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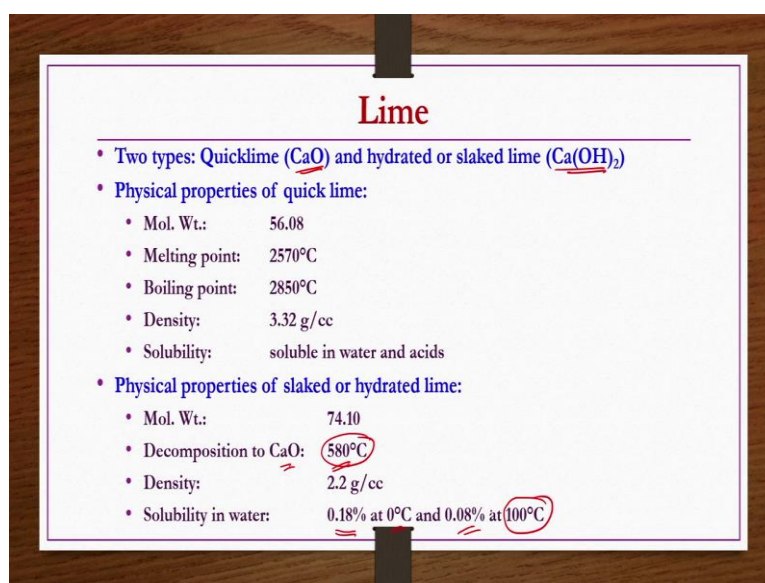
**Lecture - 26**  
**Cement and Lime Industry - Lime**

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Cement and Lime Industry - Lime. In the previous lecture we have seen a few introductory details about the lime and cement industries.

Then we started discussing about the cement, different types of cements, constituents of the cements, properties of the cement and then manufacturing of the cement especially Portland cement before making Portland cement. How to do the beneficiation of limestone, rock etcetera. Those details we have seen.

In addition, we have also discussed the major engineering problems associated with the cement industry, right. Now, in this lecture what we are going to see, we are going to discuss about the lime, which is also one important component or one important product coming from the limestone basic raw material.

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**Lime**

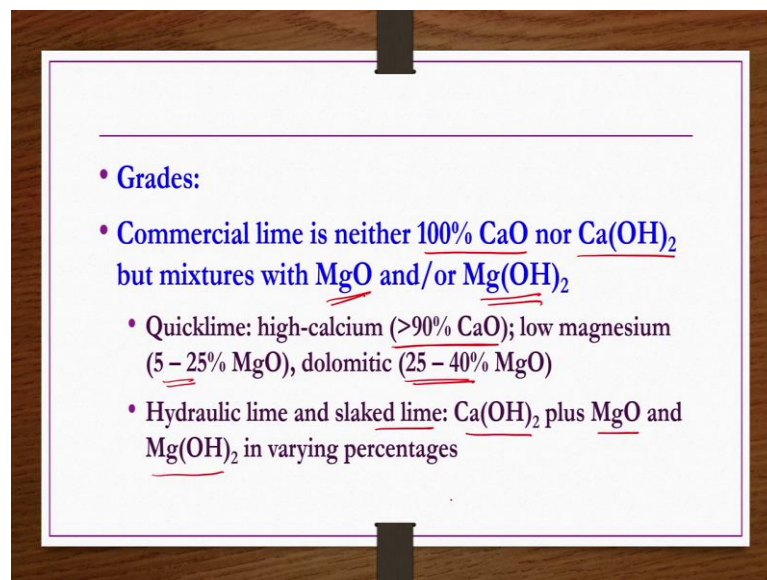
- Two types: Quicklime ( $\text{CaO}$ ) and hydrated or slaked lime ( $\text{Ca(OH)}_2$ )
- Physical properties of quick lime:
  - Mol. Wt.: 56.08
  - Melting point: 2570°C
  - Boiling point: 2850°C
  - Density: 3.32 g/cc
  - Solubility: soluble in water and acids
- Physical properties of slaked or hydrated lime:
  - Mol. Wt.: 74.10
  - Decomposition to  $\text{CaO}$ : 580°C
  - Density: 2.2 g/cc
  - Solubility in water: 0.18% at 0°C and 0.08% at 100°C

Two types of limes are possible, one is the quick lime that is calcium oxide and another one is the hydrated or slaked lime which is nothing, but calcium hydroxide. Now, we see

the physical properties of both individually. Physical properties of quick lime, molecular weight is 56.08, melting point is 2570 degree centigrades, boiling point is 2850 degree centigrade, density is 3.32 gram per cc, solubility, soluble in water and the acids.

