

**Inorganic Chemical Technology**  
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**Lecture - 25**  
**Cement and Lime Industry - Cement**

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Cement and Lime Industry - Cement. So, in this lecture before going into the details of cement, its properties, reactions and then associated flow chart process description for its production we will have a introduction about lime and cement industries.

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**Introduction**

- Processes and products to be discussed here are based on limestone, which is predominantly  $\text{CaCO}_3$
- Limestone is distributed uniformly (in 3-4 wt.%) throughout the earth's crust
- It is coming mostly from igneous rock formations
- Since it is usually available at the surface, can be collected by open-pit quarrying methods
- A few deposits are low-grade due to impurities and must be treated by beneficiation methods
- Mostly froth floatation method used to remove excess silica and alumina impurities
- Limestone based cement and lime industries are characterized by high-tonnage, low-cost, and low-margin operations which require efficient management to create a profitable venture
- Limestone is well distributed throughout India, except a few states
- India's cement industry has come a long way since the first bag of cement was packed in 1914 and now, India ranks 2<sup>nd</sup> largest producer of cement in the world in 2022

Introduction, the basic raw material for the cement as well as the lime is limestone which is predominantly calcium carbonate. And then it is distributed uniformly throughout the earth's crust in about 3 to 4 weight percent. It is coming mostly from igneous rock formations. And since it is usually available at the surface, it can be collected, open pit, quarrying methods easily.

So, you do not need to have a kind of big mining infrastructure etcetera in order to get this raw material, ok. Because it is available throughout the earth's crust ok, and then it is available at the surface only you do not need to dig too deep into the earth. A few deposits are low grade because obviously, because of the impurities. So, those impurities

must be removed and then for the beneficiation of a limestone ore usually froth floatation is used, there may be other processes as well.

So, mostly froth floatation method used to remove excess silica and alumina impurities, ok. So, what are the characteristics of cement and lime industries which are based on limestone if you would like to see? They are high tonnage, low cost and low margin operations.

So, you are able to produce in high tonnages even at low cost, but unfortunately you know margin is also low, right. Because of such reasons, you need to have efficient management to create profitable venture if you wanted to get into the cement industries or lime industries, ok.

Limestone is well distributed throughout India. So, we do not need to depend on export except a few states in India it is almost available in all states except like West Bengal, in Assam it is available in negligible quantities otherwise rest of the states it is available.

So, Indian cement industries indigenous, we do not depend on any foreign raw materials or imported raw materials. Indian cement industry has come a long way since its first bag of cement was packed in 1914 in Porbandar. And now India ranks second largest producer of cement in the world, ok. So, it is a tremendous improvement indeed.

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**Cement**

- Cement is a generic name for powdered materials which
  - initially have plastic flow when mixed with water or other liquid,
  - but form a solid structure in several hours with varying degree of strength and bonding properties which continue to improve with age
- Portland, high alumina, hydraulic hydrated lime, Pozzolana, magnesium oxychloride are a few types of cements
- Portland cement is the most common cement, which is the basis for a number of cement products
- Portland cement is defined as
  - finely ground calcium aluminates and silicates of varying compositions
  - which hydrate when mixed with water to form a rigid continuous structure with good compressive strength

*Handwritten annotations in red ink:*  
- A circle around "Cement" with an arrow pointing to "good compressive strength".  
- A circle around "compositions" with an arrow pointing to "with sand & grade".  
- A circle around "compressive strength" with an arrow pointing to "compressive strength".

So, now we see details of cement. What is cement? Cement is a generic name for powdered materials and then when you mix this powder material with water or liquids what happens? It has initially plastic flow, plastic flow in the sense it will not get back to its original shape even after you know removing the water by hydration etcetera, ok. So, you cannot get back to the initial condition. So, that is what it means by initially it will have plastic flow when mixed with water or other liquids.

Further what happens? It forms a solid structure in several hours with varying degree of strength and bonding properties and the strength and then bonding property of this material you know it increases or improves continuously with the age, ok. Now, how many types of cements are there? If you would like to list out a few Portland cement is very common, high alumina cement, hydraulic hydrated lime, Pozzolana and magnesium oxychloride are a few types of cements.

So, we will not be able to discuss all of them, but we will be discussing in details about manufacturing of Portland cement, alright. But in addition, we will be discussing about a few characteristics of other cement materials as well. Portland cement is what then? It is the most common cement which is the basis for the number of cement products and then it is defined as finely ground calcium aluminates and silicates of varying compositions ok, which hydrate when mixed with water to form rigid continuous structure with good compressive strength.

Actually, cement individually if you take it is having poor compressive strength to be frank. But this cement if you mix with water and then sand and gravels etcetera its compressive strength increases drastically and in that mixture provides a proper required strength to the construction sites, ok.

So, what are the compressive strengths of different types of cements etcetera those things anyway we are going to discuss now. Now, we have seen that cement is a like you know mixture of different types of powders which may be having aluminates and silicates etcetera.

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- Pertinent properties of cement:
- Constituents of the cement:
- (a) **Portland**

Code	Chemical formula	Type	%
C <sub>2</sub> S	2CaO·SiO <sub>2</sub> (dicalcium silicate)	Silicate	Major
C <sub>3</sub> S	3CaO·SiO <sub>2</sub> (tricalcium silicate)	Silicate	Major
C <sub>3</sub> A	3CaO·Al <sub>2</sub> O <sub>3</sub> (tricalcium aluminate)	Aluminate	Major
C <sub>4</sub> AF	4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> (tetra calcium aluminoferrite)	Aluminate	Minor
-	MgO		Minor
-	CaO		Minor

So, then what we do now? We see constituents of a cement, ok. So, that we can understand what exactly these constituents are, right, silicates, aluminates are common terminology which kind of silicates, which kind of aluminates, etcetera, now we are going to see. We see for different types of cements.

So, let us start with the constituents of the Portland cement. Now, the constituents having different chemical formulas, they have been given different codes also. Let us say C<sub>2</sub>S, here C stands for calcium oxide, S stands for silicate, C<sub>2</sub> in the sense dicalcium and then S indicates here silicate. So, C<sub>2</sub>S is nothing, but dicalcium silicate which is having chemical formula 2CaO·SiO<sub>2</sub> and then which type of component it is, it is silicate type of component and then it is present in major contributions, right.

Next chemical constituent of Portland cement is C<sub>3</sub>S. Here again C stands for calcium oxide, S stands for silica, ok. So, C<sub>3</sub>S in the sense 3CaO·SiO<sub>2</sub> that is tricalcium silicate, it is also silicate type and then contribution is major contribution. This contribution major or minor in the sense how much it is present in the cement, it is present in minor quantities or major quantities, that is what it indicates. In the overall strengths also, they have different roles, we are going to see them also now.

Now, C<sub>3</sub>A in the sense here again C stands for calcium oxide, A stands for alumina. C<sub>3</sub>A in the sense 3CaO·Al<sub>2</sub>O<sub>3</sub> that is tricalcium aluminate. So, it is an aluminate type and then it is also present in major.

C 4 AF here C stands for calcium oxide, A stands for alumina and then F stands for iron oxides. So, C 4 AF is nothing but  $4 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ , what does it mean? What is its name? Tetra calcium alumino ferrite. It is again aluminate type constituents and then its contribution is minor. Sometimes you know magnesium oxide, calcium oxides individually also they are present they are present in the minor quantities. This is about the Portland cement constituents.

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• (b) high alumina

Code	Chemical formula	Type	%
C <sub>3</sub> A	3CaO·Al <sub>2</sub> O <sub>3</sub>	Aluminate	Major
C <sub>2</sub> S	2CaO·SiO <sub>2</sub>	Silicate	Minor
C <sub>2</sub> AS	2CaO·Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub>	Mixed	Minor

• (c) hydraulic hydrated lime

Code	Chemical formula	Type	%
-	Ca(OH) <sub>2</sub>	Hydroxide	Major
C <sub>2</sub> S	2CaO·SiO <sub>2</sub>	Silicate	Minor
C <sub>3</sub> A	3CaO·Al <sub>2</sub> O <sub>3</sub>	Aluminate	Minor

*Handwritten notes:* C<sub>3</sub>A, C<sub>2</sub>S, C<sub>2</sub>AS, C<sub>3</sub>A, C<sub>2</sub>S, C<sub>3</sub>A

Now, high alumina cement if you take if you see its constituents here again, we have a C 3 A that is tricalcium aluminate in major portion whereas, C 2 S that is dicalcium silicate it is present in minor proportions and then C 2 AS it is nothing but dicalcium alumino silicate. So, it is a mixed type and then it is also present in the minor.

