Chemical Process Utilities
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Module No # 13
Lecture No # 56
Refractories

Welcome to the refractories this is the new concept and under the edges of chemical process utilities. Now before we discuss this these refractories let us have a discussion about that what we discussed in the previous lecture? In the previous lecture we discussed about the refrigeration system under this has been discussed about the cascade refrigeration system with the 2-stage cascade refrigeration system and a 3-stage gasket refrigeration system.

Then we discussed about the absorption refrigeration system with ammonia, water, gas diffusion and water lithium ARSs. And the water lithium we discussed about the 2 stages one is the single stage ARS and second one was the double stage ARS.

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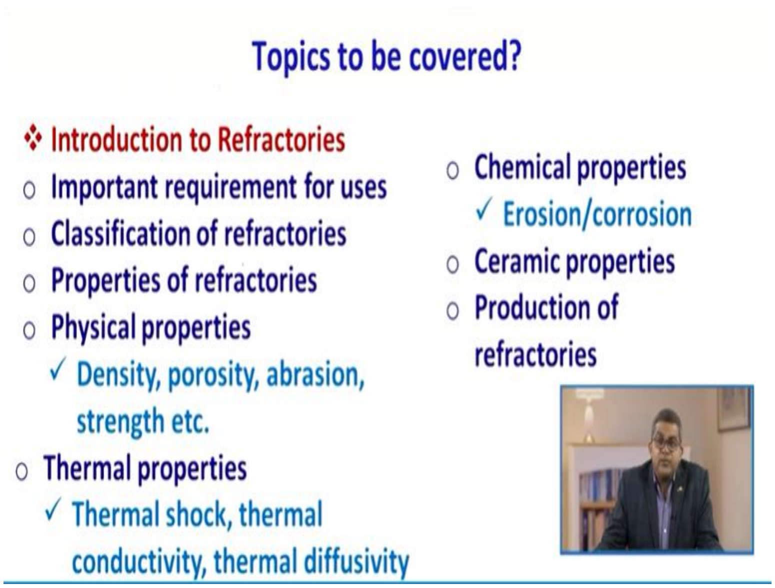

Now in this particular lecture we are going to discuss about the introduction to the refractories. Then we will discuss about the important requirement for the uses then how we can classify the refractories? Then what different kind of the properties refractories must possess? This including the physical properties which; will cover about the density porosity abrasion strength etc. Then we will discuss about the thermal properties, thermal shock, thermal conductivity, thermal diffusivity.

Then chemical properties like erosion corrosion and ceramic properties and apart from this we will discuss about the production protocols of the refractories.

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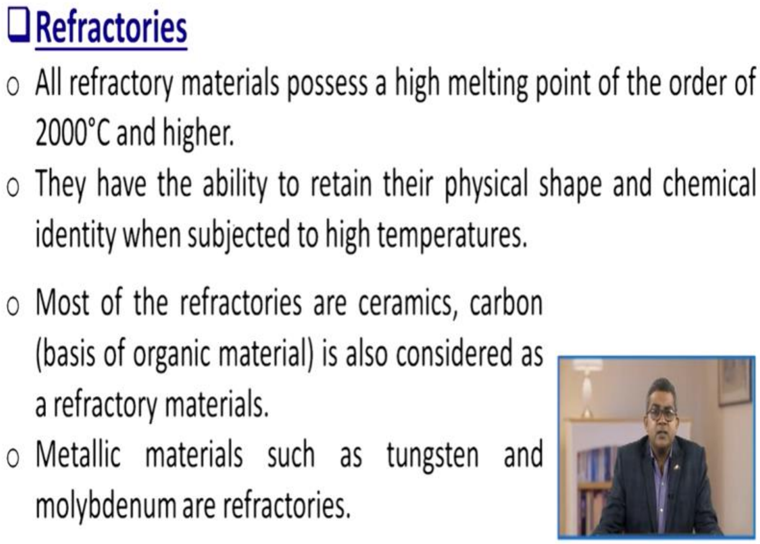

So let us talk about the refractories so all refractories material they possess a high melting point of the order of says 2000 degree Celsius and higher. They have the ability to retain their physical shape and chemical identity when subjected to high temperatures. Most of the refractories are ceramic, carbon basis of organic material and is also considered as refractory material. Metallic materials such as tungsten and molybdenum are the suitable material for the refractories.

