Admixtures And Special Concretes

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Lecture 01

Overview of cement chemistry and concrete performance: Cement history and production

Hello everybody and welcome to the first set of lectures in this course on admixtures in special concrete. The objective of this first set of lectures is to just get you up to date with an overview of cement chemistry and concrete performance which is essential from the viewpoint of understanding how the chemical and mineral additives would behave in the system that is comprised of cement, water and aggregate. So some basics about cement chemistry and how the hydration reactions actually take place, what kind of factors control the fresh and hardened properties of concrete. So those are some things that we learn in this chapter. And of course, a bulk of your textbook prescribed for the course that is the book by Mehta and Monteiro. The first 7 chapters are dedicated towards what I am going to basically cover in this very brief few lectures.

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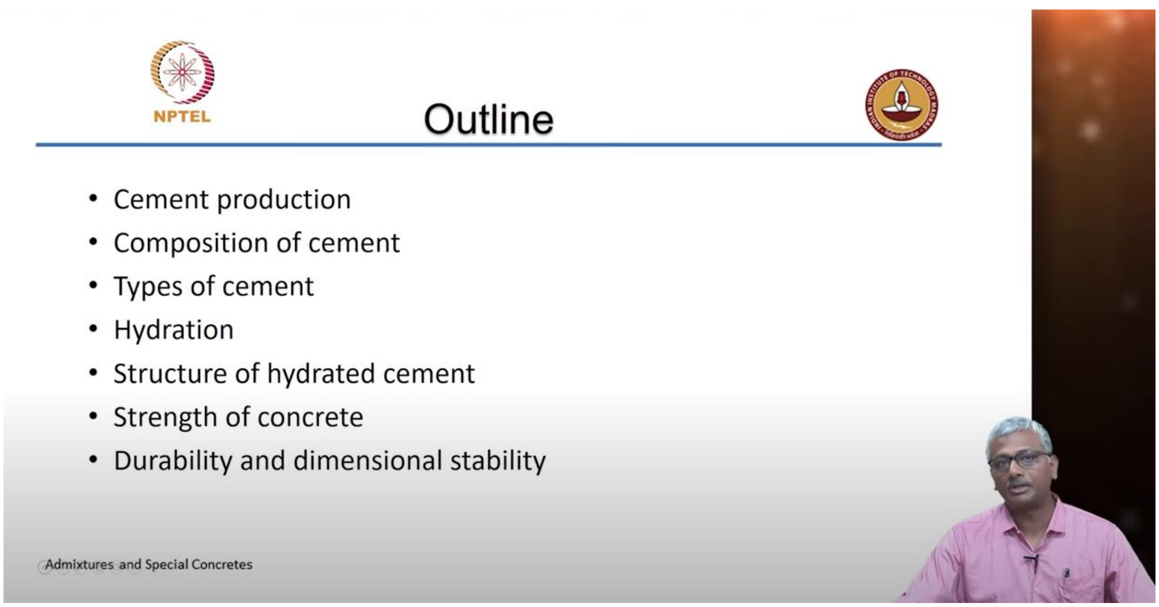

So in this lecture we will talk about,

- Cement production
- Composition of cement
- Types of cement that are available
- Hydration of the cement
- Structure of the hydrated products
- Strength of the concrete and the factors governing the strength.

Then we will talk finally about durability and dimensional stability of concrete.

History:

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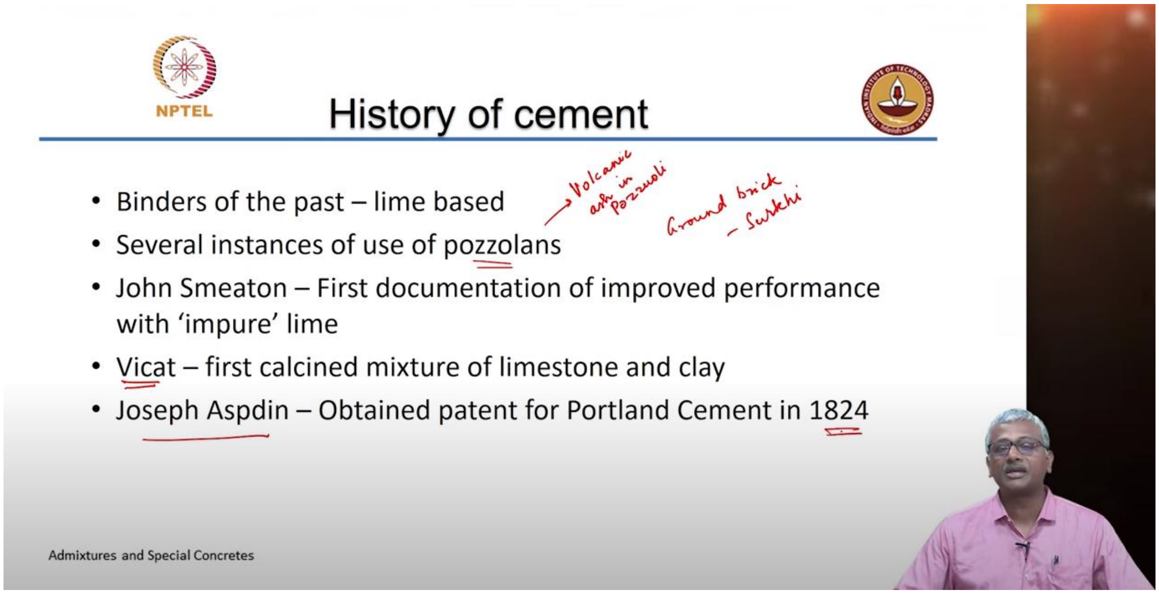

Now as far as cement itself is concerned, we have gone through a lot of inventions that have led to the development of modern Portland cement. In the past you know very well from our heritage structures that people have been using lime as a building material primarily for binding purposes. Because lime was used in conjunction with many other additives which were based on a lot of the local construction practices. In India for instance if you go to the southern part of India, a lot of the heritage monuments seem to have lime mortar in which they have actually looked at an extract of natural materials such as jaggery and kaduka. Similarly if you go up to the north, you will find that lot of dals, pulses have been ground to a very fine powder and used with the lime mortar. Just to give it the right consistency and sometimes to give it much better properties. Ground brick as a cementitious material in the past in India has been used quite significantly with lime. We used to call it surki, ground brick was called surki. The ground brick was used because it gave very good properties as a filler and perhaps to some extent also as a reactive material in conjunction with lime mortar.

Of course outside of India also there have been lot of instances of the use of alternative materials that have added to the lime mortar and that is why the term “Pozzolan” basically came into being because of the use of volcanic ash in Pozzuoli in Italy. So pozzolans started getting used in lime mortar and then later of course people started looking at how we can produce a better quality of lime by somehow incorporating some of these impurities.

For instance John Smeaton had the first documentation of improved performance with impure lime. Impure lime implying the lime that contained a significant proportion of clays as an impurity. Now John Smeaton is considered to be the first civil engineer because he was the first one outside of the military arena to really undertake construction. He constructed a lighthouse tower in the UK in 1756 and that is considered to be the first civil structure constructed by a civil engineer. And that is where he used this impure lime and he found that it was quite beneficial. From that point on, people started looking at how these impurities really play a role in the performance of lime and one of the common names that you hear in your laboratory also is the name Vicat. Viact apparatus is used to study the consistency and setting time of the cement. Vicat was a French scientist who first calcined a mixture of limestone and clay. So he burnt limestone and clay as an intimate mixture together and that probably was the first precursor to what we today know as Portland cement.

The name “Portland cement” itself comes about because of Joseph Aspdin who in 1824 got this patent for Portland cement. He saw that when he produced the cement and it reacted with water, it gave a nice grey stone like appearance and this stone resembled the Portland limestone that was found at Dorset in the United Kingdom. And based on that he obtained a patent for this material and he called it Portland cement. Of course the patent has run out a long time ago but the name “Portland cement” still sticks because people are so keen to have a brand name associated with the cement. If you just call cement as cement, nobody will really bother. But if you call it as “Portland cement’, they think you are talking about some scientific stuff but truly speaking it is just the name which has been given by the patent. So Joseph Aspdin and later his son William Aspdin basically continued the process of cement and really took it to the next level. For the last 200 years or so, cement has been produced and the technology of cement production has increased leaps and bounds. Today we have lot of sophistication in the way cement is produced.