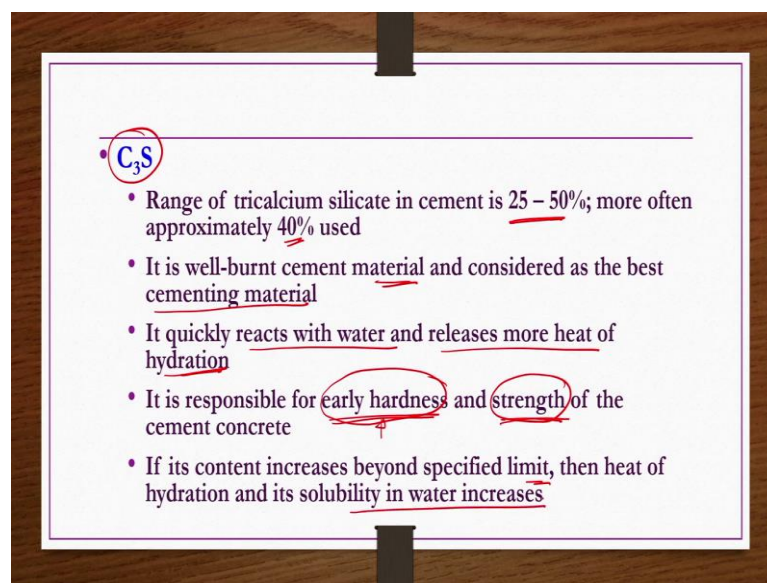
Then hydraulic hydrated lime if you take its constituents calcium hydroxide, hydroxide type and then its present in major proportions. C 2 S that is dicalcium silicate silicate type and minor proportions are present and then C 3 A that is tricalcium aluminate which is aluminate type and then its present in minor, right.

So, here each of them are having some kind of a you know role what is C 3 A is having role, what is C 3 S is having role, what is C 2 S is having role, what is C 2 AS having role, all of them are having some kind of roles in the overall mixture. Because actually the cement is nothing but mixture of C 2 S, C 3 S and then C 3 A these kind of a components are only present, right.

So, how we are making sure? We are doing some process to make sure only these things are there after purifying it. Actually, cement and lime making is very simpler or whatever the limestone is there you crush it and then try to make it purified in the minerals required and then you mix them and then you do the proper calcining in the calciners so that you can get the cement, ok.

So, systematically we are going to study them, ok. But primarily cement is having these constituents. So, then we need to know their role also.

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So,  $C_3S$  that is nothing but tricalcium silicate. Range of tricalcium silicate in cement is approximately 25 to 50 percent, but more often around 40-42 percent is used. It is well burnt cement material and considered as the best cementing material, ok. So, mostly you know over burnt is not good, lower burnt material is also not good.

What do you mean by burnt in the sense? Calcination we are doing. So, they are in general terminology we are calling them well burnt cement or over burnt cement or something like that, ok. So, it is well burnt cement material and considered as the best cementing material.

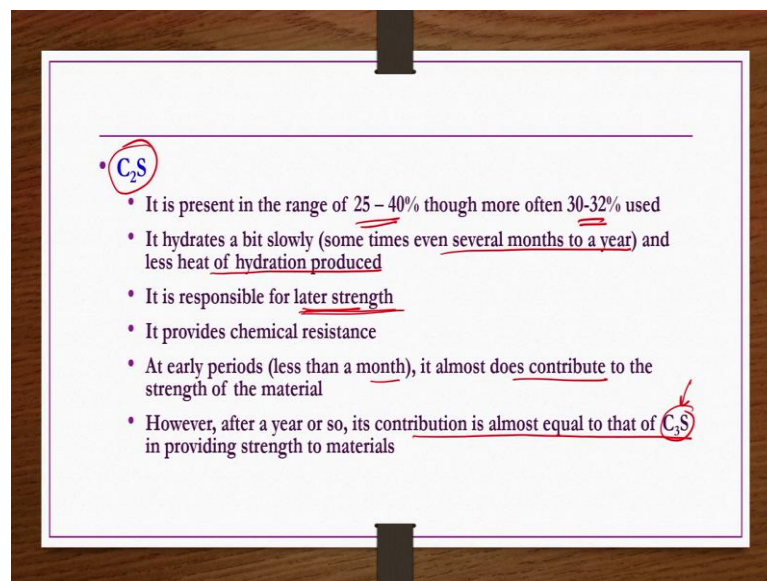
It quickly reacts with water and releases more heat of hydration, ok. So, if it reacts quickly with water and releases more heat of hydration; that means, it is possible that it may be drying up quickly. It is responsible for early hardness since it is reacting quickly

and then releasing more heat of hydration. So, then it is possible that it is giving that early hardness and then strength of the cement concrete that is mixed.

In the cement you know whatever the mixture that we have this material is the one which provides early hardness and then strength to the concrete when you mix with this sand and gravel etcetera. Why? Because let us say if it is not having early hardness or quickly you know drying up kind of thing, then what happened? Let us say when you are applying the cement so that mean if you are applying on a vertical surface that may be falling down, if it is not drying in a quicker time, ok.

So, that you need both quicker time as well as the drying you know in a slow pace both of them are required. So, this material is required for early hardness and then strength of the cement concrete. However, if its content increases beyond specified limit then heat of hydration and its solubility in water increases, ok.

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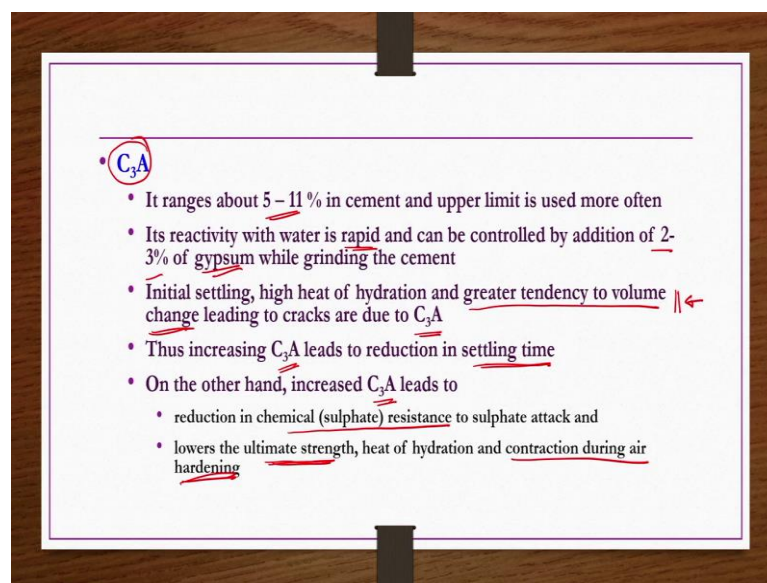
C 2 S it is present in the range of 25 to 40 percent though more often around 32 percent is used. It hydrates a bit slowly, sometimes even several months or a year also it may take to completely dry out ok, or completely hydrated out. And then less heat of hydration is produced, ok. It is responsible for later strength. Later strength in the sense, let us say if you calculate the compressive strength that is material concrete material is getting because of individual C 3 S, C 2 S etcetera.

The contribution of C 2 S in overall strength of the material is almost negligible at the early stage. But at the later stage may be after year or so the contribution of C 2 S in the strength of concrete material is almost equal to that of provided by C 3 S, ok. So, both are required sometimes. It provides chemical resistance to sulphates as well. At early periods less than a month it almost does not contribute to the strength of the material.

However, after a year or so its contribution is almost equal to that of C 3 S. Why we are comparing with C 3 S? Because C 3 S is the best cementing component that is present in the cement, ok. So, compared to this one C 2 S is also having equal importance because it provides the later strength which is also essential, ok.

If one provides the early strength so another provides the later strength, ok. That is the reason both this C 2 S and C 3 S are major contributions having in the cement overall cement mixtures as we have seen in the constituents of different types of cements, ok.

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Then C 3 A that is nothing but tricalcium aluminate. It ranges about 5 to 11 percent in the cement and then usually upper limit used more often, that is around 10 to 11 percent is used more often, ok. Its reactivity with water is very rapid and can be controlled by addition of 2 to 3 percent of gypsum while grinding the cement. So, reactivity with water is very quick and then it releases the high heat of hydration. So, but sometimes that high reactivity is not required.