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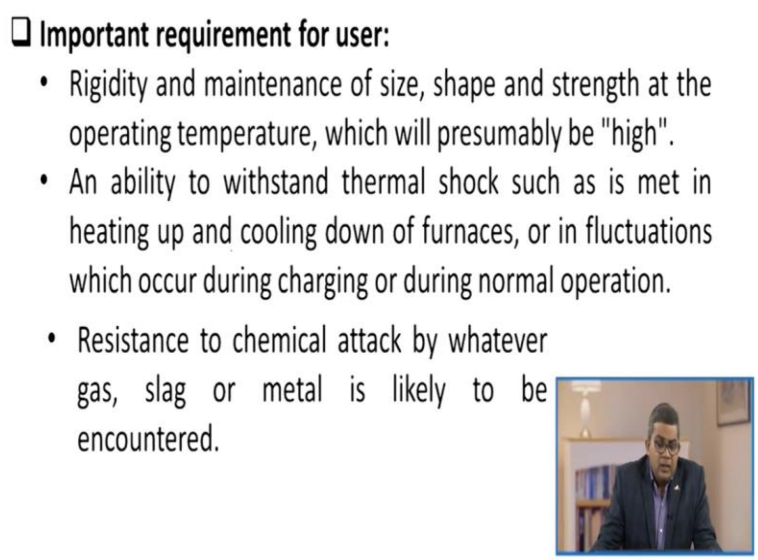

Now when we talk about the important requirement pertaining for the user, they must have the rigidity and maintenance of proper maintenance of size and shape and strength at the operating temperature which will presumably be very high. An ability to withstand the thermal shock such as it met in the heating up and cooling down the furnace or fluctuations which occur during the charging or during the normal operation. They must offer the resistance to the chemical attack by whatever gas slag or metal is likely to be encountered.

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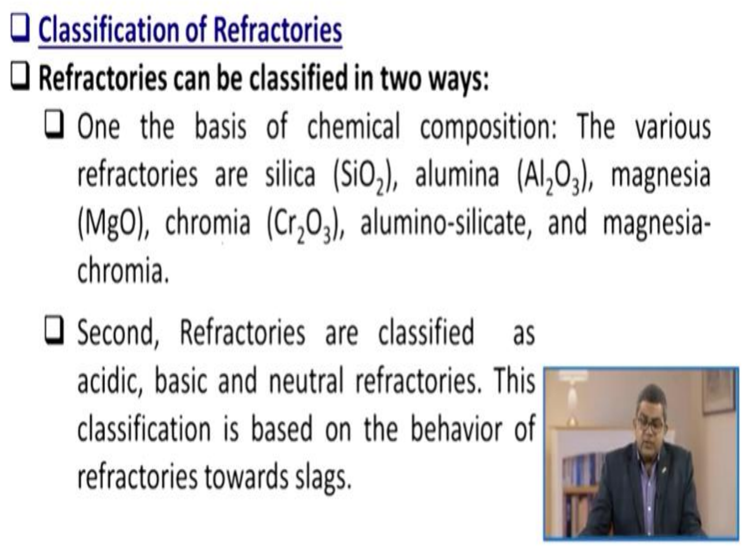

Now let us classify the refractories under the heading of the classification of refractories. Now refractories can be classified in 2 ways one is on the basis of a chemical composition the various refractories are like silica SiO_2, alumina Al_2O_3, magnesium MgO, chromia Cr_2O_3, aluminum silicate and magnesia chromium. Now second is refractories are classified as acidic basic or neutral refractories this classification is based on the behaviour of refractories towards slag.

