



Basic construction materials
Prof. Manu Santhanam
Department of Civil Engineering
Indian Institute of Technology – Madras

Lecture 25
Cement and Concrete 1 - Part 2

(Refer Slide Time: 00:15)

Raw materials for cement

- Calcareous material – Containing CaCO_3 (primary source – limestone); impurities such as iron and alumina are sometimes present
- Argillaceous material – Containing clayey matter, source of SiO_2 , Al_2O_3 and Fe_2O_3
- Gypsum – Added in the final stages of manufacture as a set regulator





Now, what are the raw materials that are required to make cement? The principal component of cement is lime. For lime, we need to get limestone. Limestone is needed to make cement. Any source that contains a large quantity of calcium carbonate is needed, mostly it will be limestone because that contains the purest form of calcium carbonate. Sometimes it may have impurities such as iron and alumina also.

The other component is clay. So the clay contains silica, alumina, and iron oxide. So limestone contributes calcium carbonate, clay contributes silica, and alumina, both of them have some little bit of iron oxide too. And then to this mixture which is burnt and then converted to what we call as clinker, I will talk about that later we also add another additive called gypsum, gypsum is added in the final stages of manufacturing to control the rate at which cement will set once it reacts with water. So we have these three principal raw materials for the manufacturing of cement.

(Refer Slide Time: 01:25)

Steps in production

- Selection of raw materials
- Grinding to correct size
- Choice of blending process
- Production of cement clinker by kiln burning of blended raw materials
- Intergrinding with gypsum to produce Portland Cement

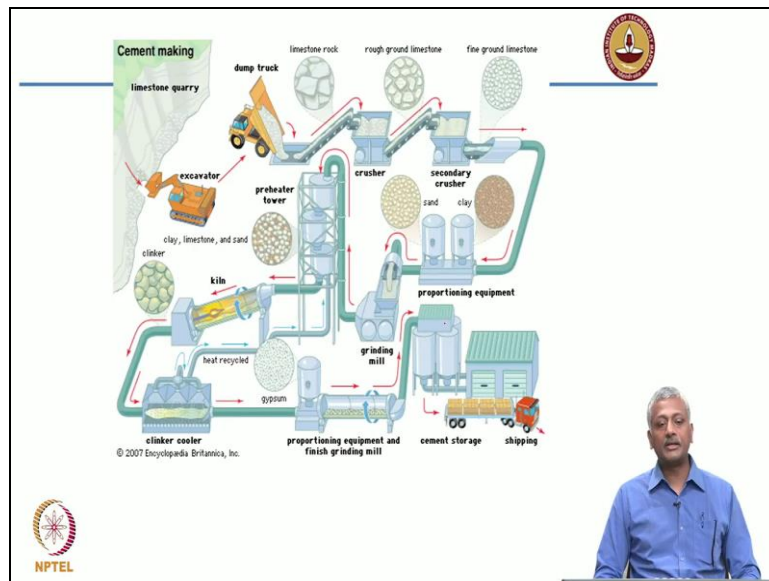


So what are the production processes that are involved? First, we need to select the correct raw materials and break them down into very fine-scale powder. After breaking them down into a powder, we mix them or blend them. And then we burn them in a kiln; we talked about vertical brick kilns, where we load the material at the bottom we have to heat, and then the gases go out of the top, and then we take the material out which has been burnt.

However, it is not the same in cement as we go with what is called a rotary kiln. In cement, we produce it with the rotary kiln, I will show we a picture of that later or a schematic that will make it much clearer. So we mix the raw materials we burn them together in a rotary kiln, leading to the production of what we call clinker.

This clinker comes out of the kiln, and this clinker is then intergrounded with gypsum to produce our Portland cement. So gypsum is not put into the burning process the material that comes out of the burning process which is called clinker, is ground together with gypsum to produce Portland cement.

(Refer Slide Time: 02:46)



So this is a schematic that describes our Portland cement production process. So we have our quarry from which limestone is getting extracted; after extraction, it goes through some crushing, we have a primary crusher, secondary crusher, and so on. Finally, we get fine grounded limestone and get it stored in silos.