So, if you wanted to control it. So, then what you do? While making the cement when you are doing the grinding so you can add 2 to 3 percent of gypsum to that cement, ok. Initial settling high heat of hydration and greater tendency to volume change leading to cracks are due to C 3 A.

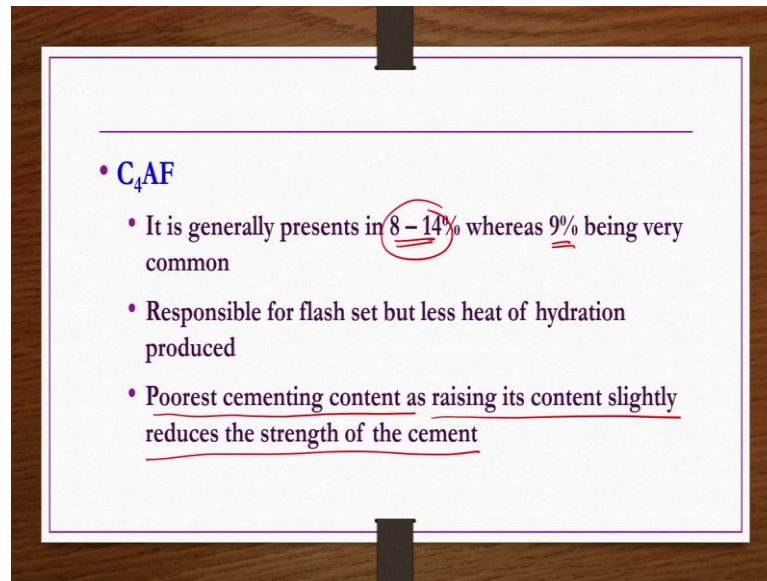
That is the problem with this one. It is least important material, because it is having greater tendency to volume change. If there is a tendency to volume change over the period of time then what happens? Either there may be contraction or expansion may be taking place.

So, whenever it is still such kind of volume changes are taking place. So, then definitely cracks would be there in the material. So, that is the problem with this one. Thus, increasing C 3 A leads to reduction in settling time. It does not require much settling time.

But on the other hand, when you increased C 3 A quantity in the cement it leads to reduction in chemical, resistance to sulfate attack and lowers the ultimate strength whatever the ultimate compressive strength that you would like to have in the final material that is also going to be lowered, ok.

So, heat of hydration is also getting lowered if you have more C 3 A and then contraction during air hardening will also take place. Actually, initially when you apply the cement sand gravel you know mixture concrete and then you allow it to air drying also, right. Contraction during air hardening will also take place. So, it is better to have this one as much less as possible and then this is the reason in the constituents of different cements, we have seen this is present in the less quantities in minor quantities.

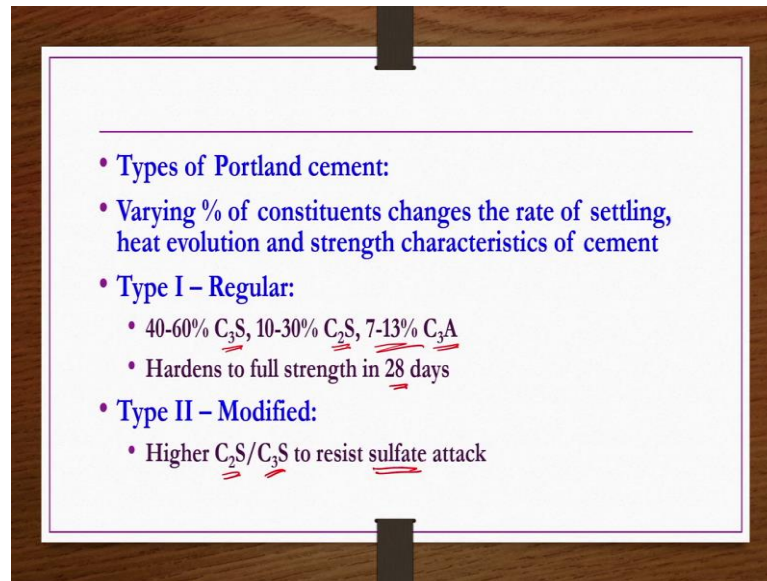
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$C_4AF$  that is tricalcium aluminoferrite it generally presents in 8 to 14 percent in the cement whereas, 9 percent is being very commonly used percentage in the cement. It is responsible for a flash set but less heat of a hydration produced. And then it is poorest cementing content as raising its content slightly reduces the strength of the cement, as you increase this percentage gradually the overall strength of the cement whatever is there that is going to be decreased in the final concrete.

So, that is about the constituents of a cement and their importance and etcetera those things we have seen. Now, we see different types of a Portland cement.

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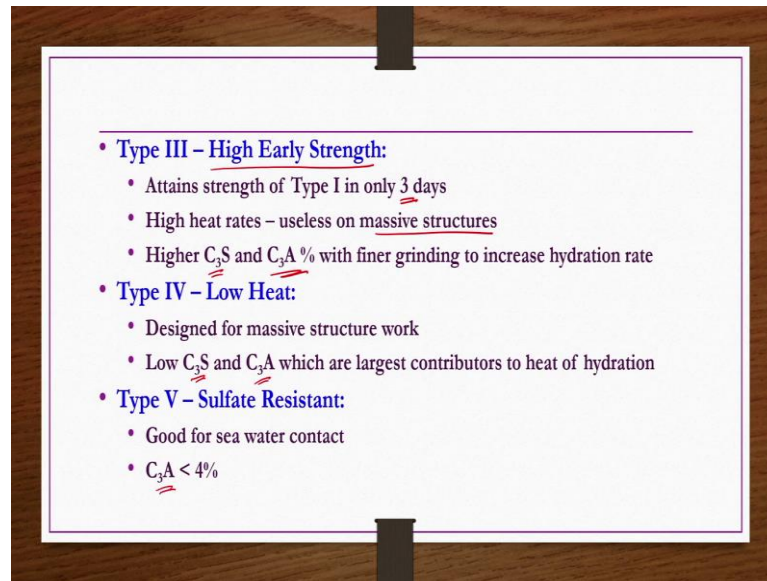


Types in the sense, depending on the percentage of the silicates aluminates that are present in the overall cement. The Portland cement is categorized as 5 different types type 1, type 2, type 3, type 4, type 5 like that.

So, those things we are going to see. Varying percentage of constituents changes the rate of setting, heat evaluation and strength characteristics of cement and then we see some of them type 1 is known as the regular one. Here you have 40 to 60 percent of C 3 S and then 10 to 30 percent of C 2 S and then 7 to 13 percent of C 3 A, only lowest one is this one C 3 A. And then hardens to full strength in 28 days.

So, whatever the full strength that this type 1 regular Portland type cement provides that can be obtained in 28 days, ok. Type 2 which is known as the modified one here higher C 2 S to C 3 S ratio would be maintained in order to resist chemical sulfate attacks.

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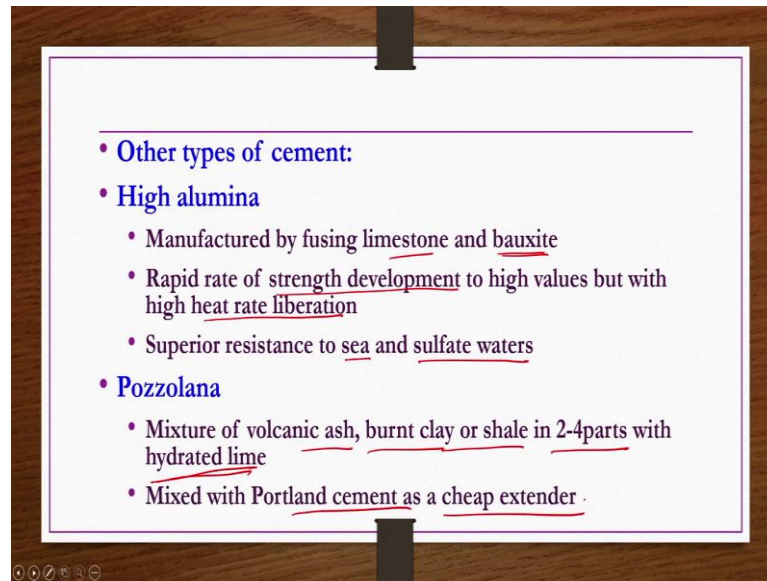


And then type 3 is high early strength if you wanted to have high early strength then type 3 is important, but obviously, high early strength is not good for the big constructions. It attains strength of type 1 in only 3 days. Whatever the strength that type 1 regular Portland cement attains in 28 days the same strength this type 3 high early strength can attain in just 3 days.

