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Lecture – 03
Cement Composition – Part 1

In the last chapter we talked about how cement was produced, what are the various processes involved, what is the importance of each process, what considerations are there are as far as the conditions and the composition in different parts of the process, how we do quality control in terms of specific parameters that we look for, primarily the oxide compositions and from that we work out some potential compound composition.

So, let us take a look at little bit more in detail as to what the composition of the cement is, in this chapter will also talk a lot about the different types of cements or classification of cements as per different standards..

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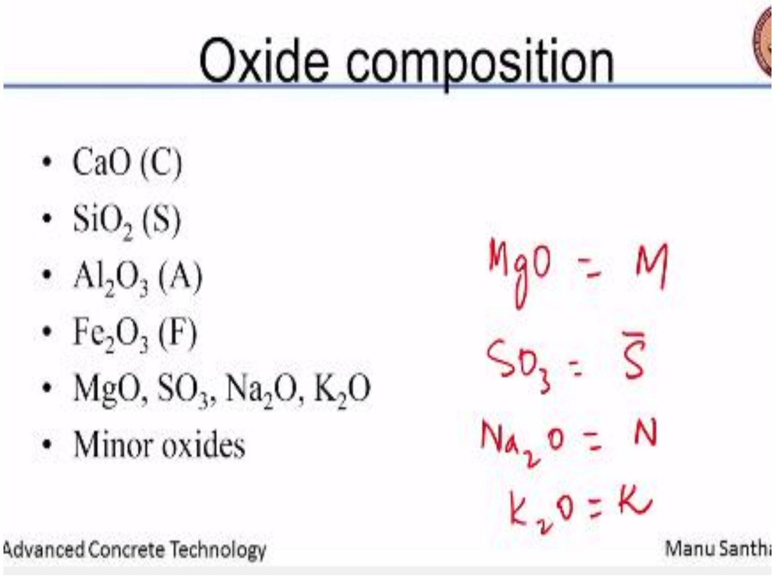

Oxide composition

- CaO (C)
- SiO_2 (S)
- Al_2O_3 (A)
- Fe_2O_3 (F)
- MgO, SO_3, Na_2O, K_2O
- Minor oxides

$MgO = M$

$SO_3 = \bar{S}$

$Na_2O = N$

$K_2O = K$

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That the 4 primary oxides in cement are calcium oxide, silicon dioxide, aluminium oxide and iron oxide, now these are represented in cement chemistry by specific notation; calcium oxide is written as C, silicon di oxide is S, aluminium oxide is A and iron oxide as written as F and apart from these, you have some other oxides which are present in fairly significant proportions and those include magnesium oxide, sulphur trioxide, sodium oxide and potassium oxide.

Where is the magnesium oxide coming from? From the calcite source, from the limestone source it may contain some impurities like dolomite. So that is where the magnesium oxide is coming from. What about the sodium oxide, potassium oxide and sulphates; where are these coming from? Well, some of the sulphate is obviously coming from gypsum, which is added in the final stages in the manufacture but you also saw earlier that attached to the clinker grains, you also have some alkali sulphates that are present like sodium sulphate or potassium sulphates.

They may be attached to the clinker grains and that is why we get the contribution of alkali oxides present in your cement. So if you have to follow the same cement chemistry notation you have to write these also accordingly, so MgO is written as M, SO_3 is written as S with a bar on top, Na_2O is written as N and K_2O is written as K, so again this is simple cement chemistry notation, it is not to be confused with what we have in regular chemistry.

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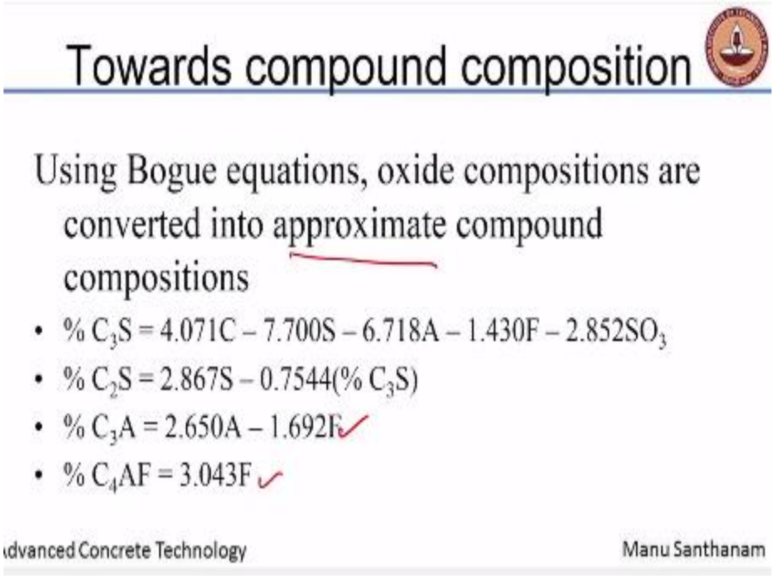

Towards compound composition

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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Of course, K still represents potassium in chemistry, N does not represent sodium in, N is nitrogen but Na is sodium but Na_2O is written as sodium oxide. So in this way if you were to work on the compound compositions, you would first have to estimate how much compound composition can actually form from a given oxide composition and for that there was a scientist named Bogue, one of the early cement chemists who was there in the first half of the 20th century.

He worked a lot with the cementitious formulations in the calculations not just with the production of cement but he also worked a lot with the hydration of cement in terms of analysing the amount of heat that is getting produced, the pore spaces that are produced and so on. There are couple of names you will hear often in cement chemistry, if you look in the history of cement chemistry, you will hear obviously about Bogue, about Vicat.

You will hear about a person called Powers. Lot of the concrete science that is practised today is obviously very thankful to the work of Powers because he was the pioneer as far as the concrete science as well. Power worked in the early part of the 20th century, so work in concrete science is obviously been there for more than 100 years now, and people have tried various combinations of materials with a basic understanding that was earlier developed by powers and of course also by Bogue.