Now, the physical properties of slaked or hydrated lime, if you see molecular weight is slightly higher, 74.10 because it is hydrated with the water. However, it decomposes to calcium oxide at 580 degree centigrade, its density is 2.2 gram per cc, solubility in water is low that is about 0.18 percent of slaked or hydrated lime is soluble in water at 0 degree centigrades which further decreases if you increase the temperature to 100 degree centigrades.

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Grades, whether quick lime or hydrated lime it is not available in 100 percent pure form commercially, so they are usually mixed. Commercial lime is neither 100 percent CaO nor 100 percent calcium hydroxide, but it makes sure with magnesium oxide and or magnesium hydroxide.

Quicklime, high-calcium if it is high calcium type, then more than 90 percent CaO would be there, low magnesium type then 5 to 25 percent magnesium oxide would be there and if it is dolomitic type 25 to 40 percent magnesium oxide would be there. Hydraulic lime or slaked lime it is nothing but calcium hydroxide plus magnesium oxide and magnesium hydroxide in varying percentages.

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- Consumption pattern:
- Uses of lime in chemical manufacture are too numerous to discuss
- Over 150 important chemicals are made with this basic material
- In fact, only five other raw materials are used more frequently than lime for chemical manufacture are: salt, coal, sulfur, air and water
- For e.g., Lime is used as a basic flux in the manufacture of steel
- Silicon dioxide is a common impurity in iron ore which cannot be melted unless it combines with other substance first to convert it to a more fluid lava called slag
- Silicon dioxide is a Lewis acid and therefore it reacts with the Lewis base lime
- $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
- Molten silicate slag is less dense than the molten iron and collects at the top of the reactor, where it can be drawn off
- Over 100 lbs of lime must be used to manufacture a ton of steel

Consumption pattern, so the application or utilization of calcium hydroxide for chemical industries is huge more than 150 chemicals are produced either by using this one directly or indirectly for the process. Such largely it is used. In fact, it is one of the top 5 chemicals, which are vastly used.

Let us say air, water, coke or coal these things are very often used in the industries most of the industries. But apart from those calcium hydroxide or calcium oxide or the lime whatever is there that is used extensively for the production of variety of chemicals. So, listing all of them is not possible. However, we see a few important understandings about utilization of this chemical for productions in some other industries.

Uses of lime in chemical manufacture are too numerous to discuss, over 150 important chemicals are made with this basic material. In fact, only 5 other raw materials are used more frequently than lime for chemical manufacture they include; salt, coal, sulfur, air and water ok.

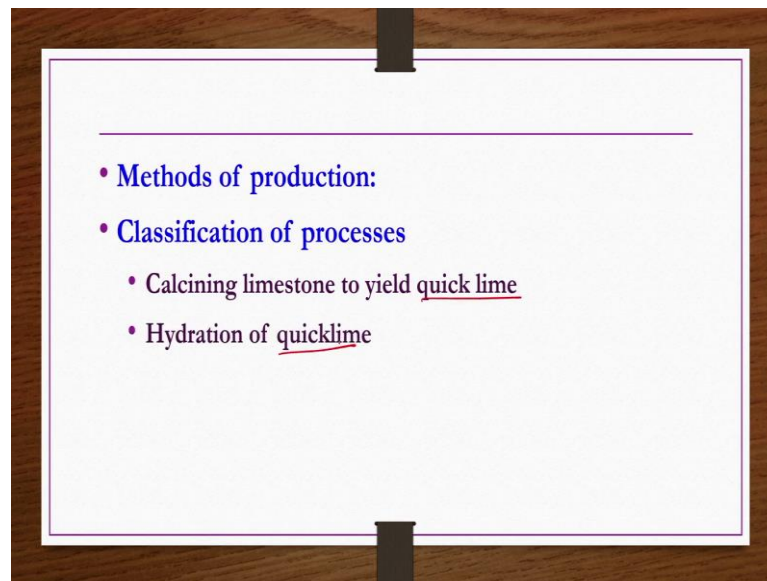
So, for example, lime is used as a basic flux in the manufacture of steel, whatever the ore that is taken for the production of steel is having so many types of silicates or silicon dioxide would be there. So, that cannot be removed because if you heat it, so then it becomes a kind of very viscous slurry kind of thing it cannot be removed.