A silo is a vertical cylindrical structure. We might have seen silos for grain silos for cement and other materials, and so on. So we store the fine ground limestone and silos we also have storage silos that have clay and probably sometimes sand depending upon the silica content that we want to do all the proportioning. And sometimes, we grind the material together with the limestone and then send it to what we call a pre-heater.

Suppose there is any free water in the limestone that is extracted from the quarry. In the quarry, the stone will not be exactly in the dry form that will be having some wetness in it. So without spending too much energy and trying to drive off this water, we may want to further send it to the preheated tower where any extra water that is then the raw material will get removed. And this water will get removed, and then the materials will again be blended properly and then introduced into this chamber called the kiln.

Now that is called a rotary kiln because it is rotating at a certain speed very slow speed. So rotary kiln is rotating and what happens is the material that comes in here basically goes around the kiln by gravity; we do not need to force it in. It goes by gravity to the other end, and if we see carefully here at the other end, we have a flame, we have a flame that is burning at the other end, which means the temperature is very high here.


So high temperature in this end and a lower temperature in this end so as the material goes from one end of the kiln to another, it is subjected to a series of different temperature scales going as high as 1450 degrees Celsius. And as a result of this burning process, these raw materials that are clay and limestone, get mixed and fuse to form certain compounds, which I will talk about later that material comes out as clinker.

And that clinker is cooled and then stored again in silos. Finally, it is proportioned along with gypsum and sent to the grinding mill, where it is grounded along with gypsum and then extracted as cement. And this cement is again stored in silos and then sent to job sites. To the job sites, typically, cement is sent either in bags or in bulk.

So in bulk, they are transported through these trucks, which are called bulkers. So depending upon the requirement of a job site, we may want to get cement in bulk or as bags. For residential construction, mostly, we will get cement in bags. However, suppose we supply it to a centralized mixing plant for concrete. In that case, we will be sending a bulker that takes a large quantity of cement and discharges that into the material storage silo available at the centralized mixing plant.



I will show those things later. So this is the overall process of cement manufacture; the most important part is that the raw materials are ground to a very fine size so that they can mix and blend well, then they are sent to a burning process in which they get fused to form different sorts of compounds and then the material comes out and is cooled and then proportioned along with gypsum to produce the final Portland cement.

(Refer Slide Time: 06:59)



Cement composition

OXIDES	COMPOUNDS*
CaO (C)	C ₃ S
SiO ₂ (S)	C ₂ S
Al ₂ O ₃ (A)	C ₃ A
Fe ₂ O ₃ (F)	C ₄ AF
MgO, SO ₃ , Na ₂ O, K ₂ O	Gypsum (CaSO ₄ .2H ₂ O)
Minor oxides	Note: Water (H ₂ O) is written as H in cement chemists' notation

So what are the compounds or the oxides present in the cement itself? From the raw materials that are limestone and clay, we get the following oxides calcium oxide, silicon dioxide, aluminum oxide, and iron oxide. If we think about cement in a nutshell, it is a mixture of these four primary oxides. In cement chemistry, calcium oxide is written as C, silicon dioxide is written as S, aluminum oxide is written as A, and iron oxide is written as F, quite different from what we see in regular chemistry.

C in regular chemistry would mean carbon, but here we are not talking about carbon; we are talking about calcium oxide as far as cement is concerned. There are also other oxides present depending upon the raw materials that we are using, like magnesium oxide, sulfur dioxide, sodium, and potassium oxides; Sodium and potassium are called alkali oxides. Then we may also have other minor oxides that do not really have a bearing on how well the cement works.

Now we all have seen that cement appears gray, and why is that gray color? It is because of iron oxide that is getting produced in the cement. And the kind of atmosphere that we have inside it is called reducing atmosphere. As I said in the kiln, burning the raw materials is mixing up and then getting fused to form some compounds. So we have these four primary compounds that are forming.