So, Bogue equations are essentially stoichiometric equation that connect the amount of potential compounds forming in the system. This is called potential compound composition or approximate compound composition, the reason for which is stated below. So, according to this, you have 4 equations for 4 different primary compounds are there in cement. Of course, you all know these are tri calcium silicate, di calcium silicate, tri calcium aluminate and tetra calcium alumina-ferrite. I will again give a description about these compounds, these are only approximate stoichiometric formulae for the compound that are actually forming inside the kiln. We cannot have an exact stoichiometry because they represent a range of different ratios between calcium and silicon for each type of these compounds.

But then we will talk about why you give this notation later. So in these equations, what you do first is you assume that all the iron that is present in the system gets combined in the form of tetra calcium alumina-ferrite, so this is your first equation here;

$$\%C_4AF \text{ is } = 3.043F$$

F is Fe_2O_3 content, so % C_4AF is obtained first. The next thing you do is; you obtain the %C_3A, which is;

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

Then you go to the first equation, determine your C3S;

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

Of course, you are subtracting this sulphate here because you are removing the potential contribution from gypsum, potential calcium contribution from gypsum because that is not going to go into the reaction with silicates and aluminates to form C_3S.

So, for C_3S formation, you only have the clinker compounds that are reacting but gypsum was only added in the final stages of cement manufactures, so the SO_3 correction is primarily for gypsum. Now, what happens here is once you calculate C_3S, you then calculate C_2S because that needs the calculation of C_3S to be completed,. Now there are certain complications with this and there are several assumptions that lead to this equation being formulated.

What are the complications? Now, just look at the first equation, % C_3S, even if I have a minor change in my silica content like even 1 or 2%, what happens then? The C_3S content will come down by nearly 7.7% that is a very large amount, right that is the major variation that can actually happen, especially with silica because the silica can come from our performance improver also, right.

Performance improver, if you are using fly ash, we are allowed it to 5% performance improver in ordinary portland cement, so 5% fly ash can potentially contribute between 2 and 3% of silica. Now, if you put that back in this formulation, your potential C_3S composition comes to be very low but in truth in the clinker, you may already form C_3S that is significantly large around 50% at least.

Because all our production processes are optimised to produce a high degree of tri calcium silicate so, these equations are better applied on the clinker to get a potential formulation of C_3S, C_2S, etc. I will tell you later how we determine the exact compound composition but for now, you have to understand that these are potential compositions more so, because there are several assumptions that are in Bogue equations.

One; the first assumption is that there are no secondary minerals present, in other words Bogue assume that these 4 are the only compounds that can actually form in the system but as I told you earlier, these 4 are not exact compounds in terms of stoichiometry, there are several other combinations possible. The average compositions are represented by these 4 components.

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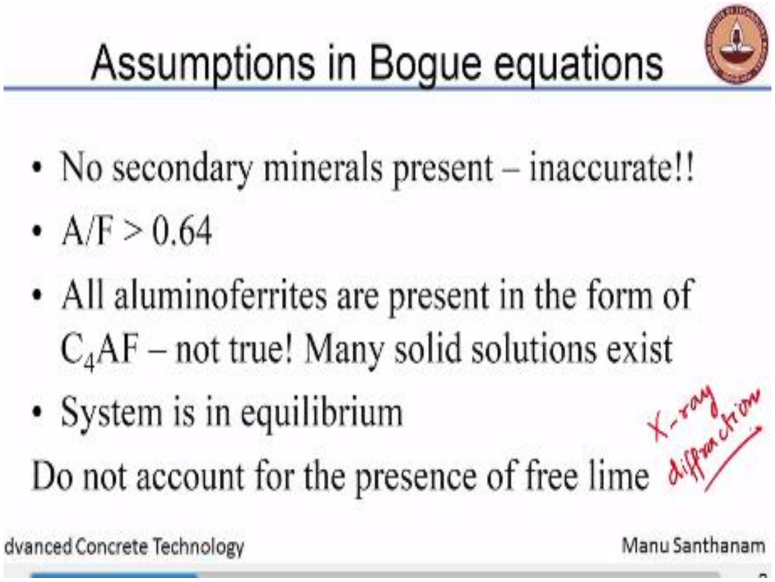

Assumptions in Bogue equations

- No secondary minerals present – inaccurate!!
- A/F > 0.64
- All aluminoferrites are present in the form of C_4AF – not true! Many solid solutions exist
- System is in equilibrium

Do not account for the presence of free lime

X-ray diffraction

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So, it is not accurate that there are no secondary minerals present, the alumina to ferrate ratio is assumed to be greater than 0.64 and there is nothing wrong with that as that holds true for the most cases. I told you earlier that the alumina ratio is in fact between 1 and 4, so quite a high ratio is typically used for ordinary portland cement. The third part is all aluminoferrites are present in the form of C_4AF.

So, it assumes that iron can only exist in the form of C_4AF but that is not correct, many solid solutions exist, I will show you later what the solid solutions are but what do you mean by a solid solution? Both the solutes and solvent are solids. Can you tell me another solid solution, commonly known solid solution? Alloys; all alloys are solid solution; steel is a solid solution, right, iron and carbon, right.

So, solid solution involves both solute and solvent are solids. So, here of course, we are talking about different variations in the formulation of calcium in combination with the alumina and iron oxide. C4AF is just one form that exists but what happens is Bogue assumed that this was the only form because of that he was able to work the calculations..

Then, the other major issue with Bogue's calculation is that he assumes that the system is in equilibrium, now we already discuss this earlier that when the raw materials come into the kiln, they spend a total of about 30 minutes in the kiln from one end to the other and in 30 minutes, it is not simply conceivable that the system would have attained equilibrium. So the system being in equilibrium is a difficult aspect to follow up it.

And this equation also does not really account for the presence of free lime but that is not really a problem, we can always do a small correction in the first equation, when you are determining the C_3S content to account for the free lime also, but that is not really a problem. The problems lie in these assumptions some of which are not necessarily correct in all situations, so because of that we call these compositions as potential compositions.

