

Advanced Concrete Technology
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Lecture - 02
Cement Production - Part 2

Good morning everybody. So in yesterday's class we were talking about the different raw materials that are used for cement. We talked about schematic layout of the processes that were involved in the manufacture of cement and we also looked at some of the challenges that cement production lays out and essentially how we can think about overcoming those challenges for the future.

One thing I did not put quite in perspective was that if we produce only ordinary Portland cement for the next so many years, our limestone reserves which are required to actually produce this Portland cement will probably last only about 50 more years. So beyond that what do we do? I am talking about the good quality limestone, please remember I told you yesterday that much of the limestone that is mined at cement plants is not usable for cement production.

Because it has got lot of impurities, so you need something which has a fairly high content of calcium oxide and only certain part of that limestone actually satisfies that requirement, because of that lot of the limestone is not usable, now as I was saying earlier the limestone reserves which are necessary for maintaining cement production over the next few years, assuming that we only produce ordinary Portland cement.

These reserves will last only for 50 years. So what we have to do obviously is to plan in a big way to ensure that we are able to produce cements which are blended for the most part that means we also incorporate other supplementary materials in the combinations with cement and ensure that we are able to extend the limestone reserves as much as possible.

And the second important aspect is, we obviously have to make some use of the material that is not usable currently in cement production that means the lower grade limestone which is found at the limestone mines that also needs to be made use of to ensure that we get the best out of all the material that is present.

Anyway coming back to the processes that we were talking about, pulverization as you know is a very important process you need to grind the material down to a smaller size to ensure that you get better blending as well as burning in the kiln.

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Blending of raw materials



- Choice of blending process
 - Wet or dry
- Wet process – more uniform mixing
- Dry process – higher output, lower power consumption (3000 kJ/kg as opposed to 5500 for wet process)
- Dry process with precalciners are the order of the day; almost no wet process plants today...some semi-wet (when limestone is wet)

So now let us move on to the next process, the blending process itself, how we actually mix the raw materials together. Now generally there are two choices as I was telling you earlier. In the past, a lot of mills were having the wet process but today almost entirely all the mills operate with the dry process. Now obviously when you mix something, when you mix powders in a wet state you can assure that the mixing is more uniform, the blending is better.

When you mix powders in a dry state, you need to be doubly sure that you have mixed it thoroughly so that there is an intimate mixture of the materials that has happened. Now obviously since water has been used in the wet process, a lot of the energy that is spent in the kiln operations will be spent towards drying off this water, removing the water whereas in the dry process you do not have that problem.

So in a wet process approximately for every ton of raw material that goes in into the kiln about 1-ton extra water is also there. So you can imagine how much energy it will take to actually dry off the water. Now why does it take more energy to dry off the water because water has higher specific heat capacity exactly, amongst all the materials that are there in the raw materials, I mean compared to solids anyway water has a much higher specific heat capacity.

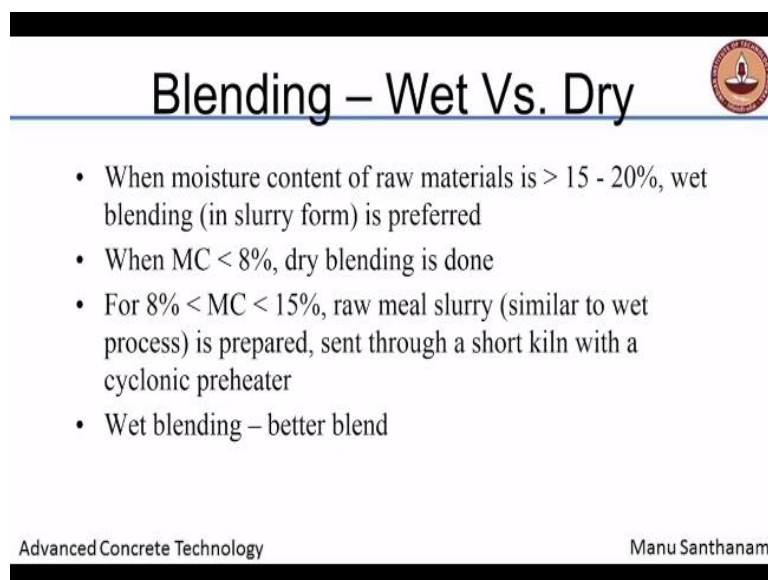
Because of which you need to spend more energy in trying to dry off the water and that can increase the length of the kilns considerably, and as a result since your half the raw material that is actually coming into your kiln is actually water, the amount of output that you are getting from this process, the amount of clinker that you generate in this process is also half of what you put in.

On the other hand, in a dry process most of the clinker, most of the material that are sent in as raw material is coming out as clinker, of course you have to account for the loss of carbon dioxide from the limestone that goes without saying in any of the processes but you can see that there is definitely higher output and lower power consumption, 3000 kilo joules per kilogram is estimated for the dry process as opposed to about 5500 for the wet process.

So it is almost half the energy that you require in the dry process for the kiln operations, okay. The lower power consumption is primarily related to the kiln operations. So dry process is definitely preferred but the issue is that sometimes you may need to make alternative choices, you may need to have a certainly different approach, because the wet process dry blending has to be decided on basically based on the state of the raw material that is being mined, much of the limestone that is getting mined must be in a wet condition.