So, then how it can be removed? It has to be reacted with the other chemical first and then formed a different chemical which can be easily removed. So, calcium hydroxide is one such chemical which reacts with the silica to form calcium silicates and then that can be easily removed in making the steel process ok.

So, silicon dioxide is a common impurity in iron ore which cannot be melted unless it combines with other substance first to convert it to more fluid lava called slag. Silicon dioxide is a Lewis acid and therefore it reacts with the Lewis base lime by this reaction that is, calcium oxide reacts with the silica to give calcium silicate.

Molten silicates slag is less dense than the molten iron, so obviously it floats and collects at the top of the reactor where it can be drawn off. Over 100 pounds of lime must be used to manufacture a ton of steel that much important is the slime in the steel industry.

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Methods of production of lime, classification of processes if you see, calcining limestone to yield quick lime and then hydration of quick lime. So, these two we are going to see. Actually, both of them can be studied in one single flow sheet itself.

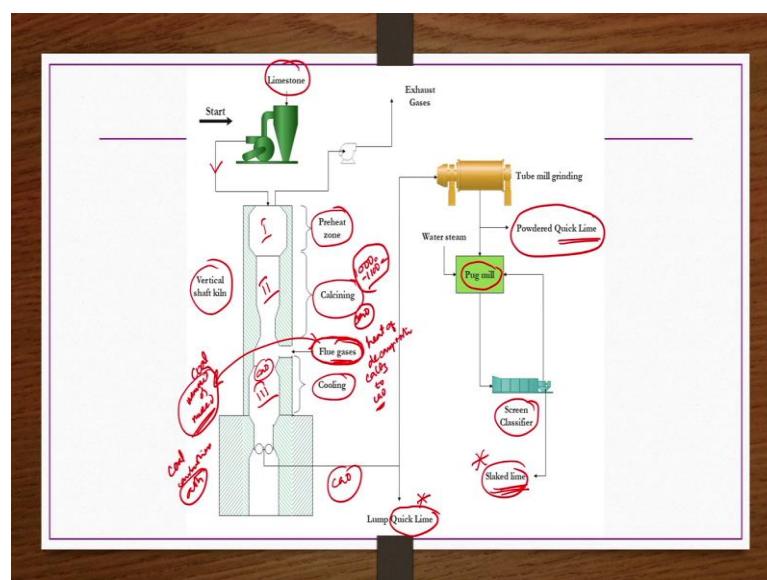
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### Quick lime process

- **Chemical reaction:**
  - $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g}); \Delta H = +44 \text{ kcal}$
- **Quantitative requirements:**
  - (a) **Basis: 1 ton CaO**
    - Limestone (pure): 1.87 tons
    - Coal: 0.3 ton
  - (b) **Plant capacities: 100 – 500 tons/day**

Quick lime process, chemical reactions if you see. If you apply heat to the calcium carbonate, you can get the calcium oxide by releasing the carbon dioxide. Quantitative requirements, if you want to produce one ton of calcium oxide, pure limestone 1.87 tons required, coal 0.3 tons required and plant capacity varies between 100 and 500 tons per day in general.

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Now, this is the flow chart for making quick lime as well as slake lime as well hydrated lime. So, we see in detail here. Whatever the limestone rock is there, raw limestone or

rock of the limestone whatever is there that will be passed through a size reduction circuit. So, that to undergo this material for the crushing, grinding and then ultrafine grinding if required, right.

The size reduced material when it is of sufficient size, then it will be sent to a vertical shaft kiln, which is having three zones one is the preheating zone it is at the top, then calcining zone that is at this middle and then cooling zone at the bottom, right. So, the size reduced material after having sufficient size that will be passed through vertical shaft kiln and then in the preheated zone, preheating of the material will be done and then in the second calcining zone the temperature is approximately 1000 to 1100 degree centigrade, right.

So, because calcium carbon decomposes to calcium oxide at around 900 degree centigrade something like that. So, then that is the reason the temperature in in the calcining zone has to be more than that one. So, approximately 1000 degree centigrade is maintained. Here most of the CO<sub>2</sub> is released and then CaO would be obtained.

And then this calcined material whatever calcium oxide is there that is sent to the cooling zone, where the cooling of that material is taking place. And then that lumps of CaO whatever is there that is collected as lump quick lime ok. So, this is the quick lime production. If you wanted to have hydrated or slake limes. So, this quick lime passed through tube mill grinding, where crushing of this lumps would be taking place, right.