That does not mean that you will have exactly these compositions when you analyse the cement when it is produced, so how do you check the exact compound composition? You will have to utilise certain characterisation techniques, the most principal one that is used in a cement plant is called the X-ray diffraction technique. Now, earlier I talked about X-ray fluorescence, which is a different technique. Fluorescence determines the concentration of elements present in the sample, X-ray diffraction is able to characterise the crystal in species that are actually present in your sample, the different crystal in species because what happens is in this case, the X-ray that comes in strikes the specimen and based on the crystals you have different orientations of these crystals at different angles, different crystals tend to reflect these X-rays.

So, we call that process reflection of the crystal planes as the diffraction of the X-rays and this happens at different angles. So because of that you can utilise X-ray diffraction to determine the exact compound composition of the cement and there are ways to quantify, there are different ways to quantify the pattern that is obtained by the X-ray diffraction and that gives you the exact compound composition.

So, if you are publishing a research paper for instance, and you determined all oxide compositions through either chemical analysis or X-ray fluorescence as the case may be, your paper has a likely chance of not getting accepted unless you are reporting your compound compositions as calculated by a proper characterisation techniques such as X-ray diffraction, if you simply doing Bogue calculation and saying that potential compound composition is so much, then if your discussion really involves the use of a compound composition.

You need to be sure that you have used some sort of a characterisation technique to come for those numbers, so very often papers get rejected because you have not done the right way of calculating these compositions. Anyway, so it is not all that simple as it sounds, there is a lot more happening inside the kiln, as you can rightly imagine the process in a kiln takes place at very high temperature.

There are several possibilities that can exist when you are processing materials in a very high temperature. Especially, the way that you cool the system can determine a lot what kind of compounds will form, what crystal sizes will actually end up forming and what will be the approximate reactivity of the compounds that form. We already know about this from the formation of igneous rocks.

Igneous rocks are formed from molten lava and when this lava solidifies within the earth's crust, we form the intrinsic igneous rocks which cool slowly and therefore, have very large crystal sizes. When you have extrinsic igneous rocks like Basalt, they form on top of earth’s surface, there is air cooling; cooling rates are rather rapid because of which you form fine crystals and then you have the pyroclastic, the ashes for example, which are cooling almost immediately which leads them to have an amorphous, siliceous nature.

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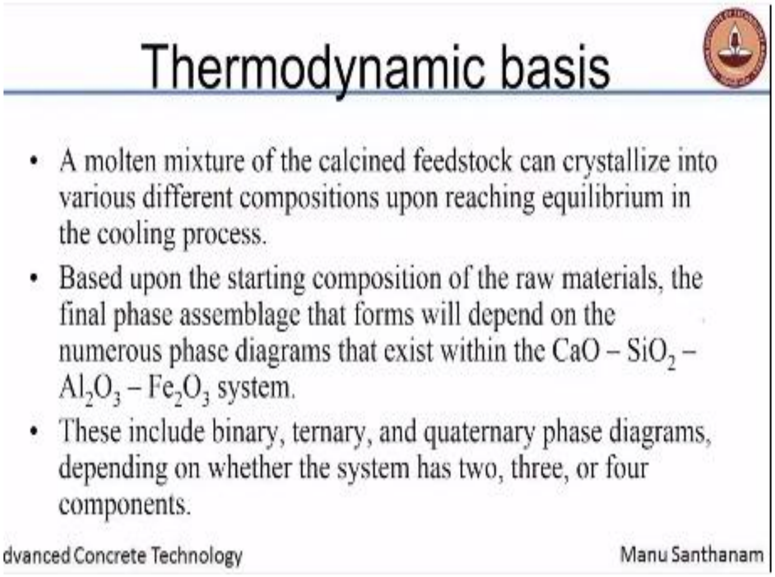

Thermodynamic basis

- A molten mixture of the calcined feedstock can crystallize into various different compositions upon reaching equilibrium in the cooling process.
- Based upon the starting composition of the raw materials, the final phase assemblage that forms will depend on the numerous phase diagrams that exist within the $CaO – SiO_2 – Al_2O_3 – Fe_2O_3$ system.
- These include binary, ternary, and quaternary phase diagrams, depending on whether the system has two, three, or four components.

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Now, you can imagine that similar possibilities obviously, exist within the kiln, where these compounds are subjected to very high temperature reaction, so there is obviously a strong thermodynamic basis, so the molten mixture of the calcined material can crystallise into different compositions based on the extent of equilibrium achieved and the cooling process. How much time the material actually spends in the system and what is the rate at which the cooling happens can determine to a large extent, the kind of compounds that end up forming in the system. We know that the 4 principal oxides are calcium oxide, silicon dioxide, aluminium oxide, and iron oxides, so essentially ours is the 4 component system. Now, this 4 component system does not mean that all the compounds or all the oxides are interacting with each other.

There can be instances when you can work with certain binary compositions, certain ternary compositions, sometimes quaternary compositions. Phase diagram being quaternary means there are 4 variables involved, there are 3 compositions and 1 temperature, a ternary phase diagram implies there are 2 compositions and 1 temperature and binary means, there is a single composition along with temperature.

So, phase diagrams are something that you have learnt in your basic chemistry, you must have learnt basic thermodynamics, when you talked about how you can determine the congruent melting of certain mixtures, you can determine temperatures at which you can form complete solutions and so on and so forth. The simplest example obviously is a solution of sugar and water right.