What are these compounds C₃S is a mixture of calcium oxide and silicon dioxide. So it is typically written as C₃S to mean that it has three parts of calcium oxide and one part of silicon dioxide. C₂S is two parts of calcium oxide and one part of silicon dioxide, C₃A is three parts of calcium oxide, and one part of aluminum oxide, and C₄AF is four parts of

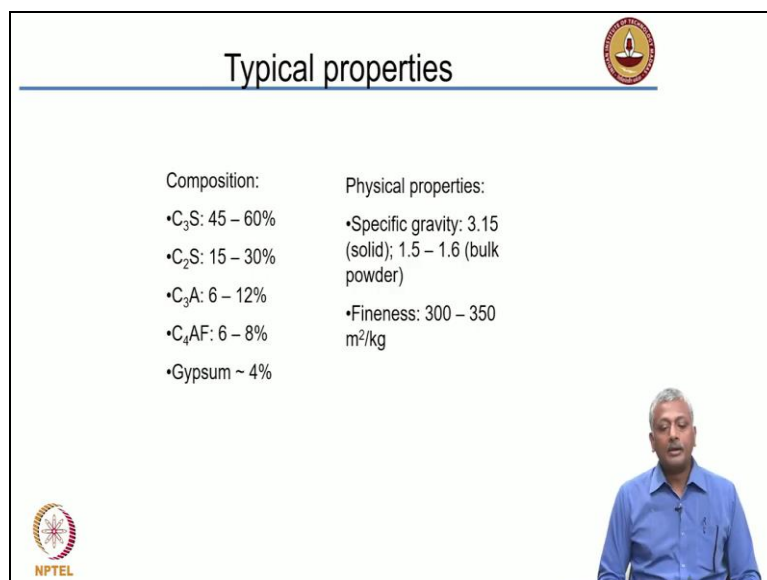
calcium oxide and one part of aluminum oxide and one part of iron oxide. It is very complicated because these compounds do not represent actual stoichiometric compositions of the materials that we see inside the cement.

When we think about compounds like calcium carbonate in chemistry, it is got a very well-defined stoichiometry. We do not write calcium carbonate as CaO dot CO_2 because it combines well to form calcium carbonate. Here the exact composition of the material is not very well known. The approximate compositions are represented here by these compound compositions C_3S , C_2S , C_3A , and C_4AF .

Gypsum, as we all know, is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and if we want to write gypsum in the language of cement chemists, we would be writing it as calcium sulfate dehydrate. So in cement chemistry, gypsum will be written as CS with a bar on top, or sometimes it is written as SSH_2 . Do not confuse yourself with this; do not worry about it. It is just the way that cement chemistry notation works.

For the most part, we need to remember these four principle products that come out in the form of clinker; of course, gypsum is added after the clinker comes out and proportioned together with the clinker to make your Portland cement.

(Refer Slide Time: 10:37)



The slide is titled "Typical properties" and is divided into two columns: "Composition" and "Physical properties". The composition column lists the percentages of C_3S , C_2S , C_3A , C_4AF , and Gypsum. The physical properties column lists specific gravity (solid and bulk powder) and fineness. The slide also features a logo in the top right corner and an NPTEL logo in the bottom left corner, with a small video inset of a speaker in the bottom right corner.

Composition:	Physical properties:
• C_3S : 45 – 60%	•Specific gravity: 3.15 (solid); 1.5 – 1.6 (bulk powder)
• C_2S : 15 – 30%	•Fineness: 300 – 350 m^2/kg
• C_3A : 6 – 12%	
• C_4AF : 6 – 8%	
•Gypsum ~ 4%	

How much of these compounds are present inside the cement? Typically when we think about modern cement, most of it is C_3S , nearly 50% or more than 50% is C_3S . There is a reason why this is, so I will come to that in just a minute apart from C_3S , I said we have C_2S ,

which is typically about half or less than half of C_3S then we have C_3A and C_4AF , which are much smaller quantities.

If we combine the C_3S and C_2S , it will be nearly 80% of our cement, and of course, the remainder will be made out of our aluminates and gypsum. So nearly 80% of cement will be a mixture of C_3S and C_2S . So primarily, our cement is calcium silicate. In the last chapter in stone brick and mortar, we talked about hydraulic lime produced from impure limestone burning of impure limestone.

Again that leads to the formation of calcium silicates. It forms smaller forms of calcium silicate here; it forms larger forms of calcium silicate like C_3S and C_2S . So what do these compounds impart to the cement? We will take a look at the reactions and the chemistry in just a few minutes. But what does the resultant cement have in terms of its basic physical properties? So the specific gravity of the cement is 3.15 that means if we take each and every grain of cement and somehow we can calculate the mass and the volume of each grain, what we will get by dividing mass by volume is the true specific gravity of the cement that is a solid specific gravity of the cement. However, when we take it in bulk and put it in a container, the particles do not come very close to each other there are voids or air gaps that we have inside.