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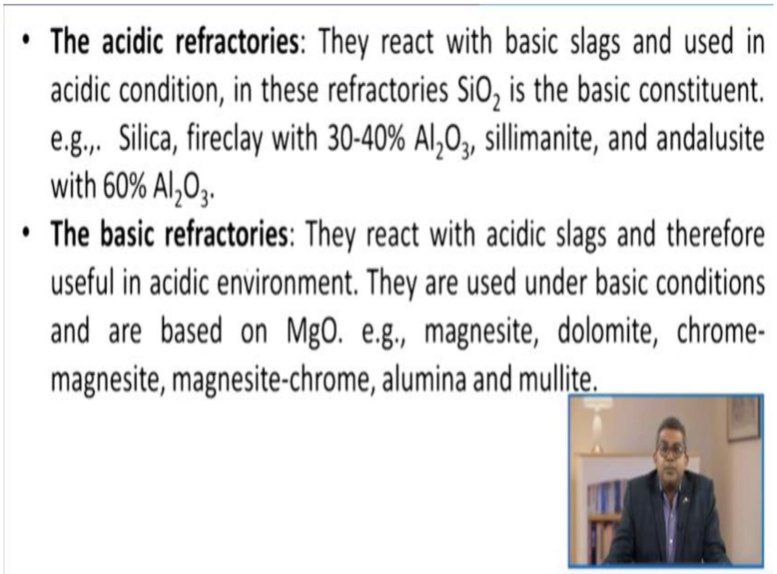

The acidic refractories they react with the basic slags and use in acidic condition. Now in these refractories SiO 2 is the basic constituent like silica fire clay with 30- 40% of Al_2O_3 sillimanite and andalusite with the 60% Al_2O_3. The basic refractories they react with the acidic slag and therefore useful in acidic environment. They are used under basic condition and they are based on MgO that is magnesite, dolomite, chrome magnesite, magnesite chrome, alumina and amulite.

Neutral refractories they do not react with either acidic or basic slags hence useful in both acidic and basic media that is the carbon chromite $FeO.Cr_2O_3$ and fosterite 2 MgO SiO_2. Now certain refractories are grouped under the special refractory such as zirconia, thoria, barilla.

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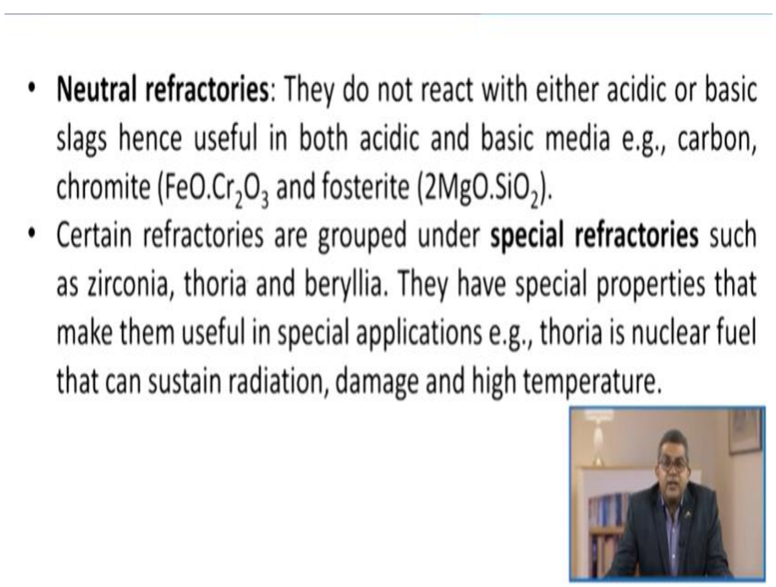

They have special properties that make them useful in special application that is thoria is nuclear fuel that can sustain radiation damage and high temperature.