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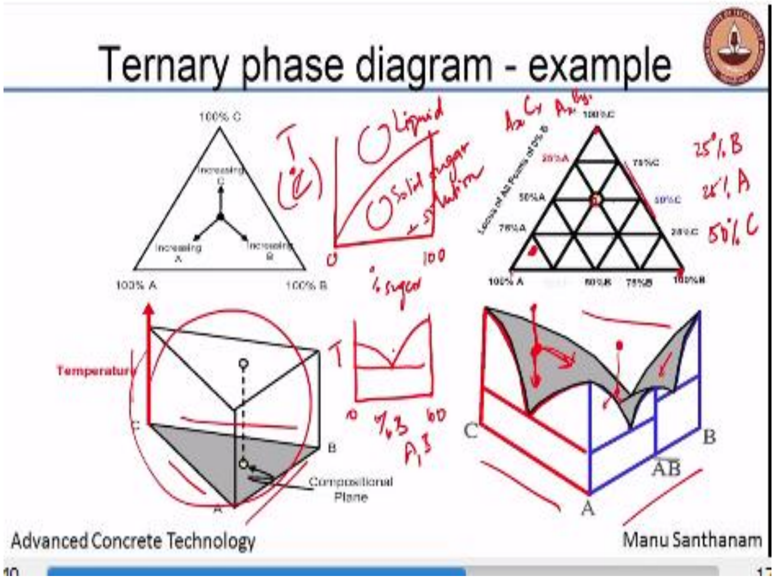

Ternary phase diagram - example

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If you have a solution of sugar and water, what will happen? As you keep on increasing the temperature, the solubility of sugar will keep on increasing. To plot the diagram, of sugar, with temperature in degrees Celsius on the y-axis and concentration of sugar on x-axis. So, as the temperature increases, what will happen?

How will this graph look like now? So, here 0, you have 100% sugar, as I increased the concentration, I need greater and greater temperature to make it a liquid solution, so obviously at 0% sugar, where am I? I do not need; I basically can make a solution at any temperature, right, at 100% sugar, I need to have very high temperatures, so my diagram will look like as shown in above slide.

That means that when I am above the phase line, I have completely a liquid phase, when I am below, I have a mixture of solid sugar and its solution, and probably I will come to a temperature beyond which sugar will not dissolve at all, I may not be starting here from 0. Beyond a certain temperature, the sugar may not dissolve at all. So at that point you actually have 2 phases existing that is solid sugar and liquid water.

So, here what we are talking about is the simple phase diagram between sugar and water. Now when you have 2 solids, which are interacting with each other like an alloy, you have a slightly different system, so if you plot the 2 solid phase diagram as a binary phase diagram, you will have, let us say the 2 solids are A and B, so if you plot the diagram in terms of percentage B starting from 0 to 100 and that is your temperature axis, what happens in that case.

You often see that for example when you have a copper and zinc phase diagram to form brass or copper and tin to form bronze. You often see some kind of behaviour which looks like the graph right below the phase diagram, you see some congruent melting, that means for combinations of materials, the melting temperature goes down. That means at a lower temperature for a certain combination of A and B, you are able to form from the liquid state, a completely solid mixture.

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So, what will happen here in these 2 regions? There will be a liquid phase and the solid phase in both these regions, depending on which side of this point, you are at you will have either have more of B in the solid phase or more of A in the solid phase. In the iron carbon system we have a point called the eutectoid point, which is a 0.077% carbon. If you are exactly at the eutectoid point and you reduce the temperature from above 727°C to below 727°C, the austenitic phase gets completely converted to a phase called perlite; perlite is the mixture of ferrite and cementite and that transformation happens exactly at a known concentration of carbon and a perfect temperature of 727°C.

But that again all these phase diagrams assume that there is some equilibrium in the system, now when there is no equilibrium in terms of rapid rates of cooling, you actually end up forming very different microstructures, so those of you who learnt steel would have learned that there is different kinds of steels that can actually form from the austenitic phase not just perlite, you can form from ferrorite, you can form benite, right you can form martensite, depending upon the rate at which you are cooling the system, right.

All these phases that form in the steel have very unique characteristics with respect to their strength and their ductility. So similarly in a cementitious system what we have to do is; work through these 4 components that is calcium oxide, silicon dioxide, aluminium oxide, iron oxide and try to represent or try to understand the interactions that can take place at these different temperatures between these 4 components.

The problem with the 4 components system is that a 4 component system cannot be represented easily in a 2 dimensional plane, why? Because 4 components are almost like the 4 corners in a tetrahedron and then representing the temperature axis becomes a very difficult task, so what we tend to do is; we break it into 2 ternary systems.

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We break it into the C-S-A ternary system and the C-A-F ternary system. Now in all these cases when I talked about sugar water, when I talked about alloys like A and B, right, I was talking about a binary system, I had only 2 components. In a ternary system, I know I have to keep 3 components, so when I have 3 components, how do I still represent the temperature?

What I can do is; composition can be represented in terms of this triangle, in the plane and temperatures is represented as the normal to the plane. So temperature is represented here as the normal to this plane, while the composition is exactly a triangle. So, how do we represent composition on a triangle? Each vertex represents the pure phase or pure component.

What is the difference between a phase and a component? from your understanding of the thermodynamics; so in the sugar water phase diagram, which are the components? Sugar and water. What are the phases? It is a liquid, solid, the solution that is right, so those are the phases. So phase and components are different, in this case, what happens is; in a ternary diagram, you are plotting a diagram in such a way that each vertex of the triangle is a pure phase.
So, 100% A, 100% B and 100% C in the ternary diagram and all these lines that are parallel to the opposite side from a given vertex, The line you draw parallel to that those are composition lines for component A that means that if you are 100% at one line, other could be 75%, 50% 25% etc.

Whereas, similarly this is 100% C that 75% C, 50% 25% and this line is A and B line, right, so you are not getting any C in that case, C is 0%, so that way, you can actually represent the 3 components phase diagram and this point marked here is what now, what is a composition that that represents? Here, that means it is 25% B, with respect to A it is here, again is 25% A and 50% C.

So, that will be the composition that is reflected by that point there. So now what you have done is; broken down this first of all we broke down the quarterly phase diagram into 2 phase diagrams; C-S-A and C-A-F. To tell you how this diagram is actually constructed, now you have the compositional plane and then you draw the normal to that plane and mark that as a temperature.

Now, these 3 components; A, B and C, when they are in a molten state and you start cooling down from that molten state, you can have several different interaction taking place, some of these interactions will be binary interactions that means compounds A and B may have binary interactions for example, what is shown on this side, the blue curve is all the binary interactions that take place between A and B.

The red curve is all the binary interactions that take place between A and C, on the other side; you will actually have the binary interactions that take place between B and C. And then in between you see these surfaces which are slopping in different directions. Now if you are at a temperature that is here what sort of a phase do you have? You only have a molten liquid phase because there is no possibility of a solid forming.

