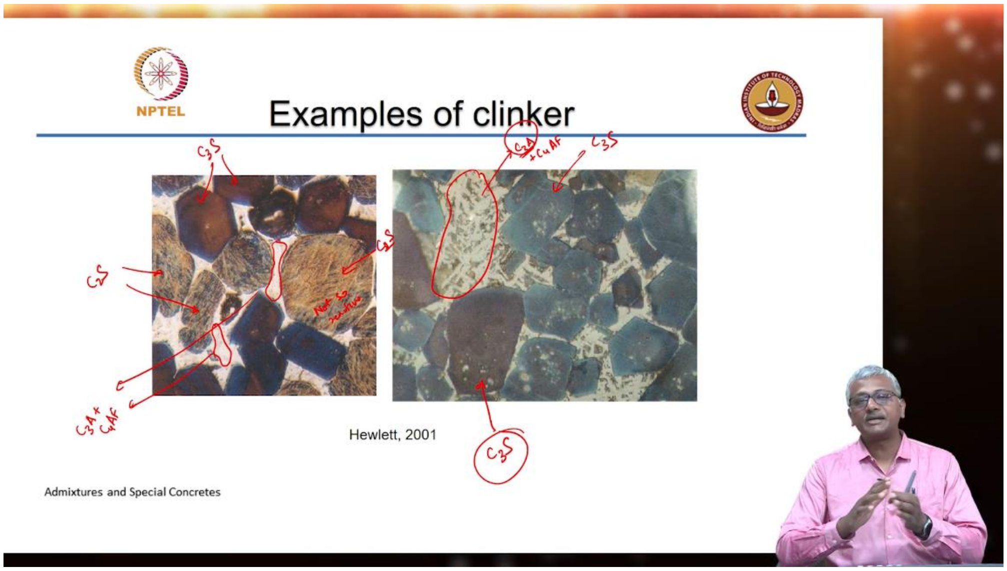

Examples of clinker

Hewlett, 2001

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So, I will show you a couple of pictures. So here it is an example of clinker that you can see. Here these are the irregular crystals that you see of C_3S. Here more rounded crystals of C_2S. Again, you can see another rounded crystal of C_2S and you see this ground mass that is present here. That is basically, a mixture of C_3A plus C_4AF. In this picture, all of these are basically, C_3S, that is also C_3S. All these irregular crystals are C_3S. So, you have a cluster of C_3S particles together but you have a large amount of this ground mass C_3A and C_4AF.

Now, obviously the crystal size and the presence of the impurities in the system will have a large bearing on the reactivity of these phases. Because C_3S has such an irregular structure it lends itself to being highly reactive. Whereas, C_2S which is more rounded is not so reactive. And further, your C_3A, is another very reactive material. C_4AF could be reactive but the problem is that for reaction to happen your material should first dissolve in the water and then react. Because iron is present, the extent of dissolution is very limited. So, C_4AF almost does not even react much at all in the cementitious system.

So, reactivity is very high for C_3S and for C_3A. So, most modern cement where we want early-age performance relies a lot on the reactivity that we get from C_3S and C_3A. We really do not get too much from the other components that is C_2S and C_4AF.

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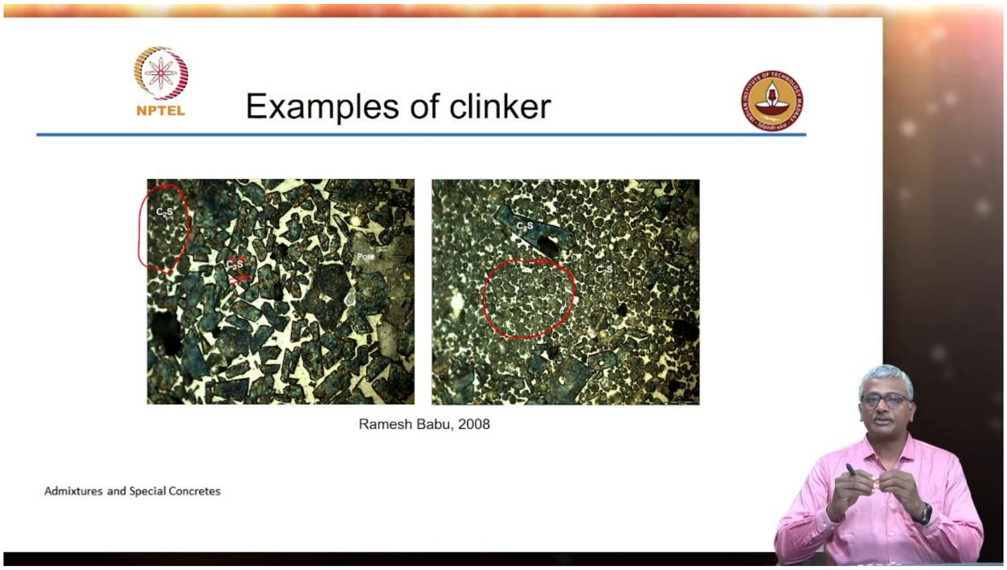

NPTEL

Examples of clinker

Ramesh Babu, 2008

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Again, another example of a clinker which is seen under the optical microscope, which shows you C_3S particles and a cluster of C_2S. Here again, you see a large cluster of C_2S with some C_3S in the system here. So, what happens is, all these cements end up being the same ordinary Portland cement. In India, we have graded cement 53, 43, and so on. So, they are all ultimately going to be ordinary Portland cement but their internal structure could differ significantly and all these characteristics of the way that the clinker has formed inside the kiln can have a bearing on the actual reactivity and performance of these cements.

So again, it is fairly complex to truly predict a cement performance just based on its structure or its composition. You need both angles to be looked at carefully.