You know that in any quarry whenever you dig for the stone, you will also get lot of water, right, and this water essentially makes the raw material extremely wet.

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Blending – Wet Vs. Dry

- When moisture content of raw materials is $> 15 - 20\%$, wet blending (in slurry form) is preferred
- When $MC < 8\%$, dry blending is done
- For $8\% < MC < 15\%$, raw meal slurry (similar to wet process) is prepared, sent through a short kiln with a cyclonic preheater
- Wet blending – better blend

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So if the moisture content is very high more than 15 to 20%, the wet process maybe a viable alternative to doing your kiln operations. So, because you already have so much water present in the raw material you only need additional little bit of water to actually get the slurry prepared for the wet process to do the blending and then this water has to be driven out in the kiln operations.

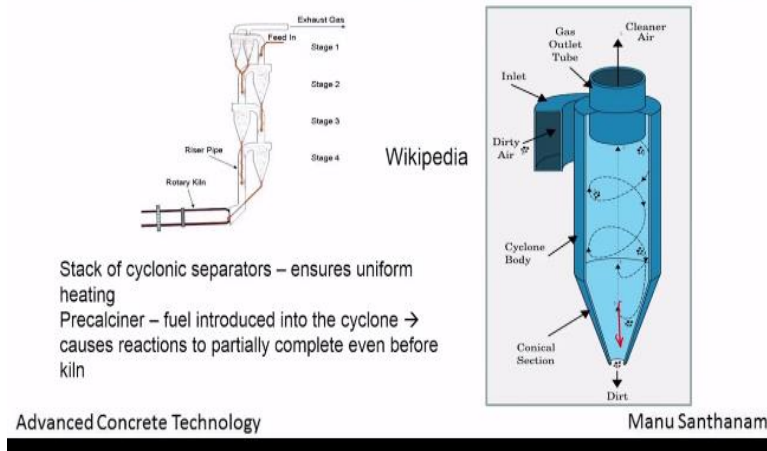
So essentially it goes to state that if you have moisture content which is very high in the raw material, you may be benefitted by using the wet process. On the other hand, when you have extremely dry material, less than 8% moisture content, dry blending is good enough, for between 8 and 15% of moisture content, it is usually good to have a precalciner with the dry blending apparatus.

So essentially you have a preheater or precalciner and then you send it to the kiln. Now the aspect that you need to worry about here is what impact does this have on the economy of the mill. For example, is it beneficial for you to actually go for a longer kiln and eliminate the preprocessing that you have to do for the raw material. So all that is basically an economic consideration that leads people to decide one way or the other.

But today it has turned out that almost all the plants seem to have the preheater, precalciner arrangement along with the rotary kiln and they prefer the dry process. Alright so, it goes without saying that for the wet blending you get a better blend but that is the material today because we usually work with the dry process, okay. Alright, so some details here are presented for the preheaters and precalciners.

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Preheaters / Precalciners



You might have heard about cyclonic separators right; cyclonic separators essentially separate out low weight material from heavy weight material or dust from heavy weight material. So here you have an example of the cyclonic separator, you see that you have a cyclonic action of the air that is coming inside, right, and then it is usually used in a situation where you need to separate dust from air.

Now in a cyclonic separation what happens is, the cleaner air with the finer dust comes out of the top whereas the coarser dust goes down the cyclonic separator. Now in this case what this does in the preheated tower is that it creates a uniform mix of the raw materials that is actually coming in because of the cyclonic action there is a uniform mix that is getting created.

At the same time, the mix is actually going down to the cyclone because it is heavier obviously than the air. So the mix actually goes down in the cyclonic separator and here instead of separation, the action of the cyclone is more intimate mixing of the raw materials. At the same time since there is cyclonic separation of the particles when you are supplying the heat, there is more uniform heating possible for the particles.

So you get several things accomplished at once not just preheating but it also blending well together and then it is coming out of the precalciner. Of course, in a true cyclonic separator what comes out is dirt but of course in our case when we talk about cement production what is coming out of this process is the blended raw material which is the input feed to the kiln.

So generally as I was telling you earlier, the preheaters are arranged in the vertical stack and the material that comes in is from the top and then it comes through a series of precalciners and then gets fed into the rotary kiln, and if it is just a preheater, please remember that we talked about this earlier in the schematic depiction, the clinker cooling process, lot of the heat that is extracted from that process is fed back into the preheater.

So you can actually save a lot of energy in this entire process by feeding back that heat into the preheater.

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Burning in kiln

- Only rotary kilns used nowadays
- Typical kilns are long ~ 30 – 70 m (5 – 6 m dia)
- Length of kiln also depends on blending process
- Temperature inside kiln varies from 850 (at inlet) to 1450 °C (at the outlet)
- Reactions are not completed inside kiln; some require cooling to occur
- What comes out of kiln is called ‘clinker’

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Now moving on to the most important operation in cement production, the reactions that happen in the kiln, okay. So obviously this reaction is termed as calcination, when we burn the raw materials in the kiln we call it the calcination of the raw materials and as I was telling you earlier we only use rotary kilns nowadays, we do not use vertical shaft kilns for the many advantages that rotary kilns actually give you.