Portland cement today:

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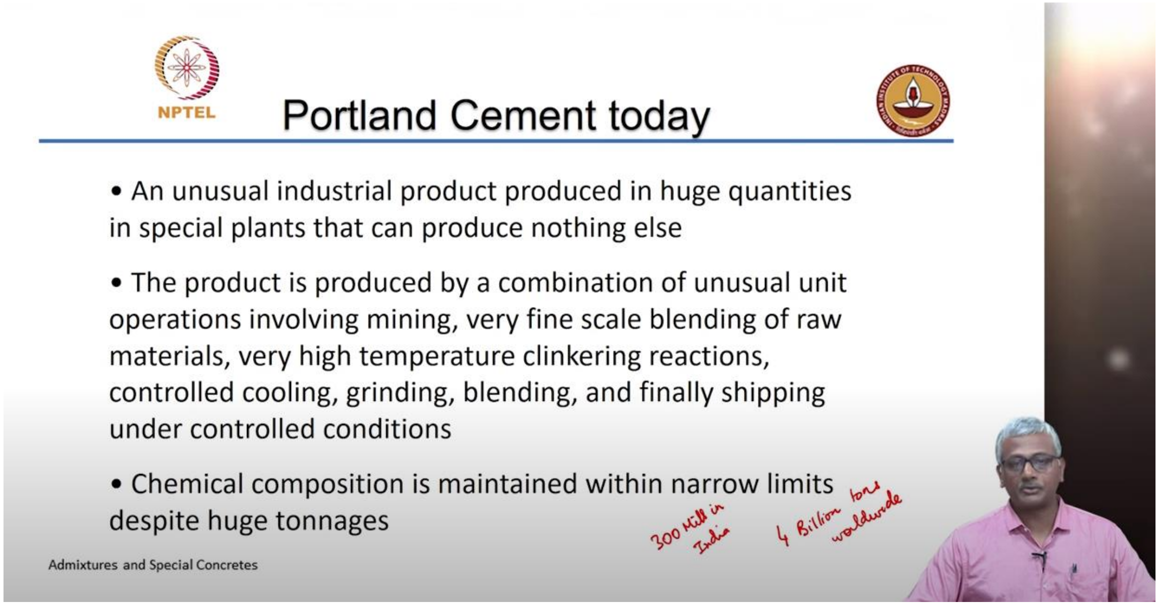

So today cement is produced in very large quantities. It is a very unusual industrial product produced in huge quantities in special plants that do not really produce anything else because the plants themselves are quite expensive, it takes a lot of money to actually produce these plants and cement is a commodity product that comes out of these plants. Very interestingly if you look at the overall production process of cement, it comes after a combination of unusual unit operations involving mining, very fine scale blending of raw materials because all of the materials have to be blended or mixed together well enough so that they burn together in the kiln and form the kind of products that you want to see. Very high temperature clinkering reactions, the reactions that take place inside the kiln produce cement clinker, so all the reactions are called as clinkering reactions. Controlled cooling is done when it comes out of the kiln and then after this controlled cooling process, there is grinding of the clinker that happens with additives like gypsum or fly ash or slag as the case may be when you are producing special types of cement and then finally shipping under controlled conditions. All of these have to be done to produce a very well controlled material whose chemical composition is retained within very narrow limits.

We produce nearly 4 billion tons of cement every year worldwide and in India of we are producing around 300 million. 300 million tons of cement and all of this has to be controlled to very narrow chemical compositions to ensure that it performs uniformly when you add it in concrete at the construction site. So all of this involves a large amount of complication and cement production units have to overcome these complications by controlling the quality of the material that they are producing.

Portland cement production:

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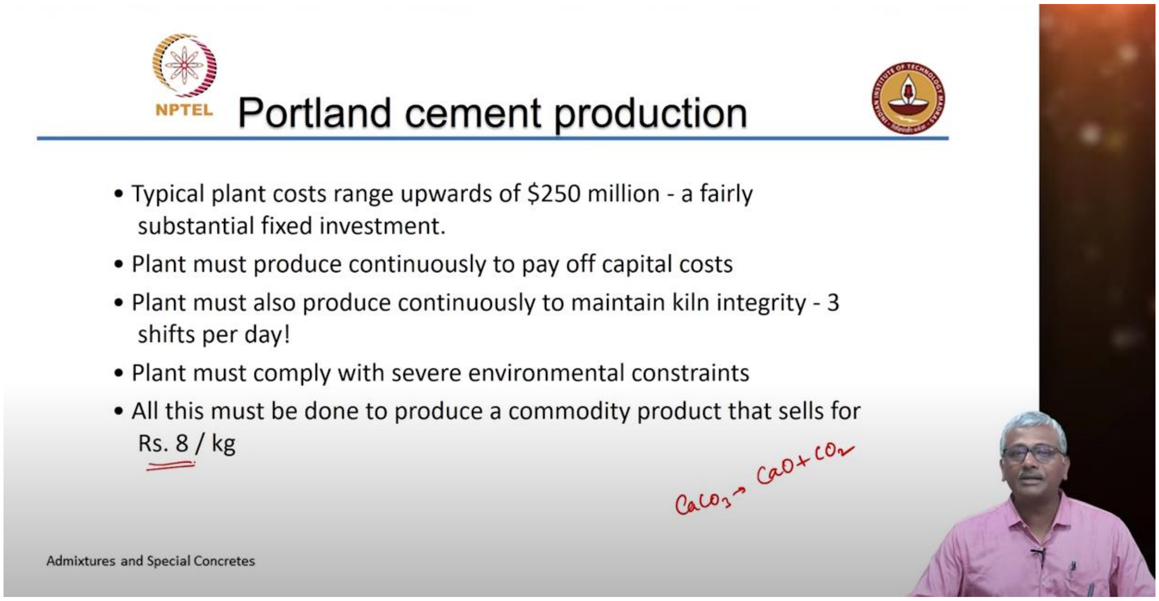

Now typical cement plants basically are costing nearly about 250 million dollars or that is equivalent to about 2000 crore rupees. That is a lot of money to invest in a plant that produces nothing else. But then again cement is required in such large quantities that is very important for all these plants to work continuously to ensure that it is able to pay off the capital costs. And if you are not working continuously, the kiln basically does not retain its integrity. So to ensure kiln integrity, one has to continuously use it. Of course there are times when the cement plants basically close down for maintenance because otherwise they will be getting a lot of problems in their production process. So they have these annual maintenance shutdowns but the downtime that happens because of any shutdown can be quite large and because of that they want to avoid that to a large extent possible and you really need to ensure that you are producing cement almost on a continuous basis. 3 shifts a day, day to day process almost 24×7 until the plant shutdown actually happens for maintenance.

And you all know very well that the environmental regulations are getting stricter by the day. Needless to say, we are burning a lot of different types of fuel and we are going to be obviously emanating a lot of different toxic gases into the atmosphere. One has to be able to devise processes that are able to control the extent of toxicity that comes out of these gases like SO_X and NO_X. Sulphur oxides and nitrogen oxides and the biggest culprit of them all is carbon dioxide. Because we are using limestone as a primary raw material in cement, the burning of the limestone, calcium carbonate inevitably gives out carbon dioxide.

$$CaCO_3 \longrightarrow CaO + CO_2$$

So burning of limestone that is calcium carbonate gives out carbon dioxide and it turns out that for every ton of limestone that is burnt, you are producing an equivalent of nearly half a ton of carbon dioxide. Of course it is a gas, it does not have a mass but equivalent of half a ton of carbon dioxide is getting produced. Now combine this with the CO_2 that will get produced when you burn the fossil fuels inside the kiln. If you combine everything, it turns out that for every ton of cement that is produced, you are actually letting out an equivalent of one ton of carbon dioxide. So that is a significant amount of CO_2 emissions that come out of cement production. So all of this has to be kept in mind. Today a lot of the carbon tax initiatives of different governments are coming into place.

By 2070, India is expected to become net zero with respect to carbon emissions and all of these indicate that we need to have a strict control on this production process to minimize CO2 impact on the environment. Nevertheless, cement production still leads to a very large amount of CO_2 production. And of course we have to keep cement cost controlled to such an extent that we are able to sell it as a commodity product.

Currently cement is selling in bags, it is about Rs. 8 / kg. If you buy it in bulk, it is going to be Rs. 5 to 6 / kg depending upon the location in the country that you are in. So imagine a material that is cheaper than bottled water but it is produced through a unique combination of so many different processes that have to be finely controlled. So all of this tells you that cement production is a process that has a high degree of control and requires the strictest quality control measures to be adopted.