That is the reason it is known as high early strength type which is numbered as type 3. High heat rates, but it is useless on massive constructions because such rapid drying is not good. Higher  $C_3S$  and then  $C_3A$  percentage with final grinding to increase hydration rate is being done in these type of Portland cement.

Type 4 low heat it is designed for massive structure work and then low  $C_3S$  and  $C_3A$  which are largest contributors to heat of hydration. Type 5 sulfate resistant type good for sea water contact and then  $C_3A$  should be less than 4 percent. So, these are the 5 different types of Portland cements.

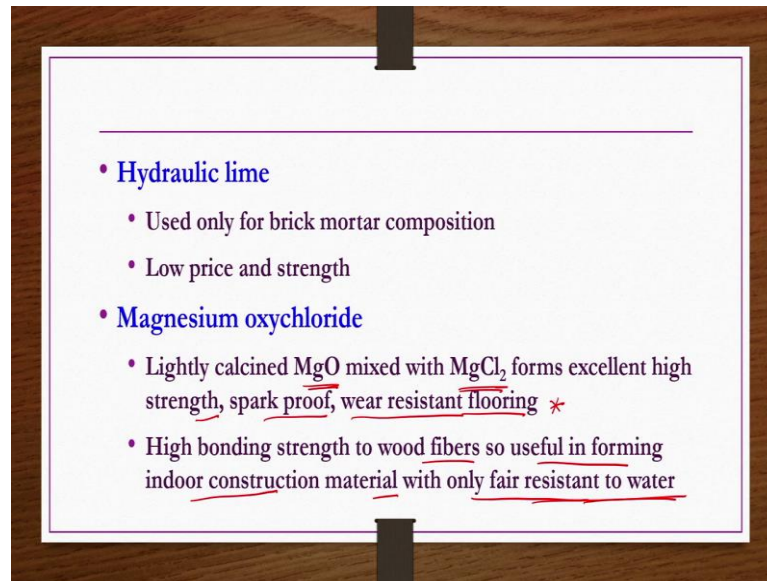
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Other types of cements if you take, high alumina cement manufactured by fusing limestone along with the bauxite and then rapid rate of strength development to high values, but with high heat rate liberation as well is one characteristic of this high alumina cement. It is having superior resistance to sea and then sulfate waters.

So, near sea if you have the construction, it is better to have a high alumina cements. Then Pozzolana cement it is a mixture of volcanic ash, burnt clay or shale in 2 to 4 parts with hydrated lime. Hydrated lime is nothing but calcium hydroxide those things are also we are going to see now. It is mixed with Portland cement as a cheap extender as well. So, that is another advantage of this one.

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Hydraulic lime is the other type of cement. It is used for brick mortar composition only and it is having low price as well as the low strength. Magnesium oxychloride lightly calcined magnesium oxide mixed with magnesium chloride forms excellent high strength, spark proof, wear resistant, flooring etcetera. So, because of these characteristics it is this material is often used for a indoor constructions, ok.

High bonding strength to wood fibers so useful in forming indoor construction material with only fair resistant to water. Because indoor constructions anyway they are not exposed to water anyway.

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• Relative compressive strength characteristics:

• Cement when mixed with other ingredients such as sand and gravel is used for structural purposes under compressive loading since it has very poor tensile strength

Type	Mortar composition	1 cement : 3 sand + H <sub>2</sub> O		
		Compressive strength, kg/cm <sup>2</sup>		
		1 day	3 days	28 days
Portland	Type I	37	→ 120	→ 340
	Type II	28	→ 83	→ 260
	Type III	103	→ 240	→ 440
	Type IV	20	→ 49	→ 177
	Type V	28	→ 88	→ 214
Hydrated lime			14	→ 30
Aluminous		280	→ 480	→ 690

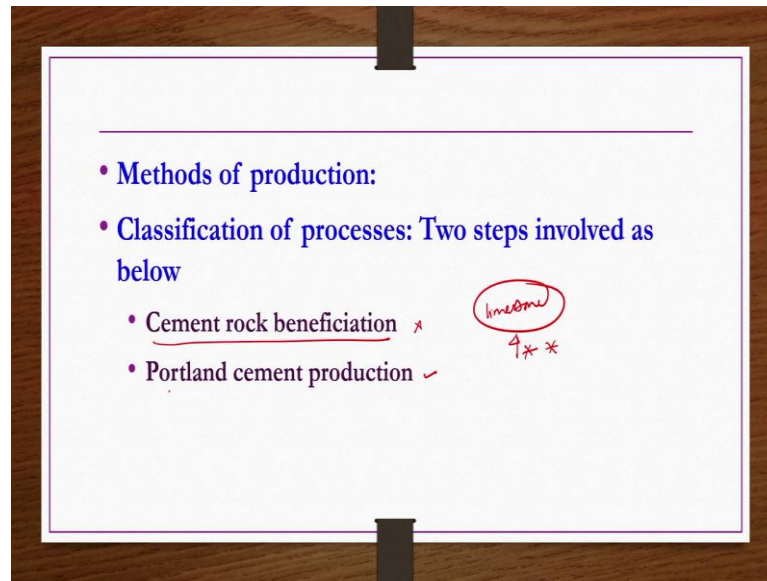
Now, we see relative compressive strength characteristics of different types of cements. Cement when mixed with other ingredients such as sand, gravel is used for structural purpose under compressive loading since it has very poor tensile strength, ok.

So, now cement one part is mixed with three parts of sand and water. Then different types of cement Portland all five types and then hydrated lime and aluminous cement if you take and then you compare their compressive strength in 1 day, in 3 days, in 28 days. Now, almost all cements you can see you know by increasing the number of days compressive strength of the concrete is increasing is not it? For all cements. So, that is good anyway.

But here what is important to observe is that Portland type 3 is having highest compressive strength even in one day that is already we have seen that type 2 material whatever the strength it gets in 28 days that you can get approximately 3 days by type 3 material.

That is the reason this type 3 is known as high early strength, high early strength cement. Because whatever the strength the other materials other types of cements are getting in 28 days that much strength this material is providing in three days only when you have one part of cement and then three parts of sand and water mixture, ok.

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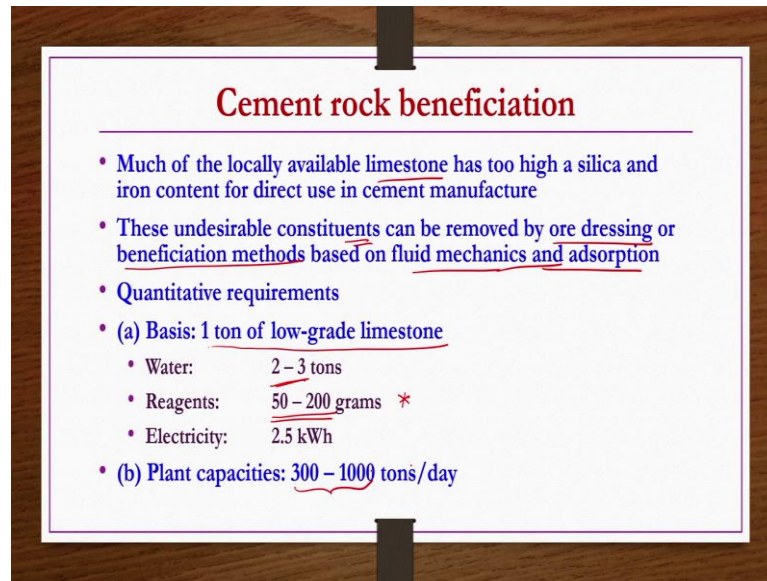


So, now we see methods of production. Classification of process two steps involved as below. One is the cement rock beneficiation another one is Portland cement production. Actually, you know whatever the limestone that is the basic raw material for the cement production that we understand. If it is having sufficient characteristics especially, from the requirement to make Portland cement production point of view.

So, then this step is not required, directly you can start going to Portland cement production that we can see. But most of the sources most of the raw materials that we have or most of the limestone that we have they are low grade that means, they are having so many impurities. So, beneficiation is required. So, we start with cement rock beneficiation then we go to the Portland cement production.