The length of the kilns we discussed earlier for wet process can be as much as 70 to 100 meters, for dry process it is probably of the order of 30 to 40 meters, okay especially when it is connected with the precalciner and then you have a diameter of about 5 to 6 meters. So you have a significantly large cylindrical steel barrel that is basically used as a kiln and I was telling you earlier that since the interior of the kiln is subjected to very high temperature to protect that steel you need to also line it with appropriate heat resistant bricks.

And depending upon the temperature variation inside the kiln, you can choose different types of bricks to line the interior, okay. So temperature varies from about 850 degree Celsius at the inlet to about 1450 degree Celsius at the outlet. Now I will show you in the diagram later that there are two temperatures that you need to look at, one is the temperature that is produced by burning that means the temperature of the gas in the kiln.

The other is the temperature of the raw materials itself. Please remember that the reactions of raw materials will get accomplished when the temperature in the raw materials reaches that level. It is not the gas temperature but the raw material temperature that is very important. So the gas temperature at the outlet maybe even higher than 1500 but the raw material temperature is only about 1450 degree Celsius when it comes out of the kiln.

Now one important aspect to understand is, the process of cooling that happens after the kiln process is absolutely required to complete the reactions, okay. The reactions do not get completed inside the kiln, okay. Now in one of the cement manufacturing processes like for example for the calcium aluminate cement, the processes get completed inside the kiln itself, the material is formed inside the kiln whereas for Portland cement that is not the case.

For Portland cement generally the reactions subsequently which happen in the clinker cooler, okay or the stabilizing part of the clinker cooling leads to the ultimate development of the cementitious composition, so that is an absolutely important aspect to remember and the material that comes out of the kiln we call it as clinker, cement clinker, and I showed you earlier the picture of cement clinker.

It is very nodular because it is formed out a fusion of different particles and when this clinker is then ground later along with the gypsum you get the finer particles of cement. So now let us look at the reactions that happen in the kiln.

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Reactions in the kiln



- The clinkering reactions involve conversion of mixtures of calcium carbonate and silica and alumina-bearing components to a mixture of special crystalline components capable of reacting with water to produce controlled setting and strength gain
- The major components in clinker are impure but well crystallized fine (ca. $<50\ \mu\text{m}$) crystals of tricalcium silicate and dicalcium silicate

So these are extremely important to understand and figure out the way the sequence in which the reactions actually take place. So there are obviously calcium carbonate materials and there is silicoaluminate materials which have to combine in some way or the other to produce the cementitious compounds. So, what you ultimately want to result in is a material that has a controlled rate of reaction with water.

You do not want the material that reacts very slowly, you also do not want the material that reacts extremely fast and that leads to a complete setting or strength or development of hardened characteristics without sufficient development of the structure. So you want something that is slow and steady and you know very well from your basic background in science that crystalline materials are definitely a lot more controlled with respect to their reactivity as supposed to amorphous materials.

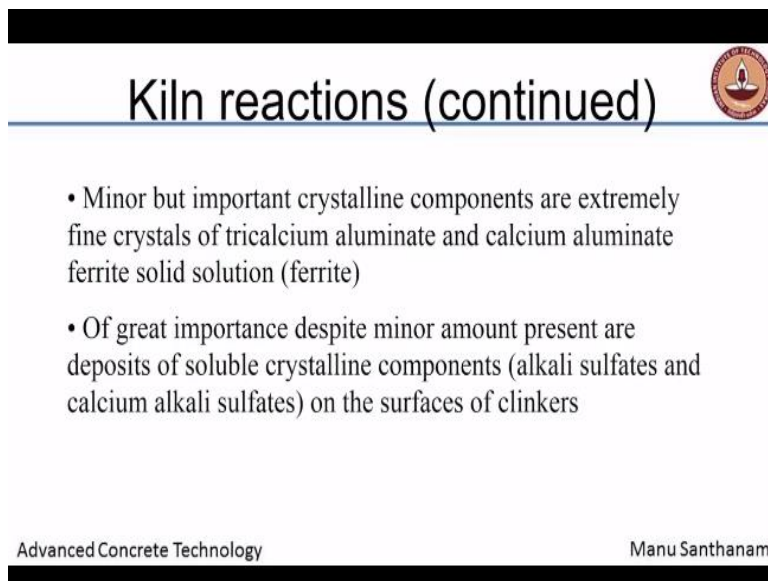
So you want the reactions to produce crystalline components, and these crystalline components should have a controlled rate of reactivity. At the same time, the crystalline nature should not be such that the reactivity is extremely low, for very stable crystal structures the reactivity can be very low. For example, if you take a look at quartz, quartz is a very stable, well organized structure and it does not have much reactivity at all.

On the other hand, there are other minerals which have a lot of irregularities in their crystal structure itself. Further the other aspect that drives the reactivity of crystalline materials is the extent of impurities that will be present inside that, okay. So here in this case of cement the

crystalline compounds that form have significant amounts of impurities and those impurities are the ones which lead to a higher level of reactivity in these phases.

So major components in clinker are, impure but well crystallized fine crystals of tricalcium silicate and dicalcium silicate. So those are the major proportions typically about 80% of your clinker is silicates, calcium silicates 80%, the remaining 20% is your calcium aluminates, okay, so more or less that balance will be maintained. Any type of cement that you take that balance is more or less maintained, that 80% is calcium silicates and about 20% is calcium aluminate.