Whatever the fine particles; very fine particles of quick lime are there, which are cannot be sent to a subsequent operation they will be collected as powdered quick lime which are very fine in general. So, other than this fine material the remaining material is sent to a plug mill in which water steam is also provided.

So, that you know required hydration can take place and then this mixture is sent to a screen classifier, then after this screen classifier whatever the materials having sufficient size something like 2 mm or 2 centimeters etcetera. They will be taken as a slaked lime, whereas the other size material would be sent back to the pug mill for the subsequent hydration etcetera.

So, this is the production of slake or hydrated lime production. So, both the process we have discussed here.

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• **Process description:**

- Limestone is quarried or mixed and put on conveyors feeding the mill crushing unit
- Limestone of several sizes is produced with
  - jaw or gyratory crushers used for hard rock and
  - hammer or roll mills used for soft rock
- **Size depends on type of calciner as follows:**

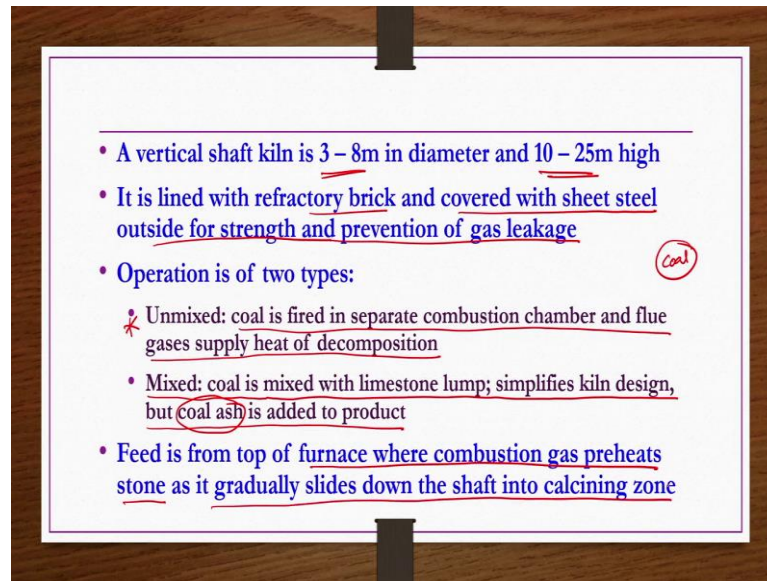
|                         |              |
|-------------------------|--------------|
| • Vertical shaft        | 10 – 20cm    |
| • Moving bed:           | 1 – 10cm     |
| • <b>Rotary kiln:</b>   | 0.5 – 5cm    |
| • <b>Fluidized bed:</b> | 0.5 – 0.05cm |
- Vertical shaft or rotary kilns are usually specified

Now we see description of this process here. Process description limestone is quarried or mixed and put on conveyors feeding the mill crushing unit, limestone of several sizes is produced with jar or gyratory crushers used for hard rock and then if the rock is soft rock then hammer or roll mills are used especially when the soft rock is there. Size depends on the type of calciner as follows, different types of calciners are there in general that is what it means by.

So, if the size is between 10 to 20 centimeters then you should use vertical shaft, if the size is 1 to 10 centimeters then it is better to go for the moving bed calciner, if the size is very small like 0.5 to 5 centimeters then rotary kilns are better option, if the size is very fine like 0.5 to 0.05 centimeters then fluidized beds are important. So, such important is the size reduction operation.

So, size reduced material depending on the size of the size reduced rock you have to select the which type of calciner you should use. But however, mostly vertical shaft and then rotary kiln are preferred, rotary kiln is much more preferred because of its advantages as we are going to discuss subsequent slides ok. Vertical shaft or rotary kilns are usually specified.

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A vertical shaft kiln is 3 to 8 meters in diameter and 10 to 25 meters high that whatever the flowchart we have seen that is usually having 10 to 25 meters high and then 3 to 8 meters diameter. It is lined with refractory brick and covered with a sheet steel outside for strength and prevention of gas leakage. Operations are two types because in this kind of material the coal is also mixed sometimes.