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### Cement rock beneficiation

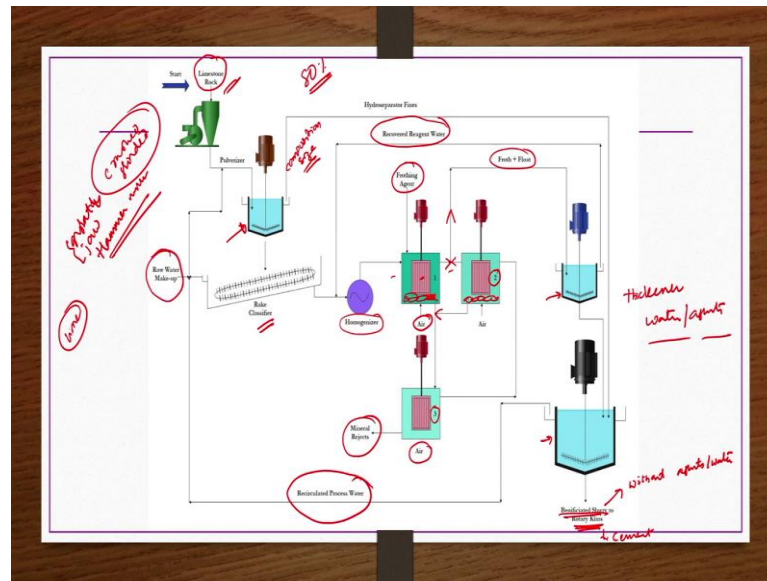
- Much of the locally available limestone has too high a silica and iron content for direct use in cement manufacture
- These undesirable constituents can be removed by ore dressing or beneficiation methods based on fluid mechanics and adsorption
- Quantitative requirements
- (a) Basis: 1 ton of low-grade limestone
  - Water: 2 – 3 tons
  - Reagents: 50 – 200 grams \*
  - Electricity: 2.5 kWh
- (b) Plant capacities: 300 – 1000 tons/day

Cement rock beneficiation: much of the locally available limestone has too high a silica and iron content for direct use in cement manufacture. So, obviously, it has to be beneficiated by over dressing or froth flotation etcetera. So, that is what we are going to see now.

These undesirable constituents can be removed by ore dressing or beneficiation methods based on fluid mechanics and adsorption, ok. So, quantitative requirements we start with. If you wanted to do the beneficiation of one 1 of low-grade limestone how much water is required? 2 to 3 tons.

Reagents 50 to 200 grams. These reagents are required to have in a kind of froth forming reagents that we are going to see anyway in flow sheet and then electricity 2.5 kilowatt hours. Plant capacities usually vary between 300 and 1000 tons per day.

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Now, this is the flow chart for a beneficiation of a cement rock, ok. Whatever the limestone rock that is there that usually crushed and then grinded to a required size specified size suitable for a undergoing you know Portland cement production, ok.

So, what we do often this material is usually crushed in a gyratory crushers or jaw crushers etcetera. Then we pass them to mills, several mills or hammer mills etcetera so that to reduce its size and then that size reduced material will be pulverized and then taken to a hydro separation unit. This is the hydro separation unit, ok.

Here what happens? The overflow of the hydro separation unit is usually having fines. Actually, what happens here in this hydro separator you add water and then mix it with and then based on the density difference as well as the size difference you know finers would be floating and then heaviers, bigger particle as well as the having heavier density you know they will be settling at the bottom.

Required ore whatever the lime, quick lime is there or whatever the lime we are expected to have to make cement that is usually floats on the top as a fine, ok. So, because of its less density and then smaller size compared to the mud and other kind of impurities or bigger size particles that are present at the bottom, right. Not only the size the constituents, composition also we have to see.

If the composition as well as the size is very much essential in the cement industry and then 80 percent of whatever the power is being applied in the cement industry is utilized for this size reduction and then drying these kind of operations, ok. So, if the size and then composition of the fines is sufficient enough that it can be directly taken to beneficiated slurry tank, right.

So, this directly will be taken to a rotary kiln where we can start making cement. If the size and then composition is not sufficient enough to directly send it to the rotary kilns for the cement making then what you do? You take that mixture to a classifier to which raw water make up water is supplied. Here what you try to have? You try to do the size separation of the material basically.

So, whatever the material which is having sufficient size that you take to the homogenizer, right. So, whatever the bigger size material is there that you can take back to the further processing again going through the so called you know size reduction etcetera again. So, this size reduced material will be sent to a homogenizer where homogenization of this material will take place by some kind of agents, right.

Then this mixture homogenized ore whatever is there it is basically in wet condition actually. So, it will be passed through a circuit of froth flotation. The circuit because we are calling circuit you can see that they are closed actually, right. So, this material is taken to a froth flotation unit this unit to which frothing agents are added and then air is being supplied and then the mixing mechanically mixing or agitation is being done.

When you do this one because of the frothing agent that is nature of this agent is to generate froth. So, then bubbles will form, right. These bubbles will be carrying the finer ores which are good for the subsequent process they will be attached to the surface of the bubbles, ok. And then they will be taken as an overflow from the top as if along with the froth, ok.

So, that will be taken to a final thickener unit thickness. Here actually these thickener units are what they are doing? We are removing the water and then agents etcetera whatever are there that are attached to the particles mineral particles they all be removed. And then that recovered reagent water is sent back to homogenized section again, right. So, then once removing the water and agents etcetera the minerals are taken to the rotary kiln for cement making, ok.

If this can be done in 1, 2, 3, 4, 5 depends on the nature of the basic limestone that you have the number of froth floatations and then size, design so many factor should be there. So, there may be some cases 5 floatation cells may also be required, ok. So, now let us say the top one whatever is there that we take as a like sufficiently good quantity and then it is having of characteristic which is suitable to make cement both size wise and then composition wise that you can take it to the thickener, right.

If it is not, if it is not then are the bottoms which are the heaviers one which are having the mud etcetera other kind of impurities all those things you take to the other floatation cell unit where similar operation is being done and then minerals rejected which are not suitable or not required for the cement making they are rejected here. Whereas, the other ones they are floating on the top along with the froth they may be useful.

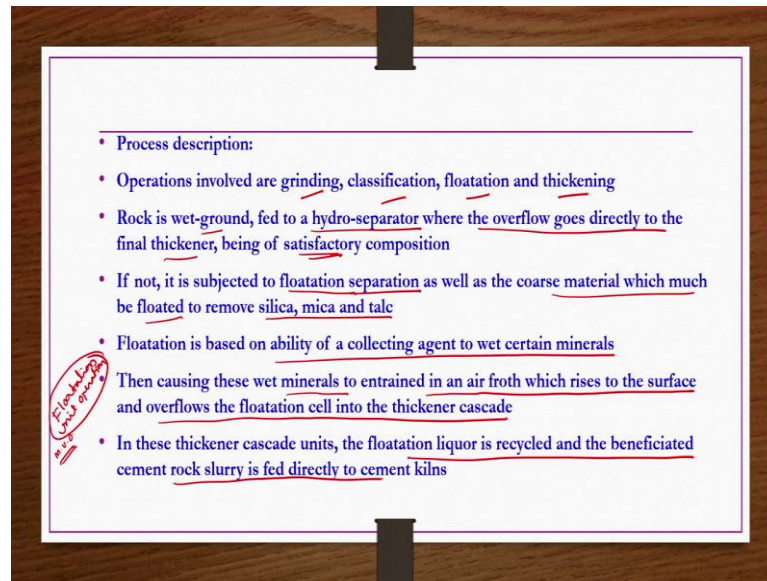
So, then they will be taken to a another floatation cell and then similar operation would be taken here right, by using air etcetera. So, the wastage whatever the bottoms are there bottoms may not be completely waste material there may be some important minerals which are good for cement making may also be there. So, then what we do that bottoms we take to this line again and then we do the similar processing.

Whereas, the froth or bubbles whatever floating at the top because of the froth formation they will be having the minerals or minerals attached to the froth and then they will be taken from the top as a overflow and then froth plus float floating material are taken to the thickeners.

In the final thickeners water and then whatever the frothing agents would be the attached to the minerals they will be removed in this thickeners and then whatever the recovered reagent water is there that is fed back to the homogenizer. And then beneficiated slurry without any agents or water etcetera are there they will be taken to the rotary klin where subsequent calcining will take place in order to get the cement ok, that we are going to see.

Actually, this is the flow chart for you know getting this beneficiated ore, in order to get beneficiated ore you know this is the process after removing ore the mud etcetera. So, in the thickeners whatever the process to water is there that is often recirculated and then used along with the raw water as maker, ok. The same information we are going to discuss here in the text.