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Kiln reactions (continued)

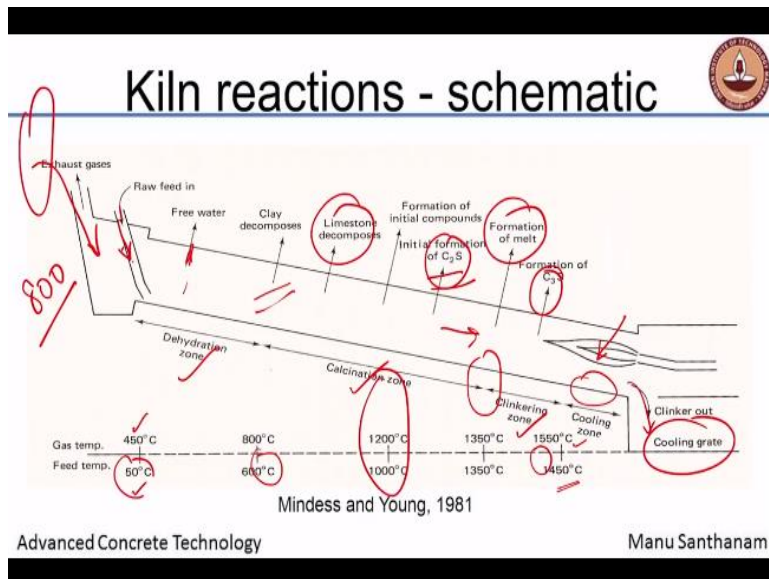
- Minor but important crystalline components are extremely fine crystals of tricalcium aluminate and calcium aluminate ferrite solid solution (ferrite)
- Of great importance despite minor amount present are deposits of soluble crystalline components (alkali sulfates and calcium alkali sulfates) on the surfaces of clinkers

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The minor but important crystalline components are the aluminates obviously, one is calcium aluminate, the other is a combination of calcium aluminate and calcium ferrite, so we call it aluminoferrite, okay and apart from these what really gives cement its unique characteristic is the presence of the impurities and these are generally the soluble crystalline components like alkali sulfates and calcium alkali sulfates, that are attached to the surfaces of the clinker grains.

And these have extremely interesting characteristics because they lend the reactivity of the crystals that ultimately decides the early phase of cement chemistry.

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So this is the all-important diagram which tells you what is happening in different sections of the kiln. So again, if you look at this kiln, the way it is shaped obviously the material is coming in from here, the raw material is getting fed in from the upper end where the temperature again is mentioned in two scales, one is the gas temperature and the other is the feed temperature, that is the temperature of the material.

So here for example, it says 450 degree Celsius at one end and about 1550 at the other end and the material temperature comes to about 1450 at the other end, okay. Now this can vary if you have a preheater here. Then, obviously the temperature of the raw material that is coming in is already around 800 degree Celsius, because I told you earlier when you have a precalciner, we increase the temperature to about 800.

So that much of the decarbonation, that is removal of carbon dioxide from limestone gets done inside the precalciner itself. So the material that is actually coming in may have a temperature close to 800 degrees at that scale, whereas if you do not work with the precalciner, your actual temperature of the feed will start obviously slowly increasing from normal temperature all the way to the high temperatures.

So that is why here the temperature at the beginning is only about 50 degree Celsius, okay. So now what happens with the kiln, as the material comes in the first material that will go out obviously at 100 degrees is the free water, and that is quite obvious because if there is any moisture in the raw materials that has to go out first. After this when you reach around 600 to

700 degree Celsius the next aspect that takes place inside the rotary kiln is the activation of the clay.

Now, you know very well that clays are layered structures, okay, they have silicoaluminates basically with alumina octahedra and silica tetrahedra forming layers, different types of clays have different combinations of layers, some are 1:1 clays, some are 1:2 clays and so on, right, and what is between these layers typically, water molecules are there between the layers. In some other clays, there are some ionic concentration, very high ionic concentrations are there between the clay particles.

So in the case of kaolinite, water is there, so what happens when you reach this temperature of about 600 to 700 degree Celsius, you start activating the clays by separating out the layers, the silica and the alumina get activated, the layers get separated at that temperature, okay that means they are now ready to start reacting, clay on its own is not very reactive but when you heat it, when you do a thermal activation, these components of clay start getting reactive.

So what happens next is, around 900 degree Celsius the limestone or 800 to 900 degree Celsius the limestone starts decomposing, that means the calcium carbonate starts getting converted to calcium oxide by liberating carbon dioxide. So now you have activated clay particles with silica and alumina and you have activated calcium oxide. So the next step obviously is the formation of the compounds that happens around 1000 degrees temperature.

And beyond 1000 probably close to about 1100 to 1200 you have a complete formation of C_2S that takes place in the system, C_2S is dicalcium silicate. This dicalcium silicate is two parts of CaO and one part of SiO_2 . We will look at the composition more in detail in the next class. Beyond the formation of C_2S , we still have to go further, right. In certain processes in the kiln, we can stop the process at the formation of C_2S .

Why is that, if we need a cement which is rich in C_2S . So that is called Belite cement. You might come across this in research. People have looked at various combinations of high Belite cements. In high Belite cement, the advantage is that you do not need to have very high temperature in your kiln. So obviously your overall energy spent in the processes, reduced.