So, because of the addition or not addition, the operation is two types; is one is the unmixed where coal is fired in a separate combustion chamber and the flue gases supply heat of decomposition. The other one is the mixed that is coal is mixed with limestone lump, simplifies kiln design, but coal ash is added to the product. So, it is not good that is the reason primarily people prefer for this unmixed process.

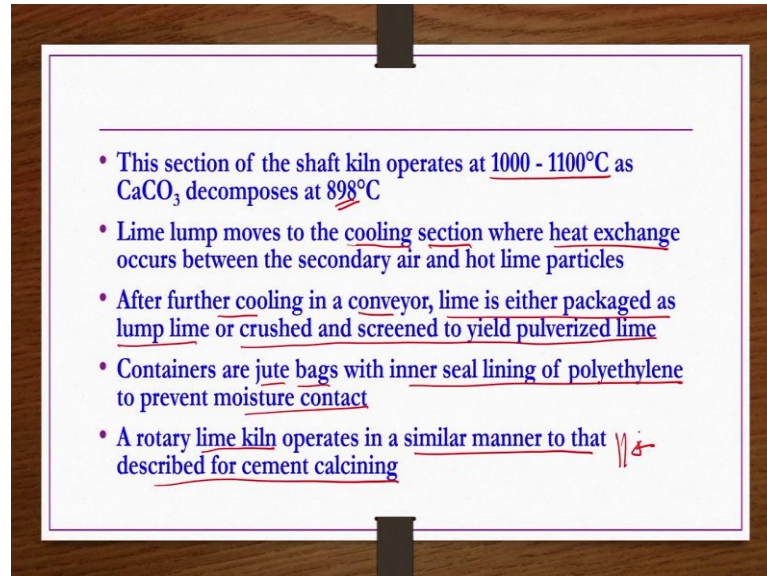
So, the purpose of this flue gas here is that this provides the heat required for the decomposition of calcium carbonate to calcium oxide. How you get this flue gas? So, then you use coal right, either unmixed or mixed with the limestone rock size reduced material. Often it is done unmixed because if you do the mixed the ash coal ash may be there or you know coal combustion may lead to ash formation that is present in the coal. So, that ash would be mixed with the product.

So, it is better to go for a unmixed operation ok that is the purpose of coal using here and because to get the flue gases and those flue gases provide the required heat of decomposition of calcium carbonate to calcium oxide. Feed is from top of furnace where



combustion gas preheats stone limestone as it gradually slides down the shaft into calcining zone.

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This section of the shaft that is calcining zone of the kiln operates at 1000 to 1100 degree centigrade as calcium carbonate decomposes at around 898 degree centigrades. Lime lump moves the cooling section where heat exchange occurs between the secondary air and hot lime particles. After further cooling in a conveyor, lime is either packaged as lump lime or crushed and screened to yield pulverized lime as per the requirement.

Containers are usually jute bags with inner seal lining of polyethylene to prevent moisture contact. A rotary lime kiln operates in a similar manner to that describe for cement calcining that we have seen.

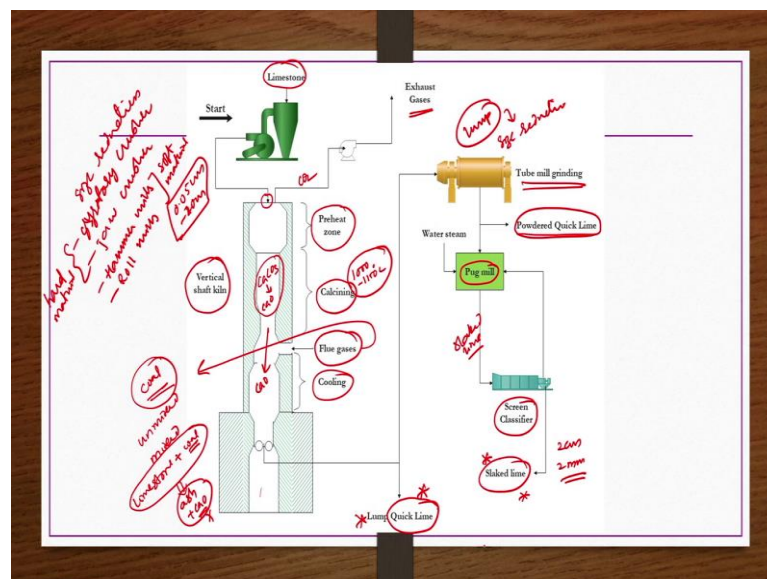
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### Hydrated lime process