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Operations involved are grinding then classification, then floatation and thickening as four different sections we have seen in the flow chart. Rock is wet ground fed to a hydro-separator where the overflow goes directly to the final thickener if its composition is satisfactory.

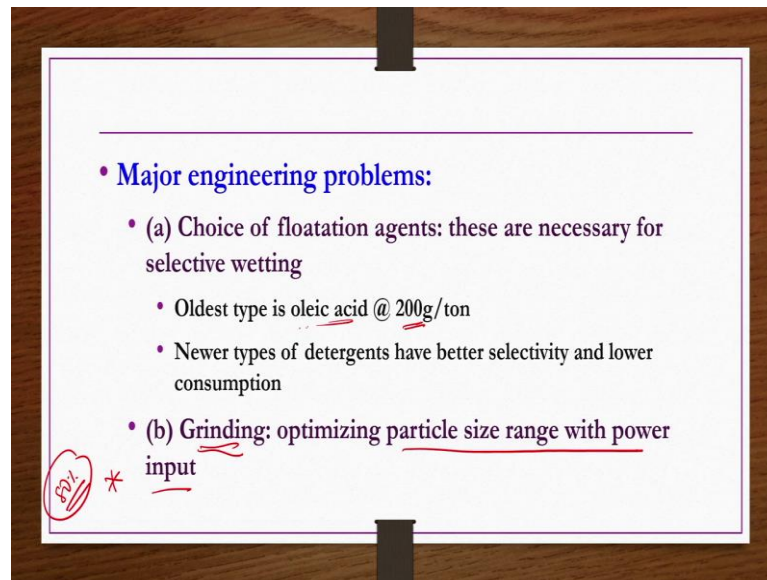
Otherwise, it is subjected to the floatation separation process or floatation circuit, circuit because it is completely closed that is the reason, we are calling a floatation circuit also sometimes used where more than one floatation cells are being used for the purpose, ok. So, the coarse material which must be floated to remove silica mica and talc.

Floatation is based on ability of a collecting agent to wet certain minerals specifically. So, here if you wanted to capture the lime. So, then you have to use a agent which is you know having ability or characteristics to wet only such kind of lime particles only it can wet and then lift it along with the froth and then take it to the next cell for the purification.

So, selection of agent is also very much important. Then causing these wet minerals to entrained in an air froth which rises to the surface and overflows the floatation cell into the thickener cascade. Actually, this floatation is a very important unit operation from chemical engineering point of view especially you know industries like cement, lime etcetera those kind of things are there.

So, this is separately studied in mechanical unit operations course where you can see the design, calculations etcetera everything you can discuss there, ok. In these thickener cascade units the floatation liquor is recycled and beneficiated cement rock slurry is fed directly to cement kilns.

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Major engineering problems of a beneficiation of a cement rock or lime stone is the choice of floatation agent. These are necessary for selective wetting and then oldest type of agent is oleic acid and approximately 200 grams per ton is utilized. Newer types of detergents have better selectivity and lower consumption.

Then second one is the grinding, optimizing particle size range with the proper input is very essential because 80 percent of the power that is utilized in industry especially cement industry like this you know mostly it goes for the run in the grinders, crushers etcetera.

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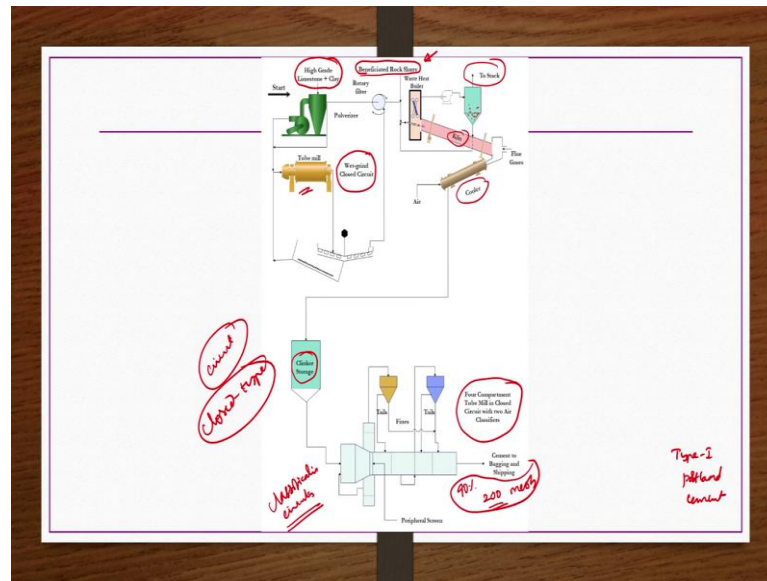
**Portland cement process**

- Chemical reactions:  
$$\text{CaCO}_3 \xrightarrow{1000^\circ\text{C}} \text{CaO} + \text{CO}_2; \Delta H = +44 \text{ kcal}$$
$$\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 \rightarrow \text{Mixture of } \text{C}_3\text{S}, \text{C}_2\text{S}, \text{C}_3\text{A}$$
- Quantitative requirements:
  - (a) Basis: 1 ton of Type I cement
    - Clay: 0.1 – 0.3 ton
    - Limestone: 1.2 – 1.3 tons
    - Gypsum: 0.03 – 0.05 ton
    - Coal: 0.25 – 0.40 ton
    - Water: 3 tons
    - Electricity: 80 kWh
  - (b) Plant capacities: 200 – 1200 tons/day

Now, we see production of Portland cement. Chemical reactions: calcium carbonate or beneficiated lime stone whatever is there that if you heat it to high temperature like 1000 degree centigrade calcium oxide would be formed by releasing carbon dioxide. This calcium oxide will be mixed with aluminates and silicates to get mixtures of C 3 S, C 2 S and C 3 A which is nothing but Portland cement ok, reaction is simple.

Process is also simple that we are going to see now. Quantitative requirements if you see to produce one ton of type 1 cement clay 0.1 to 0.3 tons required and then lime stone 1.2 to 1.3 tons required, gypsum 0.03 to 0.05 tons required and then coal 0.25 to 0.4 tons is required, water 3 tons required, electricity 80 kilowatt hours required, plant capacity usually varies between 200 and 1200 tons per day.

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Now, this is the flow chart for the production of type 1 Portland cement. Here two steps are there, right. If you have already beneficiated a rock slurry ok, or if you have high grade lime stone plus clay as initial material depending on that one process we choose. Since just now we have seen how to get the beneficiated rock slurry or beneficiated lime stone we start with this one. This lime stone is a processed through a kiln where the reactions take place at about 1000 degree centigrade, ok.

So, now here this beneficiated rock slurry is passed through a waste heat boiler right, and then whatever the material is there that is passed through kiln. From the boiler any fines gases along with the gases there may be some fines also would be there. So, they would be taken to a cyclone separator and then whatever the particles are there those particle would be fine particles would be collected and then sent to the kiln whereas, the gases would be there they will be taken to the stack, right.

While this material is passing through the kiln required a decarbonation of a calcium carbonate takes place and then you get a CaO, right. So, here you may supply some flue gases also in order to do the required operation. And then this material while going down here so then that calcium oxide whatever is there that will be cooled in a cooler by using air and then whatever the product that is there that is nothing but the clinkers that will be taken to a clinker storage.



These clinkers are passed through a classification unit or a classification circuit where size reduction of this clinker would be there and then screening of this material would be there. So, that to check the material whichever is having 200 mesh size or 90 percent of material passing through 200 mesh is that you collect as a product for the bagging.

Whereas the remaining fines you can take for the reprocessing for the size enlargement whereas, the oversize materials are recrushed and then processed for this classification circuit again to get the required size.

This is the process. Here in the classification circuit, you have four compartment tube mill in closed circuit with two air classifiers. Closed circuit in the sense the circuit the operation is completely closed only one input and one output is coming and then remaining whatever are there they are being circulated within the unit. So, that to get the most of the material is having 200 mesh size, ok.