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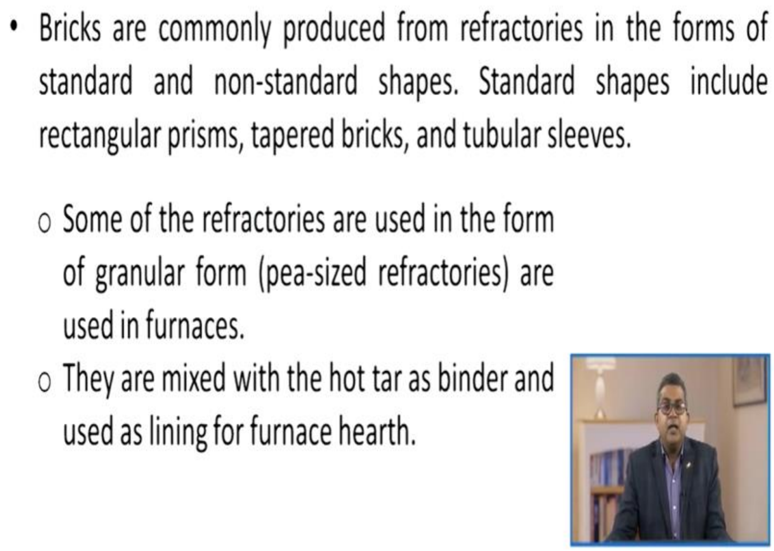

Now bricks are commonly produced from refractories in the form of standard and non-standard shapes. Standard shapes include the rectangular prism tapered, bricks and tubular sleeves. Some of the refractories are used in the form of granular form like pea-sized refractories they are used in the furnace. They are mixed with the hot tar as binder and used as a lining for furnace hearth.

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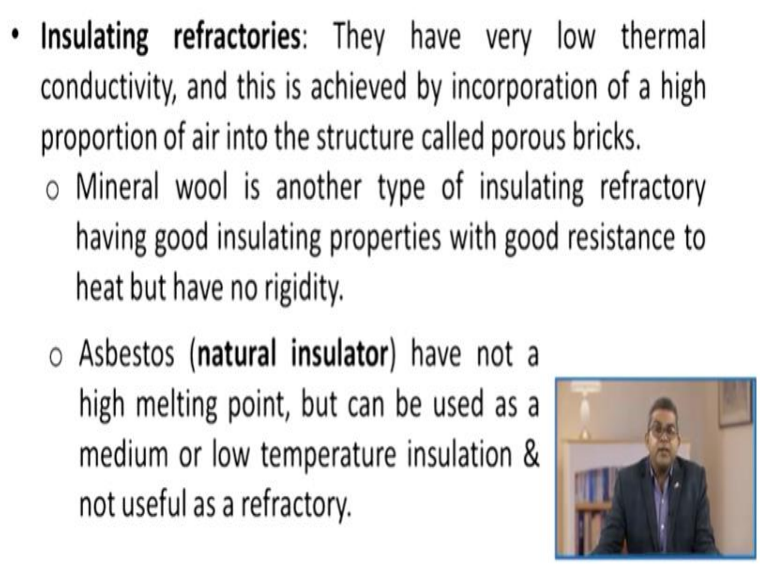

Insulating refractories, they have very low thermal conductivity and this is achieved by the incorporation of a high proportion of air into the structure that is called the porous bricks. Mineral wool is another type of insulating refractory having good insulating properties with good resistance to heat but have no rigidity. Asbestos that is a the natural in insulator asbestos have not a single melting point but can be used as a medium or low temperature insulation and not useful as a refractory.

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✓ **Properties of Refractories**

The refractories properties can be classified as follows:

- **Physical Properties**
  - Density
  - Porosity
  - Strength
  - Abrasion

Now let us talk about the properties of refractories. The refractories properties can be classified as like physical properties the density, porosity, strength, abrasion.

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- **Thermal properties**
  - Thermal shock
  - Thermal conductivity
  - Thermal diffusivity
- **Chemical Properties**
  - Corrosion/ erosion

Then the thermal properties the thermal shock, thermal conductivity, thermal diffusivity, the chemical properties the corrosion and erosion.