- **Chemical reaction:**
  - $\text{CaO(s)} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2\text{(s)}$
- **Quantitative requirements:**
  - (a) **Basis: 1 ton of  $\text{Ca(OH)}_2$** 
    - Quicklime (pure): 0.787 ton
    - Water: 0.242 ton
  - (b) **Plant capacities: 50 – 100 tons/day**

Now, hydrated lime process, here chemical reactions if you see calcium oxide whatever the lime quick lime you got that if you do the hydration then you get calcium hydroxide or hydrated lime ok. Quantitative requirements in order to get a one ton of calcium hydroxide or hydrated lime, quick lime pure one you need 0.787 tons, water you required 0.242 tons and then plant capacity between 500 and 100 tons per day in general.

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So, the same flow sheet is shown here again ok. So, the limestone whatever is there, that is usually size reduced in a size reduction unit, size reduction can be done by you know

gyratory crushers or jaw crushers. If the material is wet, these kind of gyratory crushers are used if the material or the limestone is hard material, if it is soft material then hammer mills or roll mills are used for soft material soft limestone if you are having that one you do.

And then after size reduction the particles may be anywhere between 0.05 centimeters to 10 or 20 centimeters something like that ok. Now, depending on the type of crusher or grinder or both you have selected, sometimes both may also be required not necessarily always you may be going for one this, depending on the energy efficiency ok.

So, depending on the size of the reduced, size reduced material you have to choose a kiln, right. So, let us say your material size is such a way that you are choosing vertical shaft kiln, then it is having three zones; the top one is the preheated zones to which the size reduced material is fed, right.

Next one is the calcining zone where the temperature is maintained approximately 1000 to 1100 degrees centigrades, because this is the zone at which decomposition of calcium carbonate to calcium oxide takes place and then whatever the gases CO<sub>2</sub> etcetera are there they will be taken to the exhaust gases. Now how this temperature you would be maintaining that is by flue gases.

So, this flue gases, how you are going to get you are going to get by using the coal. So, when you do the coal combustion then required energy to decompose calcium carbonate to calcium oxide would be there. So, coal combustion can be done to get this flue gases and then this flue gases would be decomposing calcium carbonate to calcium oxide ok.

So, this coal usually used either unmixed way that is separately combust the coal and then utilize the energy for you know heating this calcining zone ok, that is unmixed one. Another one is that mixed one, so that is you know this limestone whatever is there that and then coal both of them are fed together to the kiln and then within that one the required combustion is taking place.

But here what happened in the coal ash would be there obviously, inorganic constituents of coal whatever are there. So, they will be forming you know ash. So, that ash may be joined with the calcium oxide, so which is not good because you want ash pure calcium oxide lime as possible ok. So, it is better to go for unmixed operation ok.

So, now, once this decomposition taking place, the particles whatever calcium oxide particles are there they will be sliding down to cooling, where the required heat exchange will take place. And then cold lime is collected as lump quick lime ok. Now this quick lime if you wanted to get hydrated or a slaked lime from it, what you have to do?

You have to take it to a tube mill grinding where size reduction takes place, because quick lime is there in the lump size, lump to size reduction would be done in this tube mill grinding, right. Here again the size may be depending on the degree of grinding, there may be some fine very fine particles will also be there along with the intermediate particles.

So, very fine particles would be collected as a powdered quick lime, whereas the intermediate and fine products will be mixed with water in a pug mill. And then required a hydration reaction takes place to get a slaked lime or hydrated lime, that will be passed through a screen classifier to do required sizing, required sizing in the sense you may be required you know 2 centimeters or 2 millimeters size of hydrated lime only.

So, over size one maybe you can send back to the pug mill and then required size maybe you can take it as a product, alright. So, both quick lime production as well as the hydrated lime production we have seen in one flow chart.