The trick there is now, this Belite I told you earlier it is not the most reactive component in the cement. So to get some reactivity from this would need significant amount of activation when you actually mix this material with water. So Belite cements have their own drawbacks, so there has to be a significant amount of more research done to see how well we can actually bring this out to get it to a reactive state so that it can give much better strength gain characteristics.

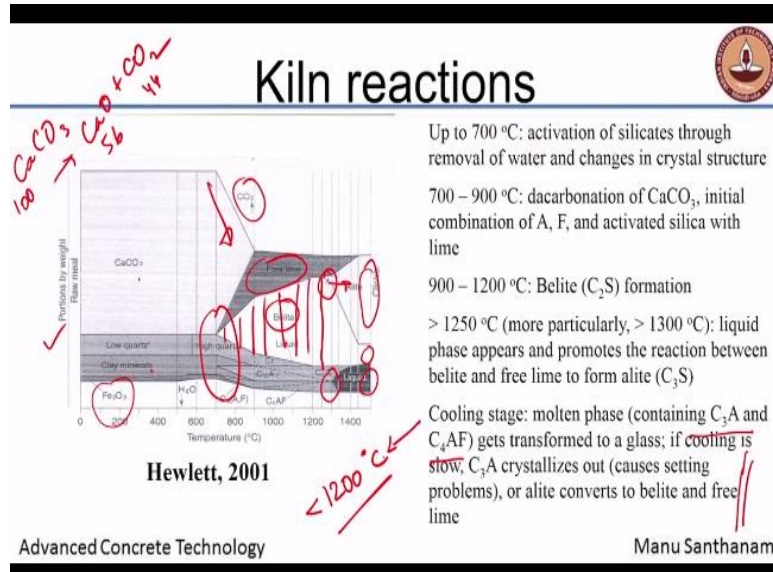
Nevertheless, what happens beyond this is that, there is an important event that happens around 1350 degree Celsius and at that point, the aluminate bearing phases that is the tricalcium aluminate and the tetracalcium aluminoferrite appear as a molten state. So appear as a molten liquid, okay, all the aluminate phases appear as a molten liquid there is the formation of melt at that point.

And what happens is, the appearance of this melt acts as a flux for the most important reaction that is conversion of C_2S to C_3S . So at 1350 when this flux appears, when this molten aluminate combination appears that acts as a flux to promote the conversion of C_2S to C_3S , okay. So this is probably from the modern cement perspective the most important process because we know that we want high early strength in modern cements and that can only be possible with the use of high C_3S contents in the cement.

So formation of C_3S happens probably in the 1400 to 1450 degrees temperature zone, and as you see here the zones are marked in the kiln as dehydration zone, we have the calcination zone, then you have the clinkering zone, and once the material is beyond the reach of the flame, right, this is the flame that is coming out from the other end of the kiln, once the material is out of reach of this flame, it is already started cooling.

But probably it is not controlling, we are not able to control the rate at which cooling is happening there, so that is why we send it to a separate cooling grate where we can actually control this rate and the control on that rate is extremely important. I will tell you the reasons in just a minute. So this is the overall process of the kiln.

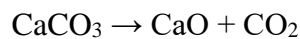
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We will take a look at it once again in a slightly different schematic which tells you about the formation of different types of compounds. So here we have the raw meal on the left side, you see the raw meal contains calcium carbonate, you have some forms of silica which may be low quartz, you have some clay minerals like kaolinite and other montmorillonite or illite whatever is present in the clay that you are using and you may have an added component of iron oxide.

If it is not sufficiently available in your raw material, you may have an added component of iron oxide that is present. What happens with increase in temperature, is that you are slowly going to convert calcium carbonate into calcium oxide. So you have CO₂ that is getting liberated, so the mass is actually getting reduced. The mass of the raw meal is getting reduced because you are liberating CO₂.

What is the reaction that liberates CO₂?



If you look at the molecular masses, CaCO₃ has a molecular mass of 100, CO₂ is 44 and CaO is 56. So what we are doing is, for every 100 kilograms of CaCO₃ that is actually coming into these process 44 kilograms of CO₂ is getting lost, equivalent of 44 kilograms. It is a gas so we do not have mass, we have mass equivalent of CO₂ is getting lost about 44 kilograms' equivalent.

So approximately, close to half of this limestone is coming out as CO₂, close to half definitely less than half but close to half, so we are experiencing a reduction in mass, right and at this point the clay is also getting activated and because of that the clay start combining to form the

initial compounds. So this is basically your free lime and that is the Belite okay or C_2S . So formation of Belite keeps on increasing so you see here that the proportion of Belite is increasing more and more until this point here.

So it is increasing all the way until here and beyond this point you start seeing the appearance of the liquid phase that is your aluminate phase, right, the aluminate and the ferrite they appear as a liquid phase as a melt, and that starts promoting the conversion of Belite to Alite. So in the end what you have is lot of Alite, some Belite and some calcium aluminates, okay. Now please remember these calcium aluminates at the end of the clinkering process are still in a liquid form.

So now these have to be cooled, okay, so this cooling stage is where this molten phase containing C_3A and C_4AF gets transformed into a glass, glass means what? Amorphous, well may be amorphous, but in this case we want still C_3A and C_4AF have to be crystalline and they are crystalline but they have extremely fine crystal sizes which makes them quite reactive but at the same time they are not uncontrolled reactive like an amorphous material.