Raw Materials of Cement:

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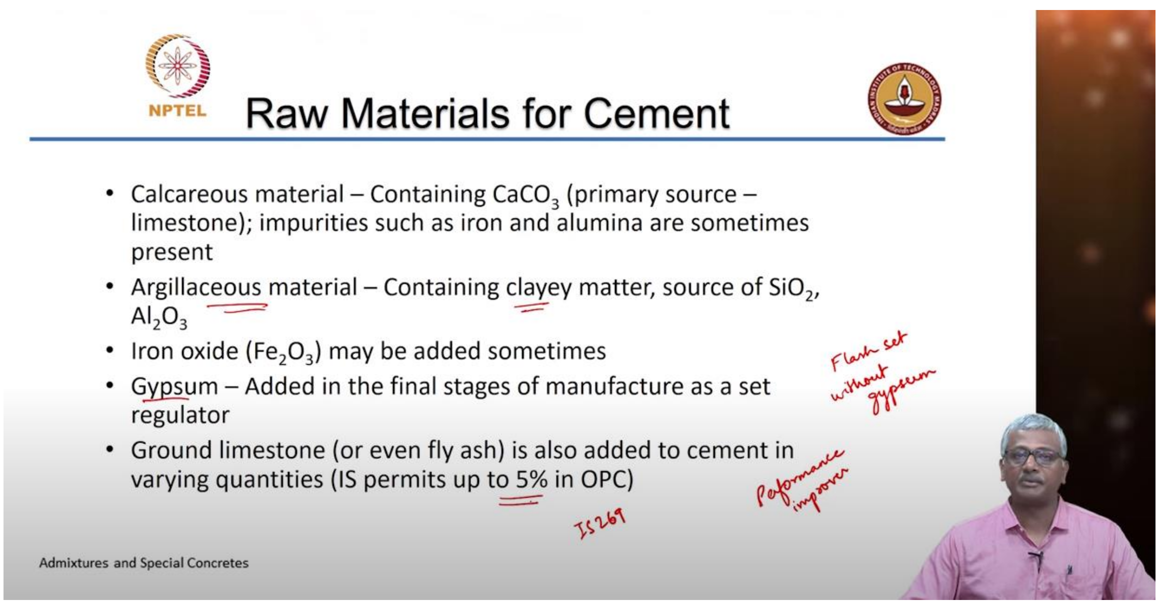

So coming back to the raw materials for cement, you need obviously limestone which is the principal source of calcium oxide that is required for all the compounds that you find in cement. So calcium carbonate is the primary source. So we call it a calcareous material, basically what is containing limestone. Sometimes you may have impurities like iron or alumina in the structure of the limestone and these are inevitably going to be there. You can have silica also present in the limestone as an impurity, but you need to ensure that for a good cement grade limestone, you have a material that is fairly rich in calcium carbonate. You then obviously have the need for silica, alumina and iron oxide which comes essentially from your argillaceous or clayey material which can provide silica and alumina and some traces of iron. But sometimes you may have to add additional iron oxides to maintain the kind of composition that you want to produce the regular ordinary Portland cement.

Most importantly at the end of the process, you have to add gypsum in the final stages of manufacture as a set regulating material. Without the presence of gypsum, your cement will undergo a phenomenon called flash set. So you definitely need gypsum to be there as an additive in the final stages of cement manufacture. And as it turns out when you are actually adding the gypsum very often in cement production, we add what is called a performance improver. If you look at IS code on cement that is IS: 269, it allows certain performance improvers to be added alongside the clinker and gypsum in the final stages of cement manufacture that is the grinding process. In that stage, we add the performance improver. It is typically ground limestone itself as a performance improver because limestone is available at the cement plant directly or you could even use fly ash of a controlled quality can be used as a performance improver up to 5% in OPC.

Now why is this performance improver added? One is that you are cutting down the extent of cement clinker that is present in cement by 5%. That means directly you have cut down the amount of material that is produced through the burning process which evolves CO_2. Here this material just added while grinding so you are not liberating additional CO_2 from this 5% material. So performance is generally here improved in terms of the sustainability impact of the cement. So this 5% is a very key component of cement characteristics but you will learn later when we talk about mineral additives that this limestone that is added as a performance improver can to some extent also lead to additional benefits in terms of the chemistry of the cement itself.