When we take a bulk measurement, we will see that the density is 1.5 to 1.6, not 3.15; specific gravity is nearly half of that when we start putting it as a powder. This we would have seen in any of the solid that we deal with. If it, takes sugar measure the density separately but then put it in a container and then measure the density, we will find that the bulk density that we have in the container is smaller than the actual solid density of the sugar.

And that is because it is not packing without any voids in it. The fineness of cement is expressed typically in terms of surface area. So if we take one gram or one kilogram of the cement and we were able to measure all the surfaces on top of the cement and represent that as a surface area, that is called a mass-specific surface area. So if we take one kilogram of cement, the mass-specific surface area would be 300 to 350 square meters.


So each and every cement grain, if we take the fineness, would be in the range of 300 to 350 square meters per kilogram.

(Refer Slide Time: 14:07)


Hydration of cement



- Reaction of cement with water
- Exothermic; heat released is called 'Heat of Hydration'
- Rate of heat evolution is faster if the reaction is quicker
- Heat evolved depends on heat of hydration of individual compounds



NPTEL



So what happens when we mix the cement with water? We might have seen what happens when we mix lime with water; it rapidly reacts with water and converts to calcium hydroxide. On the other hand, cement has a controlled reaction with water; nevertheless, the reaction of cement with water is also exothermic; it releases heat. Heat is released when cement reacts with water, and this heat released is called the heat of hydration. So the entire process of reaction of cement with water is called hydration.



Now what happens with this hydration is that we have these cementitious compounds that are C_3S , C_2S , C_3A , and C_4AF . Along with calcium sulfate coming from gypsum, they interact together and produce a certain set of compounds. We will talk about those in just a minute. If our reaction is faster, we evolve more heat rapidly. Now we can look at it in 2 ways; one is our heat getting evolved rapidly caused by a very fast reaction that means our setting and strength gain of the cement will be much faster.

However, at the same time, we also have to remember that if we are releasing much heat very fast, our potential for cracking is also more. So have to be very careful about how we control the rate of reaction of the cement, and the heat that is developed depends on the heat of hydration of individual compounds. Each compound reacts at a different rate.

(Refer Slide Time: 15:43)

Effect of constituents on cement properties

- C_3A : responsible for setting and early strength; possesses a high heat of hydration
- C_3S : early strength gain; high HOH
- C_2S : ultimate strength; low HOH
- Finer the cement, faster the rate of heat development, and quicker the setting and early strength gain



It turns out that the compound which we call **C_3A is the fastest reacting compound**. It is **responsible for setting an early strength**, and it possesses a high heat of hydration. In fact, in cement, if we do not use gypsum, our C_3A reacts rapidly with water with a lot of heat evolution, leading to what we call a flash set. So, in other words, if the cement reacts with water without any gypsum, we will lead to a condition which is called a flash set that means it will suddenly harden and it will not be recoverable beyond that.

That is why we want to add gypsum to take care of C_3A ; otherwise, the C_3A will go crazy; without gypsum. So we want this gypsum to be there to regulate the rate at which C_3A reacts. Nevertheless, the interaction between gypsum and C_3A is still giving rise to some early strengthening and setting of the cement. However, as I said, our cement is mostly C_3S because it contains more than 50% of C_3S . So C_3S is also responsible for early strength gain; that is why we want more of it.

So that we can gain strength early; like most modern construction projects, we want to finish fast and get over and go to the next stage. So for the concrete to gain strength fast, the cement should also be rapidly gaining strength. So here, the compound that is primarily responsible for the **high early strength** of the cement is C_3S . So if we want early strength gain, then use the cement with **high C_3S content**.

And of course, it does not come without any price; we have to pay the price for it. It possesses a high heat of hydration that means it evolves heat rapidly, and the potential for cracking could be significant. On the other hand, when we have cement rich in C_2S dicalcium

silicate, it is very slowly reacting and has a low heat of hydration. So it will possibly not even react in the first few days of cement coming in contact with water.