So they are still reactive but they are fine crystals of C_3A and C_4AF that actually forms. Now what happens is, this cooling process has to be done properly, so the temperature of the exit raw material is about, exit clinker is about 1450. At what temperature does Belite start converting to Alite? About more than 1200 degree Celsius, now this material at 1450, if you are doing very slow cooling what is one problem that may occur as a result, maybe the reverse reaction may occur, like conversion of Alite back to Belite.

To avoid that reverse reaction, we have to take it to a temperature where Belite is stable, it does not want to convert to Alite anymore or the reconversion of Alite to Belite would not happen, so what do we do, we should take it down immediately to less than 1200 degree Celsius. So we do a rapid cooling to take the temperature down to less than 1200 degree Celsius.

This does two things; one is, it ensures that my Belite or my Alite will not reconvert to Belite. In the cooling stage, we are taking it down from 1450 suddenly down to about 1200 to ensure that my Alite will not convert back to Belite, and secondly the other problem with slow cooling is that I will get very large crystals of C_3A and C_4AF . You know this process quite well enough based on the formation of rocks on earth.


You know that the rocks that cool very fast, they are basically the extrinsic igneous rocks, right like Basalt, Trap and so on, whereas the intrinsic igneous rocks like granite or pegmatite are formed under the earth's crust, they have very large crystals that form because of slow cooling. So when you cool something slowly you form large crystals or unreactive material. When you form something very fast, you form extremely fine crystals.


Or if you have an absolutely fast cooling process, you will form even amorphous material. For example, in a volcano which is a part that cools the fastest, the ash, right, the ash cools the fastest because of which the ash is pozzolanic, it is a reactive silica, it is pozzolanic but that same reactivity of silica you do not want in the rocks that actually formed as extrinsic or intrinsic rocks.

In this case, you want some level of reactivity from the aluminates because of which you do not want them to form large crystals, you want them to remain as fine crystals. So this cooling process is extremely important to control the reactivity of the material that we actually getting out, okay. So these are the two important aspects that, if you are having a very slow cooling from 1450 to 1200, Alite may reconvert to Belite and you may end up forming larger crystals of aluminates and ferrites.

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Clinker Cooler





Grate cooler

http://www.cementkilns.co.uk/cooler_grate.html



Cross-bar cooler

<http://www.flsmidth.com/en-US/eHighlights/Archive/Cement/2010/November/Latest+cross-bar+cooler>

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I am just showing you some snapshots of the clinker coming out of the kiln and getting cooled and passes over a grate and there is cooling water into the grate or some air is circulated to ensure that there is very rapid cooling that happens for the clinker and as it comes out finally

of the process, I showed you already the picture of clinker coming out of the overall cooling process.

It forms those nodules which are essentially cements send to temporary storage before they are ground with gypsum to form the final Portland cement. So the final step in the manufactures are obviously the intergrinding of the cement with gypsum or any other additives that you want to add in the process. We already discussed the fact that about 5% of the cement is a performance improver.

And that performance improver is typically added in this final process of cement manufacture where it is interground with the cement clinker. So gypsum is added as a set regulator. In the absence of gypsum, we will lead to a condition called flash set, this is something you all know very well but we will look at the specifics of the reactions in the later classes. There is obviously a very strict control on temperature required.

Now why is that, why do we need strict control on temperature during the process of blending or intergrinding? What do you expect the intergrinding to do? There are large steel balls in the ball mill, right, they are impacting this material, so what will be generated as a result? Heat will be generated and when the temperature becomes very high in this process what is going to happen, to cement clinker probably nothing may happen.

The gypsum has water of crystallization, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. If you have pure gypsum, if the temperature exceeds about 120, 130 it will convert to other forms of gypsum that is hemihydrate or anhydrite, that means which has no water in it. As a result, the reactivity or availability of the sulphate from gypsum for reactivity will be affected. Now, that does not mean that we have to use only pure gypsum for manufacture of cement.

We generally want to control the reactivity of the cement properly with the choice of an ideal combination of sulphates. So we need to choose components in the sulfate that are quickly available, components that are available slowly. So as a result we need to control this temperature to ensure that we get the right blend of the different forms of calcium sulphate.

Now I am only saying this much now but you will see the importance of this in several aspects of cement chemistry, cement hydration first of all, we will also look at the importance of this

with respect to compatibility of the cement with super plasticizer. So there are several issues, which the form of gypsum can actually affect as far as concrete performance is concerned.

So this is one of the ways in which you can control the kind of combination of gypsum that you have in your system. Now of course, I was telling you that this process typically happens in ball mills but today there are several other types of mills also like vertical roller mill or even a horizontal roller mill is actually available, that ensures much better efficiency in grinding.

That means, efficiency means that much of the energy goes towards the grinding and very little is actually lost out as heat. So that is an important aspect to consider for the design of a correct blending or grinding process. All the other blending material like fly ash or slag depending upon whether you are making blended cement for example, all the materials also fed into the grinding process.

And ultimately from the grinding process, the cement of the required fineness is produced but what do we typically represent the fineness of cement as, the specific surface area. And how much is that typically? About 300 square meters per kilogram, for a kilogram of cement you have 300 square meters of surface area that is how the fineness is typically represented.