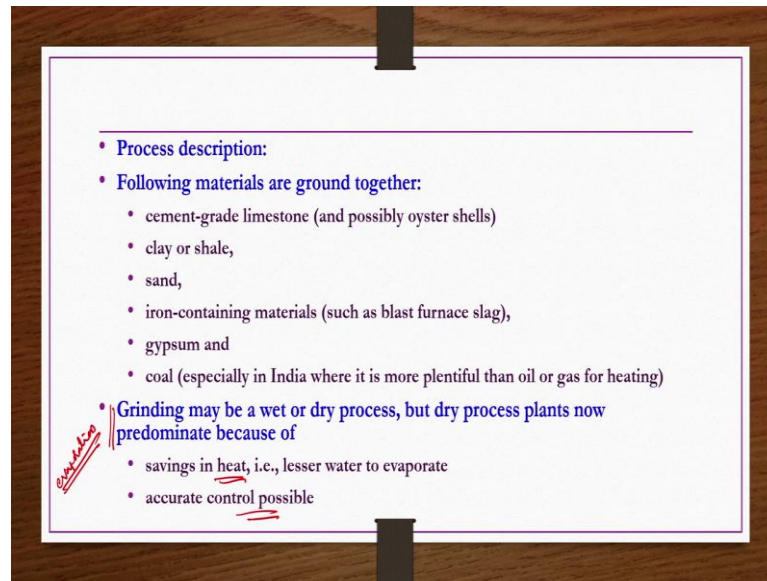
Let us say if you have high grade limestone along with the clay which is not beneficiated then what you do? You pass it through a size reduction circuit that is crushing, grinding etcetera then pulverizes and then that will be passed through a tube mill. So, after the size reduction that material is sent to a tube mill then here wet grinding taking place of this material.

This one would be sent to a hydro separator followed by the classification and then whatever the material of required size and composition is there that will be taken to a waste heat boiler and then this process continues like this, ok. So, this is crudely.

This process is you know known as the wet grind closed circuit, the air circuit because it is a grinding process only taking place size reduction and then size checking, if the size required size and composition is same then that can be taken as a product otherwise it will be sending back. That is the reason it is known as a circuit. Similar like you know floatation circuit here you know grinding circuit is there, here this one is the classification circuit is there, ok.

Circuit is the terminology is used for these operation so that to see closed type operations, ok. So, once the composition and size of the material after this wet grind closed circuit whatever you are getting it is of required specification to make cement then that will be passed through waste heat boiler and then same process continues, ok.

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Process description following materials are ground together. Actually, when you are grinding what are the materials that are grinding that is also important, not necessarily only a high grade limestone raw material there may be coal and other kind of materials may also be added depending on the type of a cement you are making. Since we are making type 1 Portland cement.

So, along with the high grade limestone you will be adding clay or shale, sand, iron containing materials such as a blast furnace slag etcetera, gypsum and then coal especially in India where it is more plentiful than oil or natural gas for heating. So, these are added together and ground, ok.

Grinding may be a wet or dry process, but dry process plants now predominant. Because in the dry process evaporation is not there a drying of the material is not there. Because before taking to the waste heat boiler is material has to be dried, ok. So, that is reduced and then obviously, savings in heat is there, right.

So, accurate process controlling is also possible if you have dry grinding process. Because if you have the wet grinding process how much moisture is there that cannot be maintained specified fixed kind of thing.

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- Sequence of size reduction may include
  - rough crushing,
  - followed by gyratory and hammer mills
  - then drying and fine grinding in tube mills
  - followed by air separation and pneumatic blending
- Dry powdered feed (or wet slurry) is then fed to a direct-fired counter-current rotary kiln
- Residence time is 1-3 hours and the feed mixture is decarbonated and fused to form the cement compounds (C<sub>2</sub>S, C<sub>3</sub>S, C<sub>3</sub>A)
- Hot clinker (3-10mm size) is dropped to a rotary cooler which also preheats combustion air for the kiln
- Product from tube milling the clinker is a powder of which 90% passes 200 mesh
- It is then bagged or bulk stored and shipped

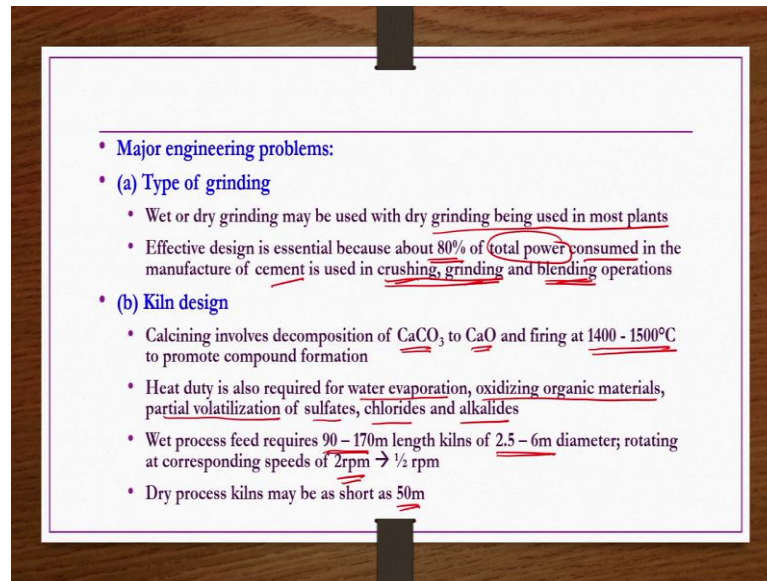
Sequence of size reduction may include the following steps like rough crushing followed by gyratory hammer mills, then drying and fine grinding in tube mills, followed by air separation and pneumatic blending. These processes are taking place in the whatever the grinding circuit that we have seen in the flowchart.

Dry powdered feed or wet slurry is then fed to a direct fired counter current rotary kiln. Resident time in the kiln is approximately 1 to 3 hours and then feed mixture is decarbonated and fused to form the cement components having C<sub>2</sub>S, C<sub>3</sub>S and C<sub>3</sub>A that is dicalcium silicate, tricalcium silicate and tricalcium aluminate mixtures.

Hot clinker which is having 3 to 10 mm size is dropped to a rotary cooler which also preheats combustion air for the kiln, then product from tube milling. The clinker is a powder of which 90 percent passes through 200 mesh size. 200 mesh size in this sense 1 linear inch, 1 inch linear inch distance if you take within this one if you have 200 openings.

Then that kind of screen whatever is there that means, a screen in which if you take a one linear inch distance and then if you count openings within that one linear inch distance you will find 200 openings. That is known as the 200 mesh such fine materials are there. So, approximately it may be around 600 or 650 micron size it is then bagged or bulk stored and shipped.

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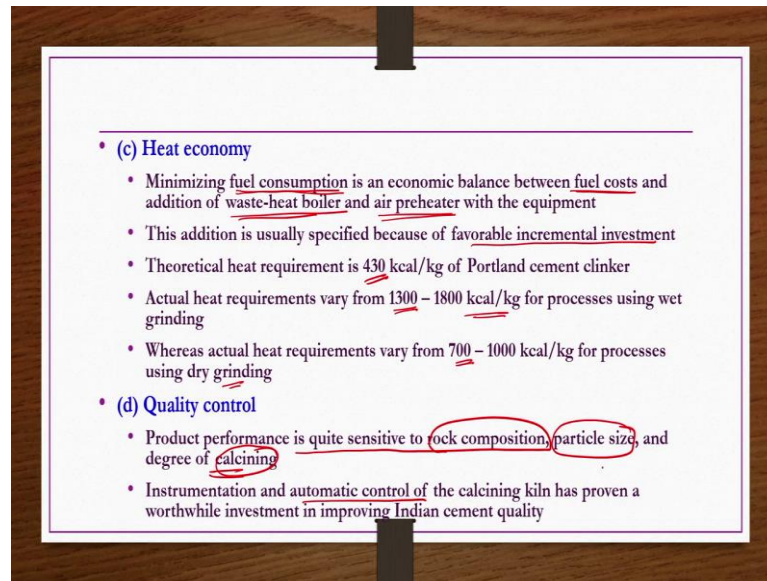
Major engineering problems: type of grinding, it is very essential because as we discuss like you know most of the power that is being applied in cement industries that is going for a you know this grinding operations. Wet or dry grinding may be used with dry grinding being used in the most plants you can use either of them. Effective design is essential because about 80 percent of total power consumed in the manufacture of cement is used in crushing, grinding and blending operations.

See crushing and then grinding are nothing but a you know size reductions, blending and mixing are the size enlargement kind of operation, ok. Klin design: calcining involves decomposition of calcium carbonate to calcium oxide and firing it 1400 to 1500 degree centigrade to promote compound formation.

So, it is very effective. Actually, in the cement making only two important things are there. Effective grinding to get the size reduced material of specified composition and then kiln in which the calcination is taking place otherwise there is nothing, is not it?