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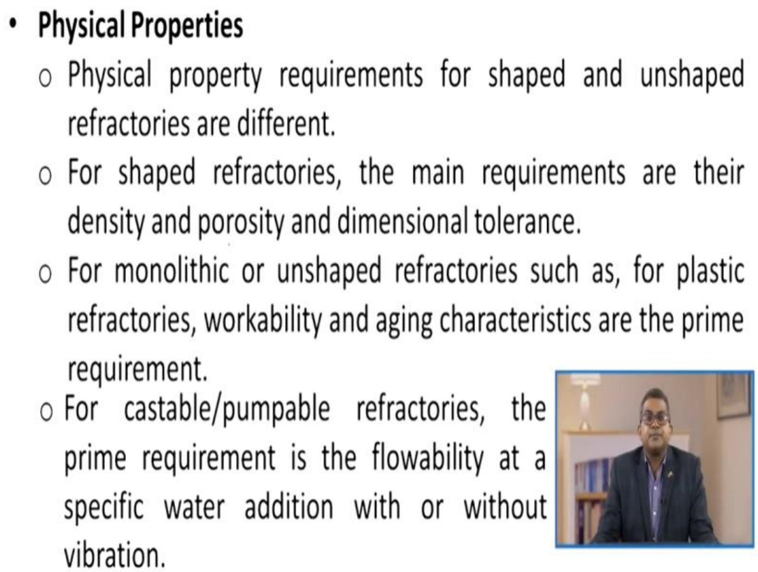

So let us talk about the physical properties. The physical property requirements for shaped and unshaped refractories are different. For shaped refractories the main requirement are their density and porosity the dimensional tolerance. For monolithic or unshaped refractories such as for plastic refractories workability and aging characteristics are the prime requirement. For castable or pumpable refractories the prime requirement is the flow ability at a specific water addition with or without vibration.

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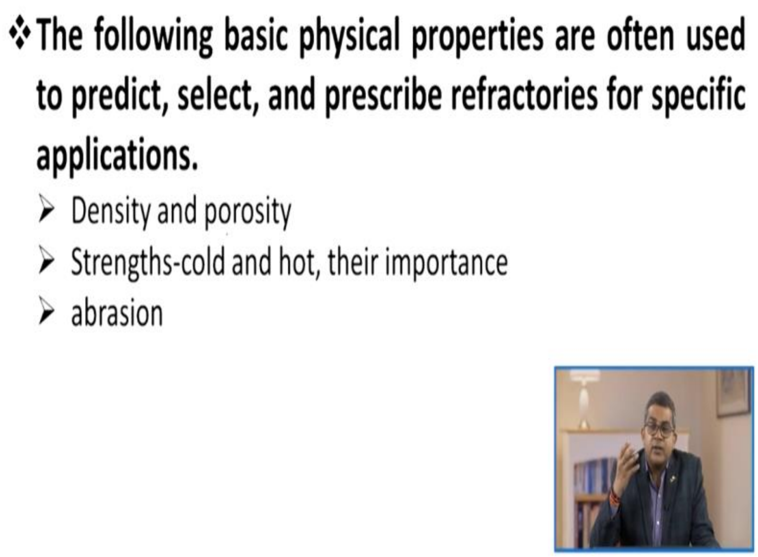

Now there are basic physical properties which are often being used to predict, select and prescribed refractories for specific application. The density and the porosity the strength cold and heart their importance and abrasion.

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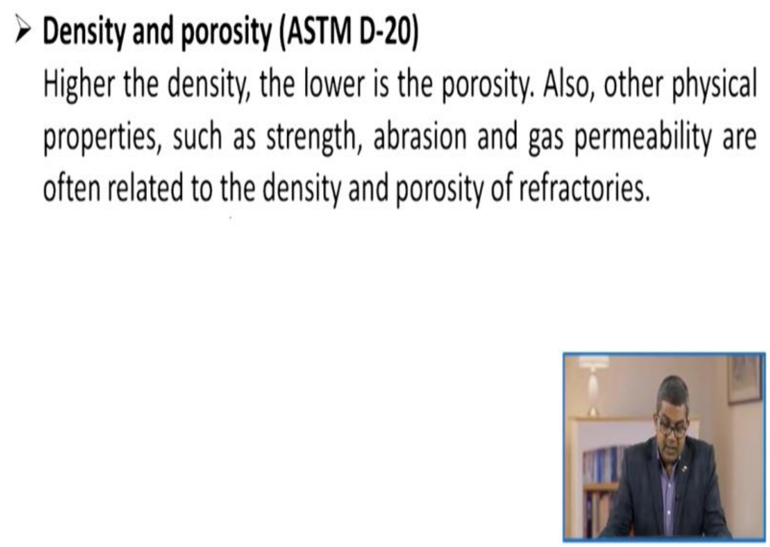