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The slide contains a list of process descriptions for quicklime hydration. The text is as follows:

- Process description:
- Quicklime lump, crushed to 2cm or less, is added along with water or steam to a vertical cylindrical pug mill containing 18 – 24 extended horizontal arms
- Operation is usually continuous
- Products from complete reaction is light and dry slaked lime
- This is classified by screen or air separators to remove any over burned (unreactive) lime that did not hydrate
- Finely divided product is packaged in bags for shipping ✖
- Steam under pressure is used to more rapidly convert MgO where dolomitic lime is used
- Product is known as hydraulic lime hydrate

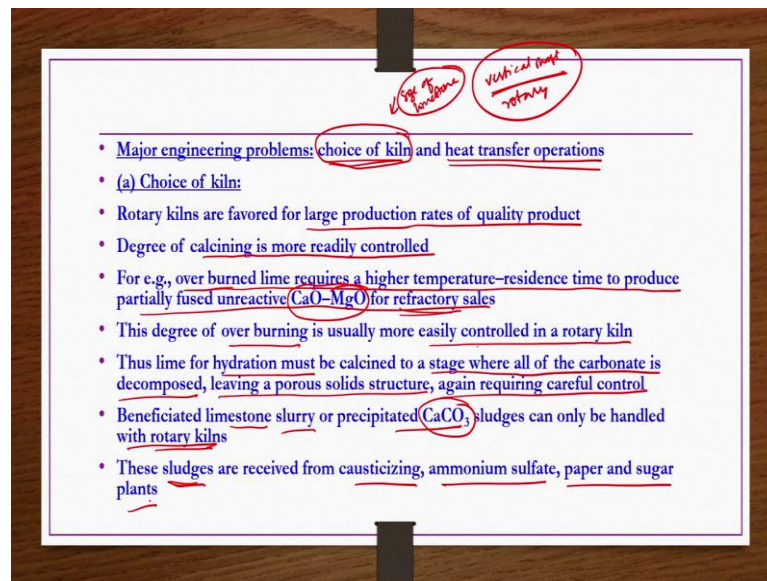
Handwritten annotations include a red checkmark next to the last bullet point, a red 'x' next to 'packaged in bags for shipping', and the word 'hydrate' written in red next to 'hydraulic lime'. The term 'MgO' is circled in red.

Process description, quick lime lump crushed to 2 centimeter or less, is added along with water or steam to a vertical cylindrical pug mill containing 18 to 24 extended horizontal arms. Operation is usually continuous, products from complete reaction is light and dry slaked lime.

This is classified by screen or air separators to remove any over burned or unreactive lime that did not hydrate. Finally, divided product is packaged in bags for shipping, steam under pressure is used to more rapidly convert magnesium oxide where dolomitic lime is used.

If the dolomitic lime is used whatever the product that you get is known as the hydraulic lime. That is the difference between, hydrated and then hydraulic lime. Hydraulic lime you get if the lime whatever you use is dolomitic lime.

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Major engineering problems of this process two important are there; one is the choice of kiln and then another one is the heat transfer operation. Choice of the kiln as I already specified in the one of the previous slide depending on the size of size reduced lime stone based on that one has to select but.

However, most of the product of size reduced limestone is suitable to use in vertical, shaft kiln or rotary kiln and then these two are better anyway ok. So, why they are better

we are going to see here. Choice of kiln rotary kilns are favoured for large production rates of quality product degree of calcining is more readily controlled in rotary kilns.

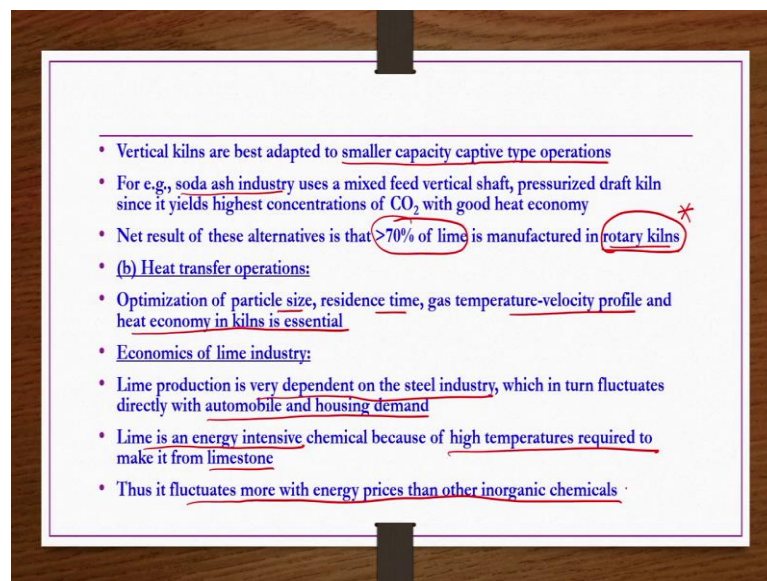
For example, over burned lime requires a higher temperature residence time to produce partially fused unreactive calcium oxide, magnesium oxide for refractory sales. Because whatever over burned material is that cannot be used for making cement, but that cannot be thrown out as well.