But that is determined by a specific process called Blaine's process, Blaine's air permeability measurement. Now we have to be very specific that when you measure the fineness and you report it, the report should also say what is the process that is used to measure it, because you may get different results from different processes. There is also another process called turbidimeter process.

From that you may get actually much lower values or fineness, so you have to be very clear in saying what is the process used for determination of fineness also. Now one thing that we do not discuss often here is, the relative ease of grinding and that is not something that I have covered in detail in this course, I would like you to do some reading on this on your own. The materials that are coming into the ball mill have varying degrees of hardness.

You have clinker then you have gypsum. Which is harder? The clinker is obviously much harder than gypsum. Gypsum is very soft material. Now supposing you have more than this, you have additional components, you have fly ash, you may have slag, if you have limestone,

so if you have all these components inside the system what happens when you are intergrinding these materials together?

Example limestone is much softer than clinker, so if you are blending limestone with clinker the grinding process may lead to a much finer limestone but coarse clinker. On the other hand when you are blending clinker with slag, slag is much harder than clinker, so you may actually grind the clinker more than the slag. So instead of getting uniform fineness, you will actually get a blend which has varying degrees of fineness amongst different ingredients.

So sometimes these processes can be quite difficult to achieve a perfectly uniform blend. So in certain cases, for example when you are combining cement clinker with materials that are significantly different in hardness, you may want to go for interblending option rather than intergrinding option. For example, like we blended the raw materials of cement manufacture together, here we are actually grinding the cement to the required fineness.

And then blending it with the other materials that are in the process, that specifically happens when you go for the route of forming blended cements, that is why you need to be doubly careful that you are blending with uniform size distribution in both clinker and the blending material. So getting that perfectly done is quite a bit of a challenge as far as intergrinding is concerned.

That is certainly something I should look at. One more aspect of grinding that we are not covering in detail in this course is, the use of special materials called grinding aids, inside the grinding machine or inside the ball mill we use something called grinding aid. Now grinding aids are essentially chemical components. These are chemicals, usually polymeric chemicals, which enable the separation of cement particles once they are ground together.

So what this does is these polymers they help in bringing down the overall energy required to grind the cement. So substantial amount of electrical energy goes into this process so if you can bring down the time required to grind the cement to a required fineness then that will be a major saving for your energy. So grinding aids are chemicals that are added to this process that will reduce the amount of energy required to grind the cement.

And I would urge you to do some more reading on your own about grinding aids. You will later realize that many of these grinding aids are also similar to our high range water reducers

that we will talk about in the later chapter in the chemical admixture chapter. Now an important aspect to understand is that we need to control cement manufacture process very carefully.


One thing we know from our field experience that between brands of cement there is a significant amount of variation, there are several cements which are sold as 43 grade or 53 grade cements but if you pick out any two different or three different brands of cement and test them in your lab there is wide variation in their properties. Of course, some of this could be attributed to the fact that one cement is ground finer than the other.

The chemical composition of the cements may be a little bit different and so on, but even in terms of performance characteristics although all of them claim to be of the same grade, the actual result you may get in the lab could be quite variable and this is something you need to contend with in a real construction project. For example, in a construction project, you need to ensure that, at the start of the project you have identified several brands of cement that are capable of being used in your project.

Because very often the supply of the cement could be erratic as a result of which you may not get the same quality of cement throughout your job, and in certain cases, the cement coming from the same plant may actually end up having lot of variability in it. Now to avoid this variability as much as possible, the cement companies have to ensure that their quality control processes are really top of the line.

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Other issues



- Cement manufacture today is a highly controlled process
- However, there is lot of variation in quality of cements (between brands, in the same brand, sometimes in batches produced on the same day!)
- Quality control during cement manufacture → done at every stage in the process

Because of which this quality control is done at every stage in the process.

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Quality control



- Sampling and evaluation should be performed after excavation from the quarry, before and after blending the feedstock, after formation of clinker, after intergrinding clinker with gypsum, and finally before packaging in the bags and drums

X-ray fluorescence

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So there are several stages in the cement manufacturing process like excavation from the quarry, blending the feedstock, formation of clinker, intergrinding with gypsum and then finally packaging the material as a final product that is cement. So at each and every stage the material is actually tested for certain properties to ensure that the quality and the composition is maintained at the correct level.

So, you may wonder most chemical analysis techniques take a very long time, so how do we ensure that this is done in fairly rapid time. So here what we do is in cement manufacture, samples of the proportion of the cement that is to be tested are sent to the quality control lab, inside the cement plant and there within 5 minutes' critical oxide compositions of the cement can be deciphered.

And this is done with the help of a technique called X-ray fluorescence. Now I do not think we need to go in details of this technique, what I just wanted to tell you this is, this technique excites the elements present in the material by an incoming radiation. So, since the radiation is X-rays we call it X-ray fluorescence but what happens is because of the excitation of these atoms by the incoming X-rays each atom produces its own characteristic X-ray.

What happens when you excite the atom in an element, there will be electrons that may get removed and because of that there will be outer shell electrons that try to fill up the inner shell electrons and the difference in energy is between the outer shell and inner shell will be released

as heat and as X-rays. So now you have an incoming X-ray which excites the elements in the sample.