Now let us talk about the density and porosity so when we talk about the density and porosity as a physical property then there must be some standards to assess this one. Then that is why the ASTM D-20 is standard this predicts that instant and porosity and this is one of the most important characterization tools. So, the higher the density the lower is the porosity and also other physical properties such as strength abrasion and gas permeability are often related to the density and porosity of the refractories.

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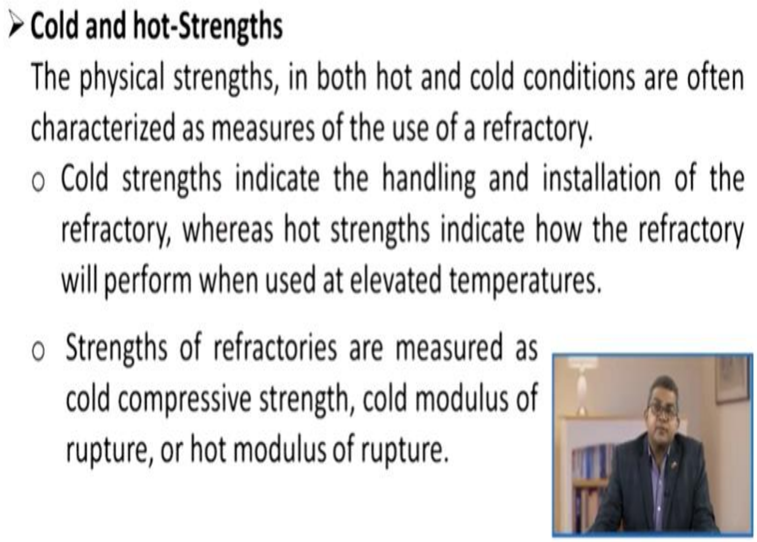

Then we can talk about the cold and hot strengths the physical strength in both hot and cold condition is often characterized as measure of the use of a refractory. Now the cold strength indicates the handling and installation of the refractory, whereas the hot strength indicates how the refractory will perform when used as elevated temperatures? The strength of refractories is measured as cold compressive strength, cold modulus of rupture or hot modulus of rupture.

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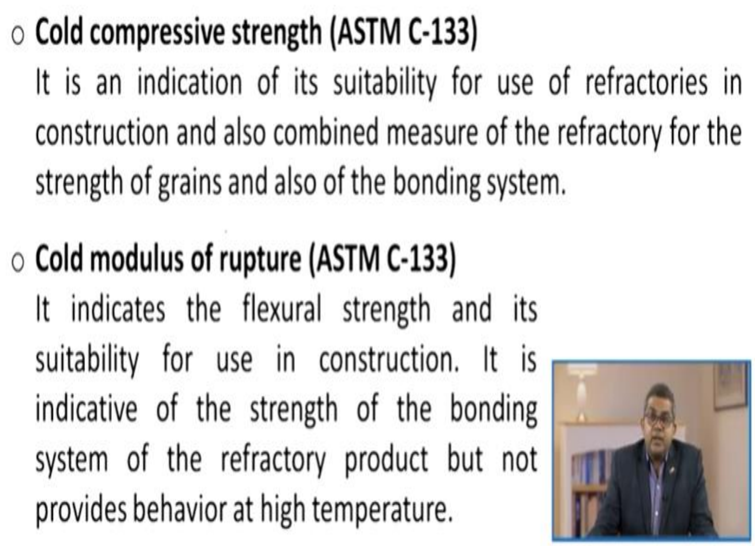

Then the cold compressive strength again we are using the American society for testing materials ASTM C-133 standard. It is an indication of its suitability for use of refractories in construction and also combined measure of the refractory for the strength of grains and also of the bonding system. Cold modulus of rupture and again we are referring to the ASTM C-133. It indicates the flexural strength and its suitability for use in construction. It is indicative of the strength of the bonding system of the refractory product but not provides behaviour at high temperature.