So, that unreactive calcium oxide, magnesium oxide mixture whatever is there, that is used in refractory sales ok. This degree of over burning is usually more easily controlled in rotary kilns compared to the other types of kilns. Thus, lime for hydration must be calcined to a stage where all of the carbonate is decomposed, leaving a porous solid structure again requiring careful control.

Beneficiated lime stone slurry or precipitated calcium carbonate sludges can only be handled with rotary kilns. These calcium carbonate sludges etcetera you can get from the other industries. And then you can use as a kind of substituted or supplementary raw material along with the you know basic raw material as we have already discussed in the previous lecture.

These sludges are received from causticizing ammonia sulfate and paper and sugar plants etcetera.

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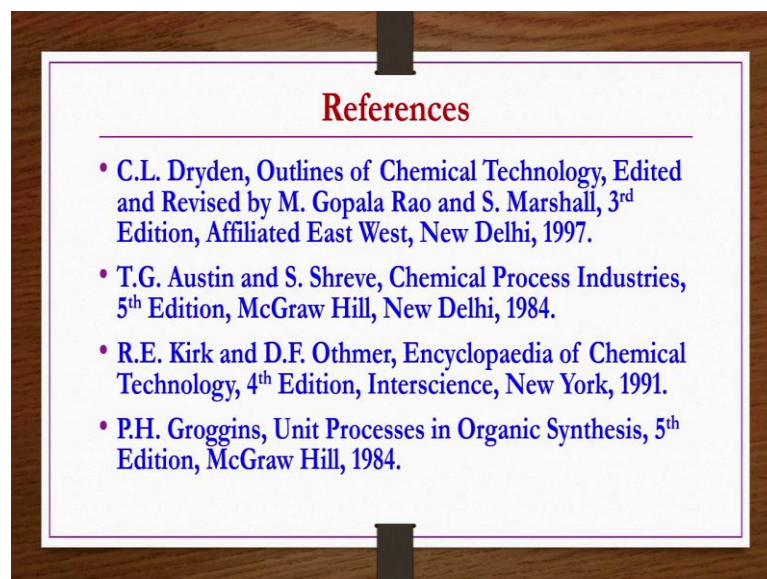
Vertical kilns are best adopted to smaller capacity captive type operations. For example, soda ash industry uses a mixed feed vertical shaft, pressurized draft kiln since it yields highest concentrations of CO<sub>2</sub> with good heat economy. Net results of these alternatives is that more than 70 percent of lime is manufactured in rotary kilns that is the reason I was mentioning that rotary kilns is better one compared to all other types of kilns.

Other engineering problem is the heat transfer operations. Optimization of particle size, residence, time gas temperature, velocity profile and heat economy in kilns is very essential. Now, economics of lime industry if you see, lime production is very dependent on the steel industry, which in turn fluctuates directly with automobile and housing demand.

Further lime is very energy intensive because in order to get the quick lime you are applying approximately 1000 or even more than that one 1000 or higher degree centigrades of temperature. So, it is very energy intensive chemical because of high temperatures required to make it from limestone.

So obviously, if the energy is required, so then it is going to be very you know important factor to be considered. Thus, it fluctuates more with energy prices than other inorganic chemicals.

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### References

- C.L. Dryden, *Outlines of Chemical Technology*, Edited and Revised by M. Gopala Rao and S. Marshall, 3<sup>rd</sup> Edition, Affiliated East West, New Delhi, 1997.
- T.G. Austin and S. Shreve, *Chemical Process Industries*, 5<sup>th</sup> Edition, McGraw Hill, New Delhi, 1984.
- R.E. Kirk and D.F. Othmer, *Encyclopaedia of Chemical Technology*, 4<sup>th</sup> Edition, Interscience, New York, 1991.
- P.H. Groggins, *Unit Processes in Organic Synthesis*, 5<sup>th</sup> Edition, McGraw Hill, 1984.

References for today's lecture are provided here, *Outlines of Chemical Technology* by C. L. Dryden edited and revised by Gopal Rao and Marshall 3rd edition. Then *Chemical Process Industries* by Austin and Shreve 5th edition, *Encyclopaedia of Chemical Technology* by Kirk and Othmer fourth edition, *Unit Processes in Organic Synthesis* Groggins 5th edition.

Thank you.