But when you start reducing the temperature from that point onwards, you come to the boundary of that surface. Now from that boundary of the surface; since it is not a curve, and actually a surface, you can go down in several directions. So based on the initial starting composition, you will have a defined part which the melting line will take or the solidification line will take.

Talking about the grace surface that is inside, I have plotted melting temperature. You bring down the temperature,you intersected this solidification surface and you can come down in different ways across the surface. So at a temperature below that you start solidifying different phases.

Now, what phases you solidify will depend on where you are in the compositional plane. So supposing you are somewhere here in the compositional plane, what do you think would be the approximate makeup of the compounds that you get ultimately? The binary line of A and C, if you are somewhere here, what do you think will be the approximate composition that you will get?

You will definitely get a phase that is Ax, Cy. Where there is x is greater or less than y? x should be greater than y, right because you are closer to A than to C, so you will get some phase which is Ax Cy, you may also get Ax1 By1, which is obviously going to be very rich in A because B is close to 0. So depending on where you are in the composition plane, the final structure that you get will be a mixture of phases that are either rich or deficient in one of the components.

So, depending on your location in the composition plane, we can actually now figure out where you can end up with, so we know that in a cementitious system, we want to end up in a system that has a large amount of C_3S, a smaller amount of C_2S, a small amount of C_3A and probably a very smaller amount of C_4AF. So out of these, 3 of those compounds can form in the phase diagram that we call as a CSA phase diagram.

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C_3S, C_2S and C_3A, all this will come in CSA phase diagram. So again we have to choose a composition initially, so that we know exactly that we are close to the CaO rich portion; calcium oxide rich portion, when we are designing Portland cement, we need to choose raw materials so that we have a majority of calcium oxide in a system. This can be quite complicated if you have not had exposure to the phase diagrams for a long time.

You may have to do a little bit of additional reading from a basic chemistry textbooks and determine what are these phase diagrams all about, what is congruent melting and how do you detect its form and so on. Of course that is not a matter of test in this course but again from the point of your understanding what kind of components can actually form, you need to have a basic information in thermodynamics to get that idea.

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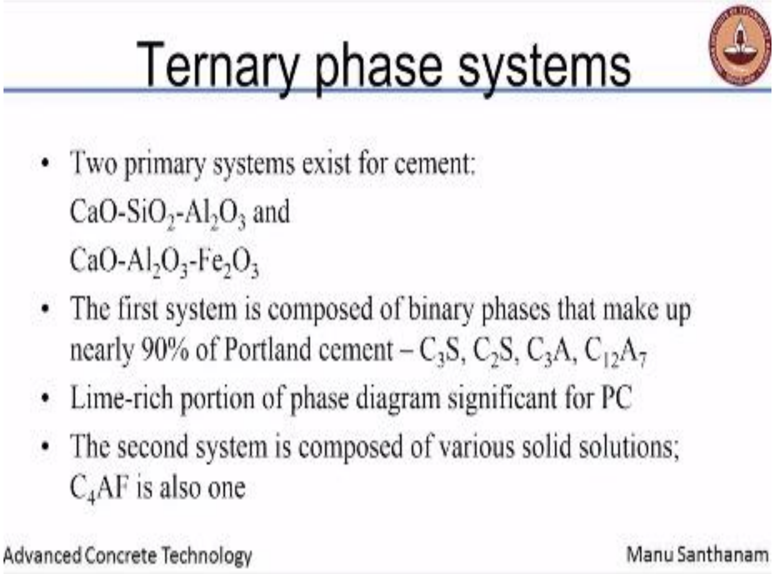

Ternary phase systems

- Two primary systems exist for cement:
  $CaO-SiO_2-Al_2O_3$ and
  $CaO-Al_2O_3-Fe_2O_3$
- The first system is composed of binary phases that make up nearly 90% of Portland cement – C_3S, C_2S, C_3A, $C_{12}A_7$
- Lime-rich portion of phase diagram significant for PC
- The second system is composed of various solid solutions; C_4AF is also one

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But anyway, so, this is how you will represent a ternary phase diagram with the compositional plane on the x-axis and the orthogonal axis is basically a temperature plane. All right, so again, as I was telling you earlier there are 2 primary ternary systems that will exist for cement; one is the CSA ternary system and the other is the CAF ternary system. Now, interestingly the first system itself solves most of our problems.

Because it is composed of binary phases that make up nearly 90% of your Portland cement, that is C_3A, C_3S, C_2S and sometimes, you also get this phase called $C_{12}A_7$, depending upon the extent of alumina you may have in your cement. The lime rich portion is the one that is significant, as we talked about steel alloys, about the iron carbon alloys for steel, the portion that is relevant is obviously the one which is rich in iron.

Because if you have too much carbon in you steel, it becomes very brittle and becomes unusable as for as the structural steel is concerned, so we generally work with carbon contents of < 0.1% as for as the steel is concerned; structural steel is concerned. So, there we get sufficient amount of ductility and so on, so just like that in cement chemistry, we want to work with the lime rich portion of the ternary phase diagram.

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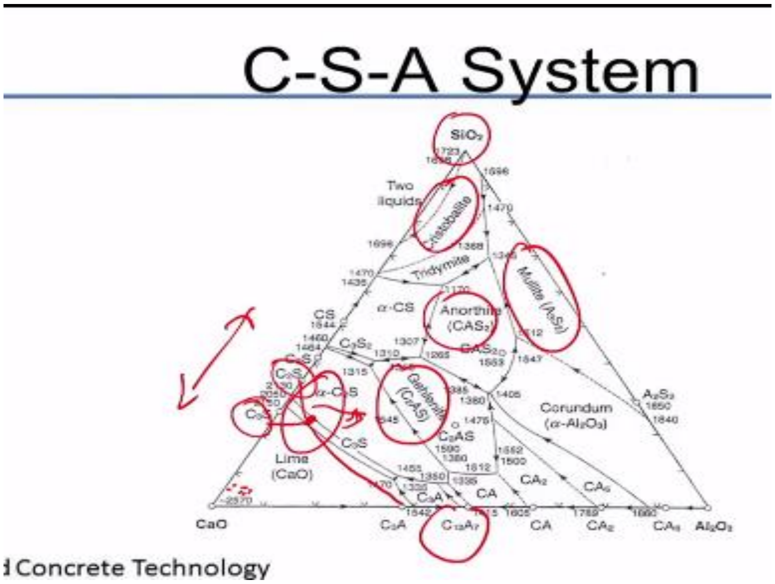

C-S-A System

The second phase diagram that is CAF is a very complicated diagram because there we have to actually analyse ternary phases which have an equivalent composition of C_4AF, so I will just show ternary diagram that is CSA because this is what is most important from our perspective of cement chemistry. So I want you to concentrate here on the lime rich portion, on the left (marked with arrow) that means we are close to the calcium oxide vertex of this triangle.