Raw Material Sources:

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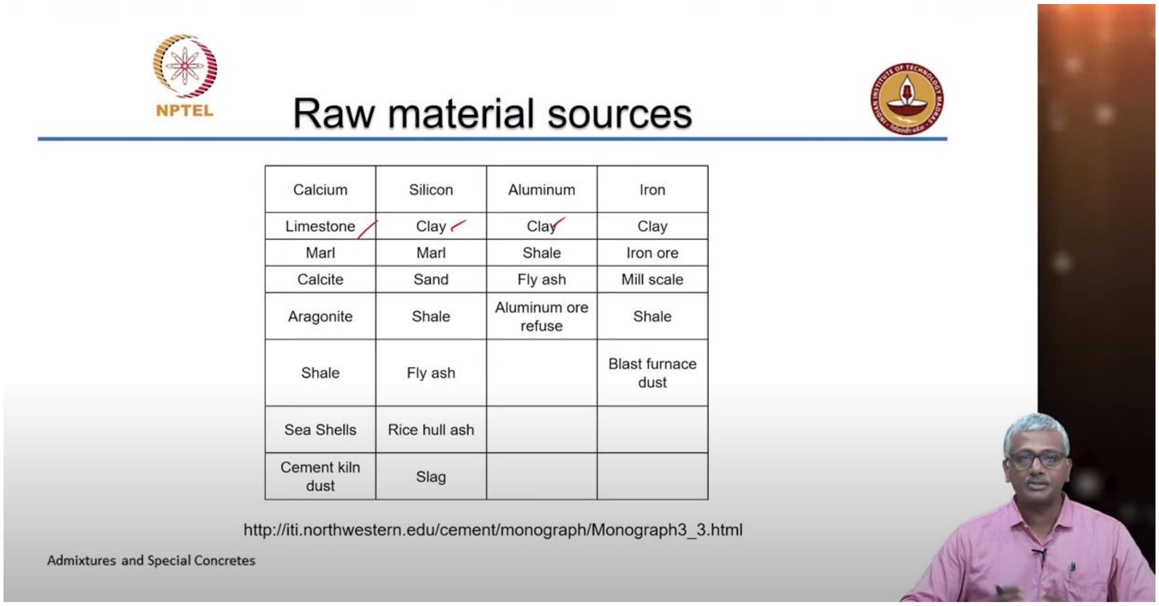

Now where do we obtain these raw materials that is calcium carbonate and silica and alumina and so on?

We have obviously mines that are rich in limestone that are available all across the world and we are extracting from these mines the calcium carbonate. So the source of calcium could be either limestone which is very high degree of purity of calcium carbonate. You could have marl which is basically a mixed clay limestone type of a combination. You have calcite of course which is much more pure form of calcium carbonate or aragonite again a pure form of calcium carbonate, shale, sea shells or cement kiln dust. The dust that comes out of the cement kiln is also having a very rich amount of calcium sources so that can be actually fed back into the cement manufacturing process and adjusted for the composition to ensure that you are getting the right amount of calcium oxide forming in the system.

Then you have silica. Silica is obviously the primary source is going to be clay silica and alumina you are primarily getting from clay but there could be other sources from which you can also obtain the silica and alumina like marl or sand or shale sometimes from fly ash or rice husk ash or slag can also be used as alternative materials to give you the sources of silica and to some extent alumina also.

Iron as I said can be an impurity present in clay or in the limestone but it can also be sometimes added additionally as iron ore or even mill scale could be added. Mill scale is basically the rust layer that forms on the surface of steel and then you have shale and blast furnace dust which can bring about significant bits of iron into your system. So all of these are potential sources from where you can actually get the raw materials but primarily we are looking at limestone and clay as the two major raw material sources from which we are extracting the oxides that are going to be combining inside the cement kiln to produce the unique product that we call as ordinary Portland cement.

Cement Production Process:

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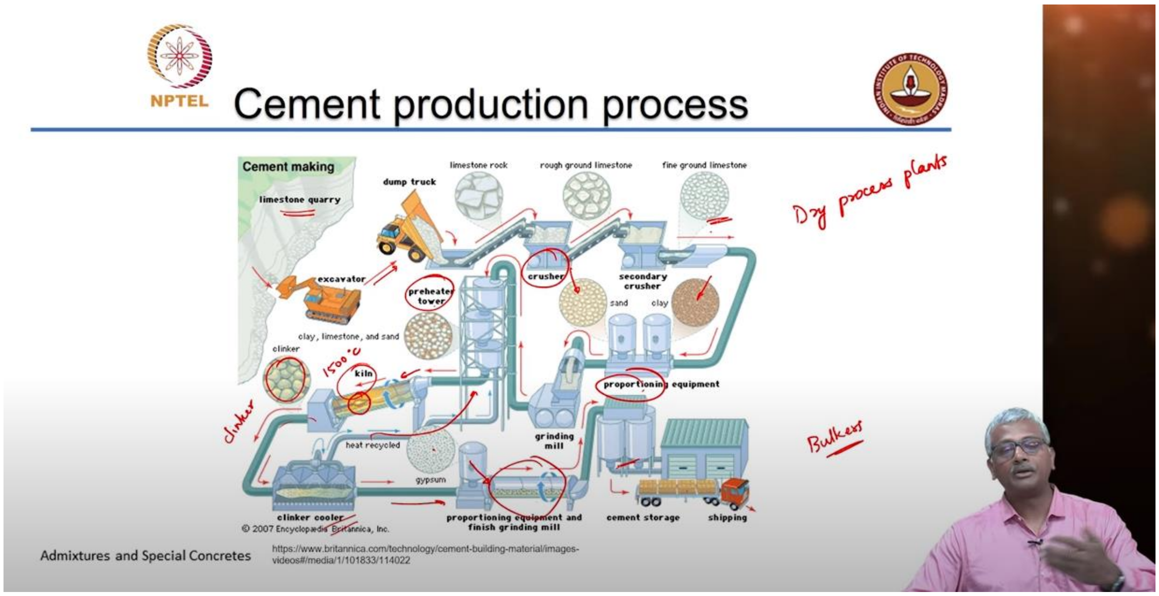

So again just to put the entire process in a perspective so you have the limestone quarry where the limestone is getting extracted and this excavator sends the limestone to a location it is getting crushed. So the first process is to crush the limestone from large boulders into very small sizes or almost like a fine powder to really enhance the extent of its blending along with the clay or the sand. So after the grinding of the limestone you have the clay or the sand which is stored in separate silos which can be then proportioned along with the limestone in a specific quantity and then sent to what we call as a preheated tower. So most of the plants today are called dry process plants.

What do we mean by dry process plants? This implies that all the raw materials are mixed in a dry state. Now compared to this in the past we used to have what are known as wet process plants. In wet process plants all the raw materials are dumped into water and then entirely mixed as a slurry. So obviously that is a much more efficient mixing process but the problem is you will need to dump all of this material in the kiln and burn off the water or heat off the water. That means you are expending a lot more energy in that process. So today all the modern plants are dry process plants. Very rarely do you find any wet process plant these days.

So you have initially the blended material coming into what is known as a preheated tower. Now the advantage of a preheater is that because of the heat that you are generating a lot of the dihydroxylation removal of the moisture present in the system from the raw materials as well as to some extent the removal of CO_2 from calcium carbonate can also take place partially inside the preheater itself. Now another advantage of this preheater is that the heat that is generated from the kiln captured in the cooler can be recycled back and taken to the preheater so that you have some heat recovery in this entire process. So the preheater is quite useful that way. In modern cement plants you always have a preheater before the kiln because the initiation of the reactions that is your limestone de-carbonation that is calcium carbonate removal of CO_2 from calcium carbonate and to some extent the activity or activation of silica and alumina from the clay can take place within the preheater itself. So that the material that comes into the kiln then starts reacting almost immediately without the need for the preliminary reactions because all of those get completed in the preheater also.

Now in the kiln itself the material is fed on one end and basically just rotates along the cylinder and comes down by gravity to the other side. You have the source of fuel on this side and basically the temperatures are going to be highest at that end of the kiln and reduce as we go along to the top. That means the cement raw feed that comes inside the kiln has the lowest temperature at the entry point and highest temperature at the exit point. Now highest temperature can go as high as 1500 degrees Celsius. And then the material that comes out of the kiln that is clinker is basically comes out and has to get cooled rapidly in the beginning and then in a controlled manner after that. So clinker cooler is an integral part of this entire system. It has to cool down rapidly in the beginning and then slowly.

It is then taken to the final step of cement manufacture that is the grinding that is done typically in a ball mill or today there are much more sophisticated roller presses that do a much better job of grinding. So here you have gypsum and gypsum is also proportioned into your system to blend with the clinker and as I said today none of the cements is plain clinker plus gypsum. You also have a small quantity of a performance improver like fly ash or limestone which is also added at the last stage in the grinding mill itself to produce the final cement. The final cement that is produced is stored in silos and then sent for packaging either in bags or in bulk. We typically see these large cement carriers which are called bulkers which transport the cement directly from the cement plant to some construction sites where they are again stored in silos to prepare the concrete.