Heat duty is also required for water evaporation, oxidizing organic materials, partial volatilization of sulfates, chlorides and alkides. Wet process feed requires 90 to 170 meters length kilns having 2.5 to 6 meters diameter, rotating at corresponding speeds of 2 rpm to half rpm. Dry process kilns may be as short as 50 meters.

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Heat economy is very essential, right. How? Minimizing fuel consumption because most of the power is being used for the size reduction and then crushing, grinding etcetera. So, minimizing fuel consumption is an economic balance between fuel cost and addition of waste heat boiler and air preheater with the equipment to the kiln. This waste heat boiler as well as the air preheater has been attached, we have seen in the flow sheet, ok.

This addition usually specified because of favorable incremental investment. Theoretical heat requirement for making Portland cement clinker is approximately 430 kilo calories per kg. However, actual heat requirements vary between 1300 to 1800 kilo calorie per kg, if the wet grinding has been done. If you do dry grinding then it increases from theoretical value of 432, 700 to 1000 kilo calorie per kg for dry grinding processes.

Quality control: product performance is quite sensitive to rock composition, low grade rock or high grade rock that is and then particle size; what is the size of the particle suitable to do the subsequent operation and degree of calcining right, degree of calcining are three important. So, instrumentation and automatic control of the calcining kiln has proven a worthwhile investment in improving the Indian cement quality.

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- Importance of substituted raw materials:
- High grade and beneficiated circuit rock will obviously beneficial from quality viewpoint
- But from economics viewpoint, these have to be supplemented by blending with burnt clays and blast furnace slag to conserve native limestone
- For e.g., at Fertilizer Crop. of India Ltd., Sindri,  $\text{CaCO}_3$  sludge is utilized in producing 600 tons cement per day
- This sludge comes from the reaction:

$$\text{CaSO}_4 \text{ (gypsum)} + (\text{NH}_4)_2\text{CO}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3$$

Importance of substituted raw materials: actually, if you have a high grade raw material then obviously, you can get a high quality cement no problem, it is very good in general. But having such high grade raw material is expensive because most of the raw materials that we get are most of the ore that we have in India it is a low grade one. So, much of purification is required.

So, you have to think of how to reduce the cost, how to make it efficient by having some other substituted raw materials also. So, that is what we see now. High grade and beneficiated circuit rock will obviously, beneficial from quality viewpoint whatever the beneficiation process we have done. So, material after beneficiation you are having for the cement making as a raw material then it is quite good from the quality point of view.

But you know you have to make sure that the venture has to be profitable. We have already seen that you know it is a low margin venture cement industry. So, then if at all any possibility of there to reduce the financial load on the plant so then it is going to be efficient. So, but from economics view point this have to be supplemented by blending with burnt clays or blast furnace slag to conserve native limestones.

For example, at fertilizer crop corporation of India limited in Sindri calcium carbonate sludge is utilized in producing 600 tons cement per day such important is this one. How this sludge is coming? This plant what is happening calcium sulfate gypsum is there, that

reacts with the ammonium carbonate to get the ammonium sulfate and then calcium carbonate.

This sludge one can use as a kind of supplement along with the quality raw material. So, that you can you know reduce the load financial load on this, ok. So, because of such reasons sometimes these plants are you know installed nearby plants where this sludges can also be utilized, ok.

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• Another e.g. of substituted raw materials involves cement production as a co-product in production of  $H_2SO_4$  from gypsum

- This process produces cement clinker and a gas-containing 9%  $SO_2$  as co-products
- The process is carried out by heating gypsum, coke and shale in a coal-fired kiln at 2500°F
- Following are some of the reactions which occur
- $CaSO_4 + 2 C \rightarrow 2 CO_2 + CaS$
- $CaS + 3 CaSO_4 \rightarrow 4 CaO + 4 SO_2$
- $3 CaS + CaSO_4 \rightarrow 4 CaO + 2 S_2$
- $2 CaSO_4 + C \rightarrow 2 CaO + CO_2 + 2 SO_2$

Another example of substituted raw materials involves cement production as a co-product in production of  $H_2SO_4$  from gypsum. In the production of  $H_2SO_4$  if you remember we have a product gypsum, right. This gypsum is also co-product; it is being produced in large quantities along with this  $H_2SO_4$ .

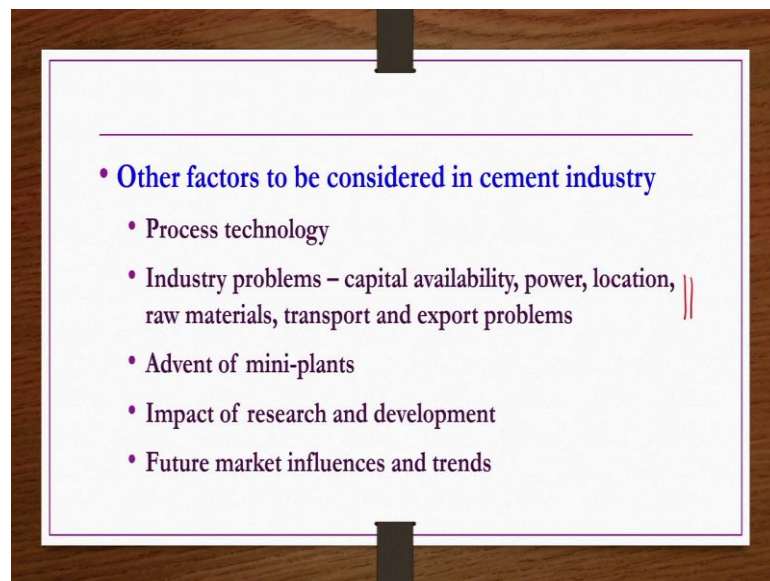
So, this gypsum can be utilized and then produce cement. So, how you can do? You can simply heat it. This process produces cement clinkers and a gas containing 9 percent  $SO_2$  as co-product. This process is carried out by heating gypsum coke and shale in a coal-fired kiln at 2500 degrees Fahrenheit. So, simple process whatever the gypsum is there along with that one you take coke and shale and then put it in a kiln, mix it thoroughly and then put it in a kiln for required heat treatment to get the cement.

Following are some of the reactions which occur if you are making cement from the gypsum co-product from the  $H_2SO_4$  plant. So, what are these reactions? So, calcium

sulfate reacting with the coke to give the carbon dioxide and calcium sulfide. This calcium sulfide further reacts with the calcium sulfate to give the calcium oxide and then this can be used for the cement production. Of course, SO<sub>2</sub> is also being produced, right.

So, these are the possible reactions in most of the reactions what you can see now here you can see the CaO is being produced, ok.

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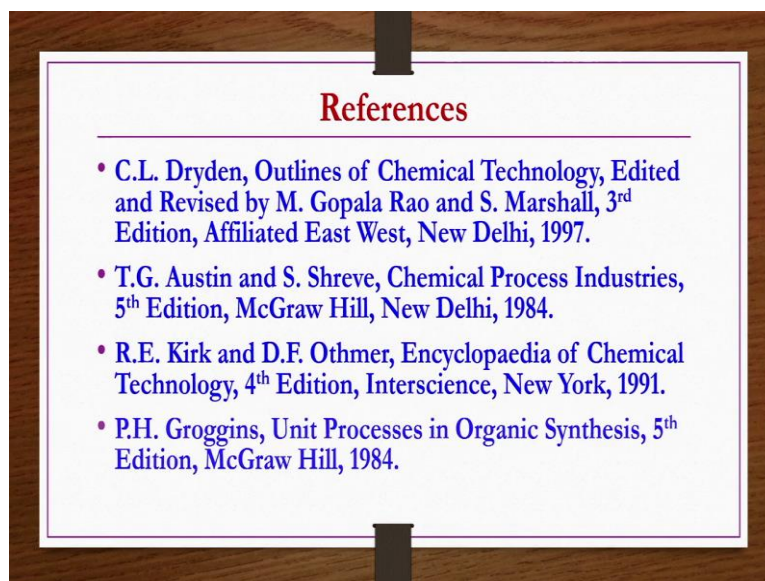
Other factors to be considered in cement industry we are just listing we are not going into the details. Something like process technology, industry problems like capital availability, power, location, raw materials, transport and export problems. These are the problems for almost all industries you know one has to take about these problems.

Then advent of mini plants, impact of research and development because when you have such kind of a high-tonnage, low-cost, low-margin production so then obviously so many research and developments may be keep coming. So, one has to be watchful about those and then try to incorporate whichever is most beneficial from both the quality as well as the economics point of view. Future market influences and trends is also very much important.

References for this lecture are provided here.



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Thank you.