So our C_2S reaction may start very late and is responsible for our concrete's long-term strength. So it will be reacting slowly as long as the water is available. It will continue to react and then provide strength over the long term. As I said, earlier higher heat evolution means faster reaction finer the cement the faster the reaction if we can grind the cement to a very fine size, we can increase the rate of reaction.


Of course, the same thing, if we take sugar and crush it into a smaller size, it dissolves much more rapidly in water. The same thing in cement when we crush it to a smaller size reacts more rapidly with water, and it will also liberate heat at a faster rate. So we need to take it very carefully to produce the cement, which has control over its setting and its strength gain properties because all this needs to satisfy the needs for a particular application.

To give an example, if we are going to construct a building, the building columns will be rapidly taking very high levels of load. So in such cases, we will want to go with the cement that gains strength rapidly. In the case of a dam, we have massive concrete very large blocks of concrete. So what is going to happen in that case? The heat that is getting liberated by the cement hydration will be so large that we may get thermal stresses in the dam.



Because the concrete section is massive, the heat generated inside does not dissipate out quite easily, so we get build up of thermal stresses that are not good for the concrete because it will lead to cracking. So because of that, we would like to use cement that produces less heat. So in those cases, we may want to go for cement rich in C_2S or adopt alternative strategies, as I will talk about later.

(Refer Slide Time: 20:15)

Products of hydration of cement



- Calcium silicate hydrate (CSH) – Primary strength giving component
- Calcium hydroxide (CH) – most susceptible to chemical attack
- Calcium sulfo-aluminates – Responsible for early stiffening of concrete



Now, what does the reaction of cement with water produce? The calcium silicates obviously have to produce some calcium silicates. The calcium aluminates have to produce some calcium aluminates. So let us see what it produces? The calcium silicates end up producing calcium silicate hydrate CSH and calcium hydroxide.

Both these solid components fill up the volume that was previously occupied by water. So if I show we a picture of cement particles in water at time t equal to 0 the cement particles have come in contact with water and slowly what is going to happen the reaction products are going to start forming on the surface of the cement particles and then occupy the space which was previously occupied by water.

So, in other words, as the reaction proceeds, space previously occupied by water gets filled by the products; what does this mean? This means that the porosity because space filled with water is basically empty space where there is no solid. So its porosity reduces as our hydration continues to happen. So, any of the solid compounds that reduce the porosity will ultimately increase our strength. So calcium silicate hydrate and calcium hydroxide both cause an increase in our strength because they contribute to a reduction in the porosity.

However, the significant component is still our CSH, and it is a primary strength-giving component calcium hydroxide can be chemically altered quite easily. For example, if there is external carbon dioxide. We have seen it in the case of lime water what happens carbon dioxide reacts with calcium hydroxide to form calcium carbonate. So, in this case, there is hydrated lime generated from the hydration reaction. And this hydrated lime can quite easily

react with chemical species coming into the concrete from outside, like chloride or sulfate, or carbonate. So it is susceptible to chemical attack, but that does not mean it is a bad product. It is a good product because it is filling up pore spaces inside the concrete. And the calcium hydroxide also regulates the pH of the cement paste.

General cement paste will have a pH of around 13 or more, which means it is highly alkaline, and interestingly, what happens is at this pH, steel is free from corrosion. When the concrete produces a very highly alkaline environment, it protects the steel from corrosion. When we have conditions that reduce this alkalinity, we will lead to corrosion of steel. So we want this highly alkaline environment, which is regulated by calcium hydroxide, present in our system.




What about the calcium aluminates? They react with the sulphate, as I said, because sulphate controls the rate of reactivity of aluminate and forms what is called calcium sulphur aluminates; these cause initial strengthening and **stiffening of the concrete**. So, long-term strength gain is all because of CSH (calcium silicate hydrate). The initial strength could be because of CSH could be because of Aluminates and so on and so forth.

Please remember that any solid product will occupy porosity or occupy the water-filled space and reduce the porosity. So as porosity reduces, the strength goes up.