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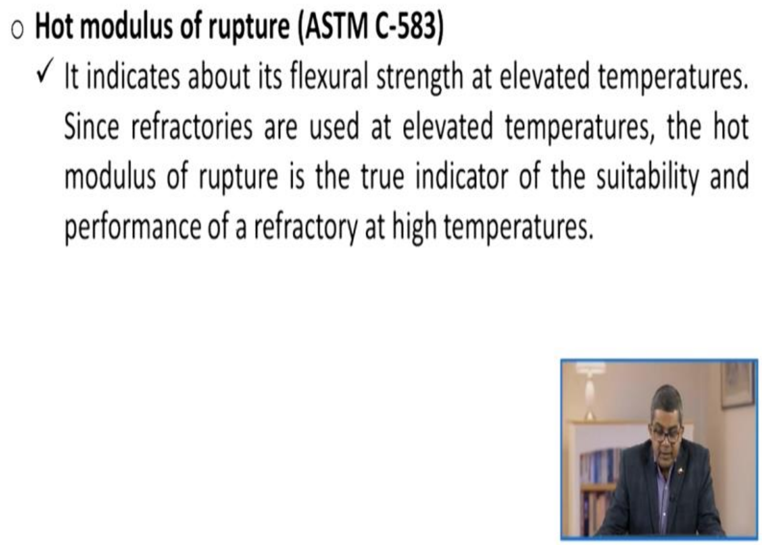

The hot modulus rupture here the ASTM standard is a bit different that is ASTM C-583. Now it indicates about its flexible strength at elevated temperature since refractories are used at elevated temperature the hot modulus of rupture is the true indicator of suitability and performance of a refractory at high temperature. Then abrasion resistance that is ASTM C-704 it is the measure of resistance of a refractory material when high velocity particles abrade the surface of the refractory.

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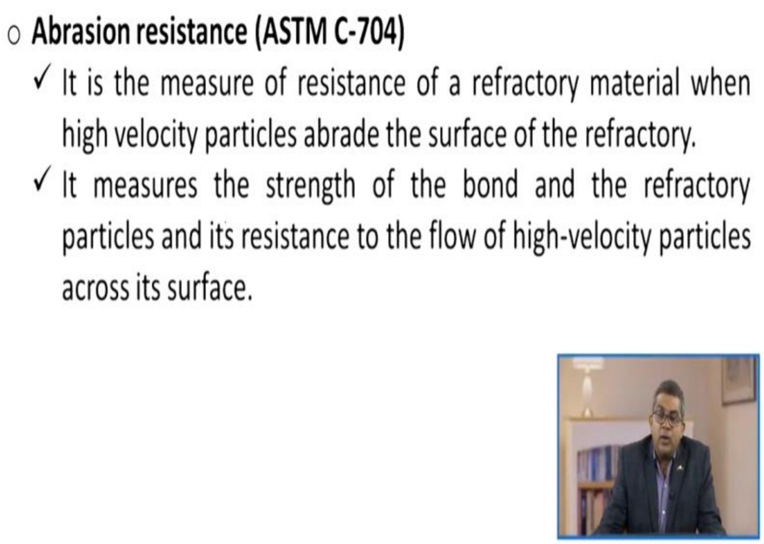

It measures the strength of the bond and the refractory particles and its resistance of the flow of high velocity particles across its surface.

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Thermal Properties

- **Thermal Expansion (ASTM C-113)**
  - ✓ This is a measure of the refractory about its linear stability when it is exposed to different ranges of high temperatures and then cooled to room temperatures.
  - ✓ It is defined as a permanent linear change (ASTM C-113) and is measured by the changes in the longest linear dimensions.