So, obviously when you are very close to lime rich portion, you are basically going to form CaO because you are driven of carbon dioxide, you will ultimately end up forming primarily calcium oxide in the system but when you are closer to the α-C_2S portion which is circled, you start interacting a lot with the silica. When you go a bit to the right, you also start forming some phases that are rich in alumina and as simple as that.

So, again if you look at this diagram here, your C_3S is located here, C_2S is located here that means in terms of oxide compositions, I should be somewhere around the region between them, so that I can end up either in C_2S or C_3S and I can form some C_3A and sometimes we may end up forming $C_{12}A_7$ depending upon the extent of alumina that I have in my system.

Now, is interesting to note that when we actually learn about different types of supplementary cementing materials like fly ash and slag, you may actually see some other phases which are representative of where they are in these phase diagrams, for example in fly ash or low calcium fly ash, where you do not have enough calcium oxide, where will you be in terms of initial composition?

You are, somewhere close to the silica alumina line. So what phase do you expect to find in fly ash? Low calcium fly ash is deficient in calcium oxide, so you are obviously close to the alumina silica line, so what crystalline phase you expect to find in fly ash? So, typical low calcium fly ash is nearly had 50% silica and about, 25% alumina.

Again, please remember fly ash has been collected from coal that is being burnt at high temperatures, so some of that fly ash will not be amorphous; it may actually have these crystalline components like, mallite, which you often find mallite in fly ash. What about slag? Now, slag has approximately equal contributions of calcium silica and probably a very high contribution of alumina also.

So, you should be close to the centre, right, so what should you form? I have already circled it, you should form the galenite phase; C_2AS phase or sometimes it can even form probably close to anorthite, CAS_2, depending upon the high content of silica. So somewhere there will be the components you may get slag; not necessarily you will, because blast furnace slag is obtained by rapidly cooling the molten slag.

And you may actually not have any crystalline phases that form in the system at all. Because of rapid cooling, you actually end up forming a highly amorphous phase but if you were to find any crystalline phases, there would be somewhere in that range, galenite to anorthite, Silicafume is almost a very high purity silica, 90%. So, if you find anything there, which is crystalline, mostly you will not because it is highly amorphous because the particle sizes are so small that cooling happens almost instantly. So there if you have to find any crystalline components, it will have to be something like cristobalite. Cristibalite is basically a high temperature form of quartz, because the industry from the silica fume is collected the temperatures can go very high up to 2000°C, so you can actually form this cristobalite phase, if indeed, a crystalline phase can form with that rapid a cooling. So silica fume that is collected typically is completely amorphous, similar to slag. Fly ash on the other hand can have sufficient degree of crystallinity also.

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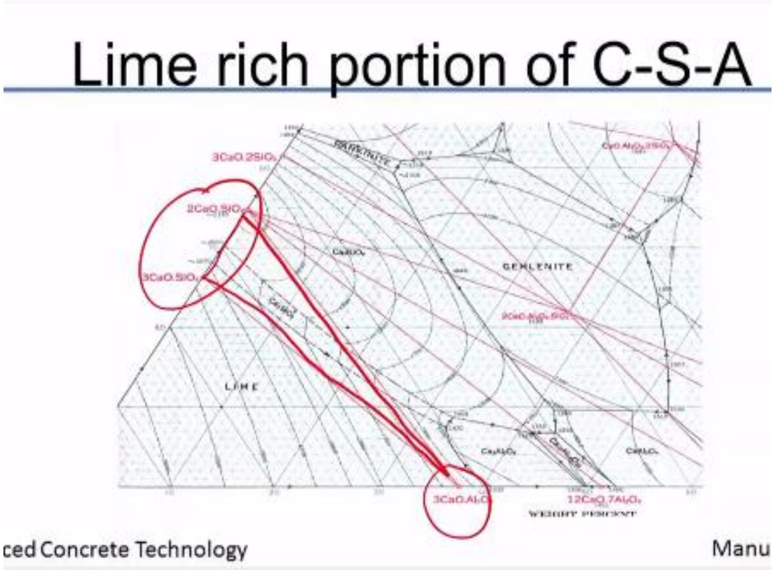

Lime rich portion of C-S-A

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So, let us move forward and look again at this diagram. Just for your understanding I have actually produce this from an actual sheet that is used by cement producing companies and this sheet is obviously is prepared by, not civil engineers of course; maybe some chemical engineers, but more importantly geologists because a real contribution from geologist can help us understand the thermodynamic basis of formation of phases and solids.

Because again, we are applying the study of rocks here, right? Solid phases are forming because of combination of oxides from a molten phase, I have shown you the lime rich portion of the diagram we can see here, you see C_3S and C_2S and you also see C_3A here and these 3 lines that are drawn here mark the boundary of the compositions that you would like to start with to make a Portland cement.

So, again our life is made easier by the fact that we already know this and we can start out by choosing an appropriate composition of a raw material to ensure that we are getting the right contributions of calcium, silica and alumina.