And the sample then starts fluorescing, that means the elements in the sample, they send out their own X-rays. So now there is a detector which can collect all these X-rays and detect what type of elements are present, and since all the elements are usually present in their oxide forms, there is a simple stoichiometric calculation, once you know the elements you can actually determine the content of the oxides that is present inside.

So within a 5-minute process the sample that is received at the quality control lab gets transformed into a specimen for this process and within 5 minutes you get a complete analysis of the oxide composition, but it is not just the oxide composition that you need to worry about, you need to convert that into certain factors.

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Quality control parameters

Lime saturation factor (LSF) = $\frac{C}{2.8S + 1.2A + 0.65F}$, where C, S, A, and F are the % amounts of CaO, SiO₂, Al₂O₃, and Fe₂O₃, respectively. x 100
 Generally between 92 – 98%; more than 100% => presence of free lime

Silica ratio (or modulus) = S/(A + F); generally 2.0 – 3.0

Alumina ratio (or modulus) = A/F; generally 1.0 – 4.0

Potential C₃S 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. Free MgO

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And the important factors that you need to look at are the lime saturation factor, the silica ratio, the alumina ratio and potential C₃S from a special set of equations called Bogue equation which we will talk about in the next class in the cement composition. Now if you look at the equation for the lime saturation factor,

$$LSF = \frac{C}{2.8S + 1.2A + 0.65F}$$

Where C, S, A and F are the % amounts of CaO, SiO₂, Al₂O₃ and Fe₂O₃ respectively. Now obviously this looks like a highly empirical equation but it is basically indicative of the fact

that it is telling you how much of the calcium is actually getting combined with the silica, the alumina and the ferrite to form the cement compounds like C_3S , C_2S , C_3A and C_4AF .

Why is that important because if there is too much lime present and much of it is unreacted it will appear as free lime, and you know from your past studies of cement that if you have too much free lime in the cement, it leads to a problem called unsoundness. Unsoundness basically relates to the volumetric expansion of the cement upon hydration, and that is because of the free lime that is present.

It is also because of free magnesia MgO or periclase that may be present in the cement that also contributes to the unsoundness, which is one of the reasons why we do not want to use lower grades of lime stone for cement manufacturing because lower grades of lime stone also have a high content of magnesium oxide. Why, because you know that there is one more form of limestone which is available naturally called dolomite, limestone is calcium carbonate, dolomite is calcium magnesium carbonate.

So this dolomitic limestone may not be entirely suitable for cement manufacturing process because it will contribute magnesium oxide which will also lead to unsoundness of the cement, okay. So this lime saturation factors, the typical levels that you want to maintain this at is between 92 and 98%, and if the value of this LSF, actually this is present as a ratio here, so it should be 0.92 to 0.98.

So this is the ratio, we need to multiply this by 100 to get the percentage obviously. So if this value comes to more than 100%, then it indicates the presence of free lime in the system which can lead to unsoundness. You are allowed certain amount of free lime, okay if you read the cement specs carefully you are allowed a certain amount of free lime but if you exceed that it will lead to the problem of unsoundness.

The silica ratio is;

$$\text{Silica Ratio} = \frac{S}{A + F}$$


It should generally be between 2 and 3. Now all this is done to ensure that we are forming cement that is rich mostly in silicates and not so rich in aluminates. We want to tilt the balance in favor of the silicates and that is why the silica ratio is generally kept at high level, 2 to 3.

And again the ratio between alumina and iron oxide is generally between 1 to 4, it is a ratio not percentage, this is not percentage these are just ratios, and then the potential C_3S from Bogue formulation is very important because again as I told you earlier modern cements have to be rich in C_3S to ensure that we have a high early strength gain. So what is the level of C_3S that you think is typically there in cement?

About 50% at least, so if you want to maintain at least 50% C_3S content in the cement for that we need to have a potential C_3S content that will be likely to be there in the system after the cement is actually formed. So it is important that we do all these calculations at every stage in the manufacturing process to ensure that we are actually ending up with the right blend.

So from now on we will talk more about what is this composition and what is creating this composition inside the kiln? What is causing these components to form in the way that they do inside the kiln and then we will subsequently talk about what is the influence of the structure of these compounds on the reactivity and finally what the hydration of the cement is like.

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Further reading

http://www.theconcreteportal.com/cem_prodn.html

http://www.lafarge-na.com/wps/portal/na/en/2_2_1-Manufacturing_process

<http://www.cement.org/cement-concrete-applications/how-cement-is-made>

<http://www.engineeringintro.com/uncategorized/cement-manufacturing-process/>

<https://cembureau.eu/cement-101/the-manufacturing-process/>

https://www.youtube.com/watch?v=tv71N_NztAw

<https://www.youtube.com/watch?v=uH6S7WpAsFU>

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So there is also some further reading that I would like to suggest. There are several websites that are given here which have some interesting information, some of these are from the sources that I have already talked about in the introduction class but there are several other sources that you can look at to get some very valuable information about cement production. Now what I have shown you is only the process and the pictures.

You can actually get very good quality animations and videos from YouTube also to get a good insight into the cement manufacturing process. I would also like you to read some more articles about how the management of the environmental constraints is done in cement manufacturing process because that has become a very important part of managing a cement plant these days.