(Refer Slide Time: 24:48)

Tests on hydraulic cement

- Consistency and setting time – Vicat test
- Initial and final setting – importance
- Soundness – Ability to retain volume after setting (related to free CaO/MgO)
- Compressive strength – as measured on mortar

So now we understood what is the chemistry of cement, how do the compounds of cement react? What happens when cement comes to a job site? How does the contractor or the person who is doing the application of the concrete? How is the quality of this material assert? We

need to do some basic laboratory investigations to understand the quality of the material that has been received on site.

The Indian standards give us the guidelines to perform the test that we need to do. The important tests required for cement analysis are the test of consistency and setting time, done with the help of a Vicat apparatus. Many of us will have this test in our laboratory classes in your further semesters. So we have to determine what is called initial setting time and final setting time.

What do we think is the importance of initial and final setting time? Now we know that when the concrete is first prepared by mixing water into it, cement and water come into contact, the concrete is still very fluid. We have some time with which this concrete can be taken and put into the formwork and then consolidated and finished on the top surface. So there is some degree of or some amount of time to complete all the operations.

After we place it in the position, it slowly starts stiffening and gaining strength beyond that point. We will not be able to rework the concrete. So the initial set is the point at which our concrete starts to set, which means the reactions just gain in speed and final setting is the point where the concrete has gained its shape or form and is not going to change the shape form beyond that.

So the initial set is the time available for us to work with the concrete; beyond that, we will not be able to mold the concrete in any way we want. The final set is the point beyond which the concrete has a definite shape. It does not mean that at the final set, our concrete gets full strength. No concrete continues to develop strength beyond that. We will talk about that later that as long as the water is available, concrete will continue to develop strength.

The other important characteristic that we want to test on our cement is soundness. Sometimes because of the nature of the raw materials and the nature of the process that manufactures the cement, we may have free calcium oxide or magnesium oxide present inside our cement. What will happen is when this reacts with water, it can lead to the formation of calcium hydroxide or magnesium hydroxide.

And that may lead to an increase in volume. So in a set cement paste, if we have too much excess of this free lime or feed magnesia, the increase in volume will lead to cracking, which is called unsoundness. So that needs to be adequately checked it is called unsoundness. So, soundness is the ability to retain volume. Unsound means that after setting, the volume increases, so we do not want that volume increase to be uncontrolled; otherwise, our concrete will not be usable.

Then we have to measure also the strength of the cement in real-life design; when engineers are working on-site with concrete, they will only be worried about the strength of the concrete that means the strength that they get from the composite material that is inclusive of water, cement, sand, and stone. However, to ensure that the cement is of quality and will produce the desired effect in concrete, we also have to test all these characteristics, and finally, we also need to test the compressive strength of the concrete.

Interestingly, the cement's compressive strength is not measured on just a mixture of cement and water; it is measured on mortar, which means it has some part of the water cement and the sand. Why do we want to use mortar to determine the strength of the cement? It is something that we should think about? The whole point of this matter is that cement does not function as a strength-giving component on its own.

It provides strength by binding the aggregate particles together in a block of concrete. That is why we want to strength test the strength of the cement with respect to its nature of binding. So we want to test the binding strength of the cement; that is why we do this test on mortar. So please remember that we want to test the strength of the cement to define its binding characteristics. How well it binds together the aggregates and keeps them in place, and provides stability and resistance to loading.

And that is the strength that we are trying to determine from the compressive strength test; that is why we do it on mortar and not on cement paste. Now the other reason we want to do it like that is that if we make a paste of cement and water, it will start shrinking once the structure hardens, there will be shrinkage. The presence of sand reduces the extent of shrinkage that happens.

We will talk about shrinkage separately when we talk about concrete, but essential to keep the volume dimensionally stable to keep the volume stable; it is essential that we do the strength test on mortar and not on cement paste. Now one thing I forgot to describe is what consistency is? Consistency is typically defined as a minimum water content required to produce a paste that has a certain characteristic that means a certain workability a certain consistency.

All these will become a lot clearer when we talk about the properties of concrete, but anyway, please remember we need to test the cement that is arrived at the job site for its consistency its initial and final, setting time, soundness, and finally compressive strength all these characteristics have to be met before the cement can be pronounced to be good enough to be used in concrete. And of course, we need to compare it with the standards. So we have to compare the cement quality that we measure on site with what is prescribed in the standards.