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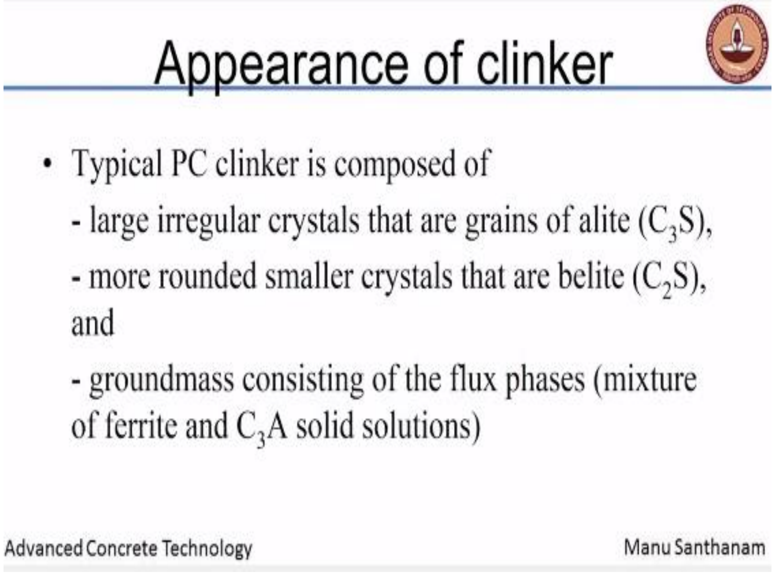

Appearance of clinker

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

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That would be confusing enough because ultimately as cement chemists or as concrete technologists, we do not really have to do much with the production of cement, we just take what we get, unfortunately a lot of current issues in concrete technology because of use of low water cement ratios, because of use of different types of chemicals as admixtures, we can also crop up because of incompatibility issues with the cement and sometimes understanding how the cement is formed in the kiln through all these reactions can actually help improve our understanding of why the mechanical behaviour or the durability behaviour or the workability behaviour is happening in one particular way. However, for a civil engineer, all this can be a little bit too much to take in.

Understanding thermodynamics, quaternary phase diagram, ternary phase diagrams could be very difficult concept for civil engineers. We have to concern ourselves more with ultimately what the composition of the cement is in terms of the compounds that are forming and in terms of the crystal size of the reactivities. For that we need to understand what is the appearance of the cement clinker under the microscope, so that we can understand what is it that contributes to the high or low reactivity of certain phase. So if you take typical Portland cement clinker and put it in under the microscope again, it is not as simple as just taking clinker and putting under microscope, what you need to do is; first embed it in an epoxy, then need to polish it to ensure that you are able to expose the clinker surfaces and perfectly maintain a flat disposition. And then, you have some sort of a liquid which is used to etch the clinker surface. Etching is required to ensure that you are able to show the distinct contrasts between the different phases that are there in the cement. So this process can be quite involved in terms of the sample preparation. Anyway, so once you do that and you look under the microscope, you will see that you will have large irregular crystals that are grains of Alite; C_3S

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You will see more round smaller crystals in some cases, smaller sometimes, you may also find bigger crystals that are of Belite or C_2S and you find that these crystals are surrounded by fine; very fine crystalline materials which form the ground mass. Ground mass is the name given to extremely fine system of crystals that cannot be discerned even by viewing under the microscope.

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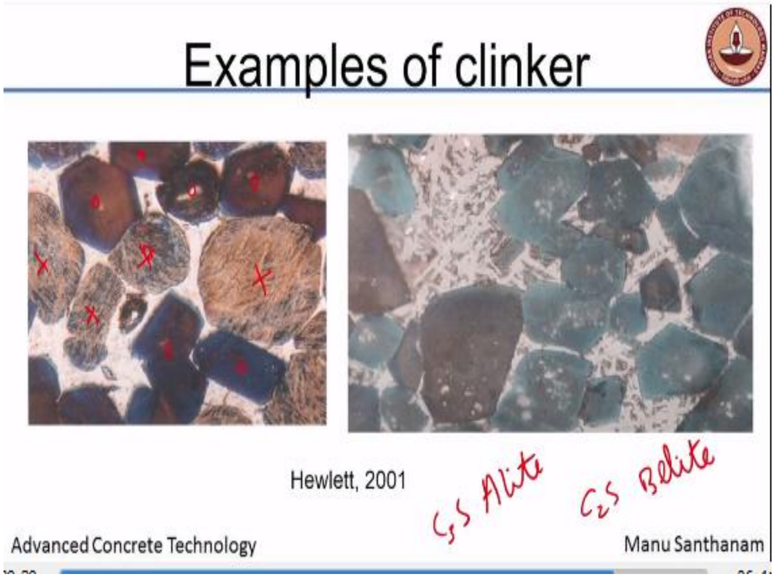

Examples of clinker

Hewlett, 2001

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Optical microscope is not good enough to figure out the crystal nature of these compounds. So you have the ground mass which consists of the flux phases, which refer to the aluminate and aluminoferrite. So just to give you an example of such an image, you see here there are some irregulars shaped crystals, there are some rounded crystals, which have a more smoother surfaces.

So, the irregular shaped crystals are C3S, otherwise we call them as Alite, the rounded crystals are Belite. Why this name; Alite, Belite? Whenever, you look at the mineralogy; study mineralogy there are all minerals which are usually given the names ending with ‘ite’. Quartzite, ettringite, anorthite and so on and so forth, so ‘ite’ is a common methodology of naming crystals. So in cementitious material somebody was quite a genius and named them Alite and Belite.

And sometimes they called C_3A as Celite; that does not mean that C_4AF is called Delite, it simply called ferrite. So the idea is to name these crystals in terms of the usual connotations that we have with crystalline components when we named them in real life as they occur in nature. So these are chemically formed crystals or synthetically formed crystals but we do give them these names Alite and Belite.

Because they are not truly C_3S and C_2S as will be shown in the next couple of slides. So here you have the rounded grains which are that of Belite. One common feature that we will find in Belite is these striations, the lines in brownish crystals in the left side image. Those striations are common features that can help you distinguish the Belite grains from the Alite grains, on the right side you actually have an image that is mostly Alite; C_3S

So, you have a cluster of Alite particles and you can also see this ground mass here what is in between, so that is basically a mixture of your C_3A and C_4AF, especially in this right side image, there is some phase that is looking browner, the other face looks very bright. So which do you think is the ferrite phase and which is the C_3A phase. You may think like brown is ferrite, because iron is there. But this is the optical microscopy. So, the intensity of the reflection from the surface will depend on the density of the material, so denser the material, the greater will be the intensity. So the iron bearing phases will actually look bright. When iron is there, the phase is very dense. Because of that the reflection will be very high, so you will see these as extremely white, whereas the brown phase will be your C_3S.

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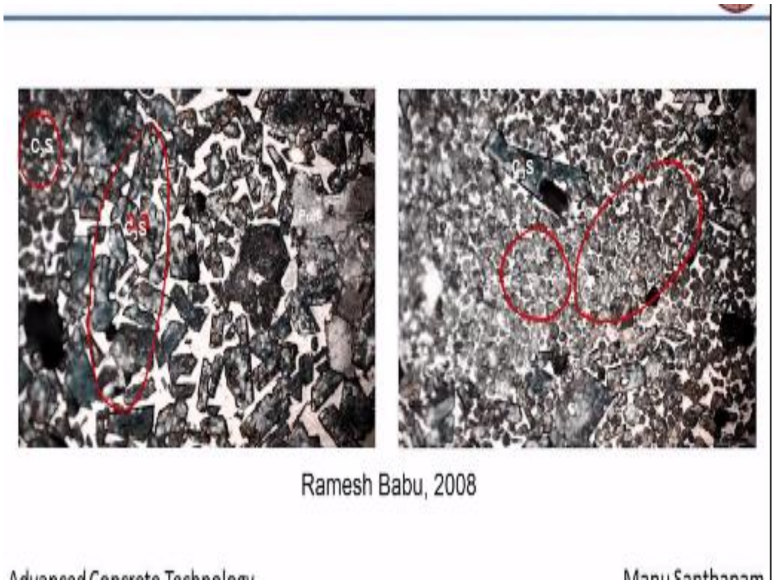

Ramesh Babu, 2008

If you have pore inside or void inside, it will be dark, pores or voids will be dark coloured or they may reflect the colour of the epoxy. Whatever epoxy is used to impregnate and polish these surfaces and those compounds may be sitting in the pore and that is what will be shown up in your optical microscopy image, I will show you another picture here and we can see here that these are crystals of C_3S, you can see very clearly on the image on left, crystals of C_3S, there are clusters of C_2S also. In the image on right side you can see the another cement which has very large clusters of C_2S and less grains of C_3S. Incidentally both of these were from 2 different cement samples that were collected as clinker and then a known amount of gypsum was added, these were ground and then they were made into cements.

There was a study on heat evolution of the cement surface done subsequently but before that we wanted to understand whether the crystal structure of the clinker can be linked to the extent of heat that is released from the cement. We will talk about that in more detail in cement chemistry but you can see here that 2 cements or 2 cement clinkers that are both intended for 53 grade cement can have quite a different microstructural make up.

So, this is because of the type of kiln operations that are processing these materials inside, so you do not always get the same appearance as I showed you in the previous, these are very classic pictures, obviously you do not exactly get that all the time. This is one of the examples that we produce from one of a recent study. So, I will end today's lecture with this slide. So we were talking about typical composition of cement.

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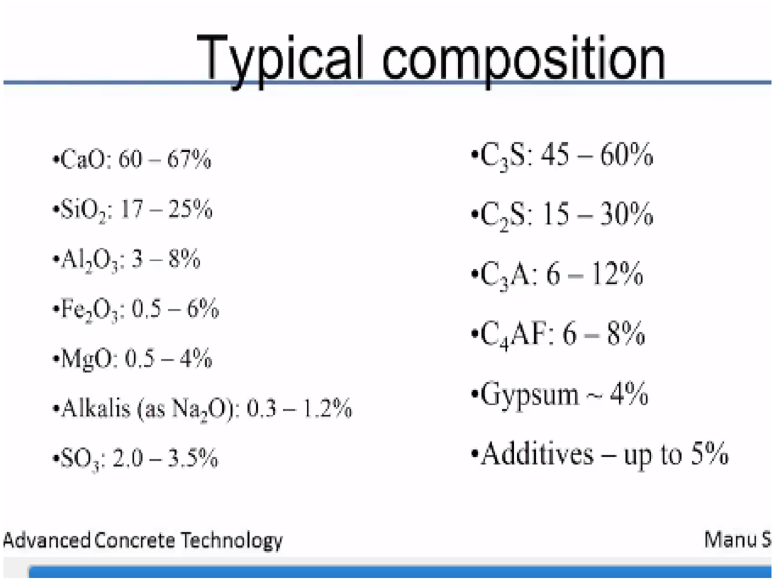

Typical composition

- 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%

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As I told you, we are in the lime rich portion of the phase diagram, so we have nearly 2/3rd of cement composition in terms of oxides is your calcium oxide, about 17 to 25% of silicon dioxide, 3 to 8% of aluminium and 0.5 to 6% of iron oxide. Magnesia can be as high as 4%, it depends on your source of limes stones, obviously. And alkalies are about 0.3 to 1.2%. You will find that alkalis in Indian cements are primarily of the order of about 0.6 to 0.8%.

Whereas, if you go abroad, most cements they would have higher alkali contents. There is a reason for this, generally higher alkali contents tend to favour early strength gain and in specific conditions where you form certain types of cement clinkers, you find that alkali contents are more in those cements. Again their special considerations as to why this is done and our cements are a quite different in that perspective.

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Sulphate is of the order of 2 to 3.5%. Most of these sulphates are obviously attributed to the gypsum that is added in the end, 2 to 3.5% is the extent of sulphate. So all these results in the compound composition once again as I told you, you want to have nearly 50% C_3S about 15 to

30% C_2S, C_3A is about 6 to 12%, C_4AF is 6 to 8%, gypsum mix of about 4.5% and you are allowed up to 5% of additives in your final Portland cement formulation.

In the clinker generally, you will see that the extent of silicate is about 80% and the extent of aluminates is about 20% in the clinker and that holds true for most types of cements, whether it is low heat cement, whether it is rapid hardening cement or any other cement that you consider, the total silicates will be around 80% and the total aluminates will be around 20%. So, we will stop with this for today.