Now let us talk about the thermal properties and thermal properties are equally important compared to the physical properties. So, first thing in this aspect is the thermal expansion and the referring standard is again ASTM C-113. Now it is the measure of refractory about its linear stability when it is exposed to different ranges of temperature and then cooled to a room temperature. It is defined as the permanent linear change and is measured by the changes in the longest linear dimension.

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- ✓ The refractory systems should always be designed in such a way that the maximum temperature attainable in the system is lower than the softening or melting temperature of the refractory ingredients (grains and bonding system).

The refractory system should always be designed in such a way that the maximum temperature attainable in the system is lower than the softening or melting temperature of the refractory ingredients, grains and bonding system.

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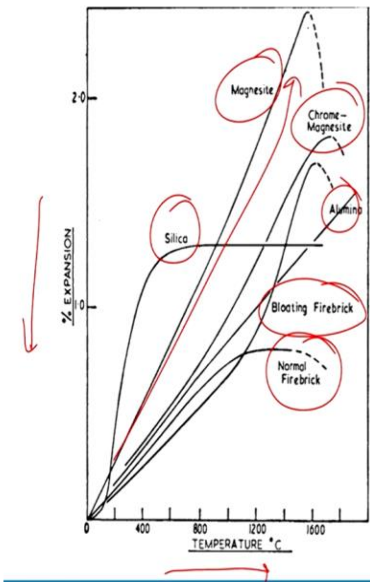

Figure: expansion curves for various refractories

Now here you see that this represents the expansion curve for various refractories and when we plot against the percentage of expansion with respect to the temperature. Here you see that we have represented various like thermal bricks, bloating fire bricks alumina, chrome magnesite, magnesite and silica. So, you see the sharp curve of this magnesite and then sharp declination in the expansion.

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- Thermal Shock (ASTM C-1100 & 1171)
  - ✓ This is measure of the refractory property when the refractory is exposed to alternate heating and cooling.
  - ✓ Refractories having structures with built-in microcracks of defects show better thermal shock resistance than with rigid systems.

Now let us talk about the thermal shock and referring standard is ASTM C- 1100 and 1171. This is the measure of the refractory property when the refractory is exposed to alternate heating and cooling. Now refractories are having structures with built in micro cracks of defects this show better thermal shock resistance than with the rigid system. Now there are 2 standard methods for determining the thermal shock resistance.

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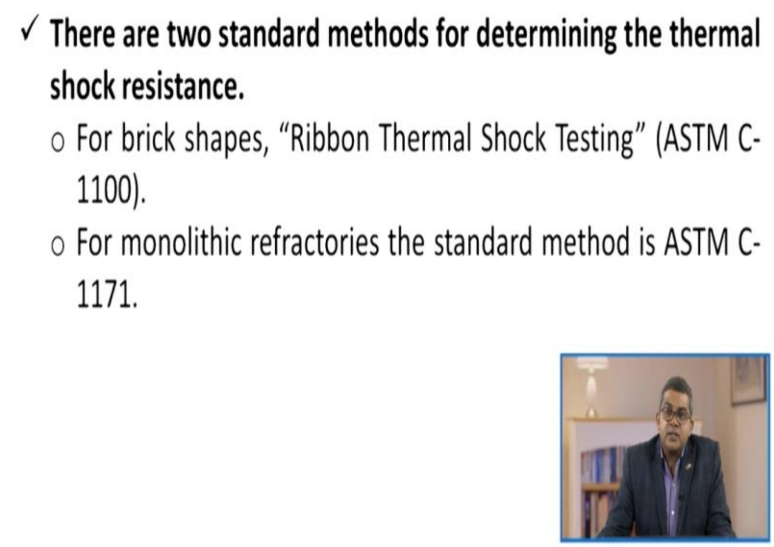

Now for brick shapes the ribbon thermal shock testing that is ASTM C-1100 and for monolithic refractories the standard method is ASTM C-1171.

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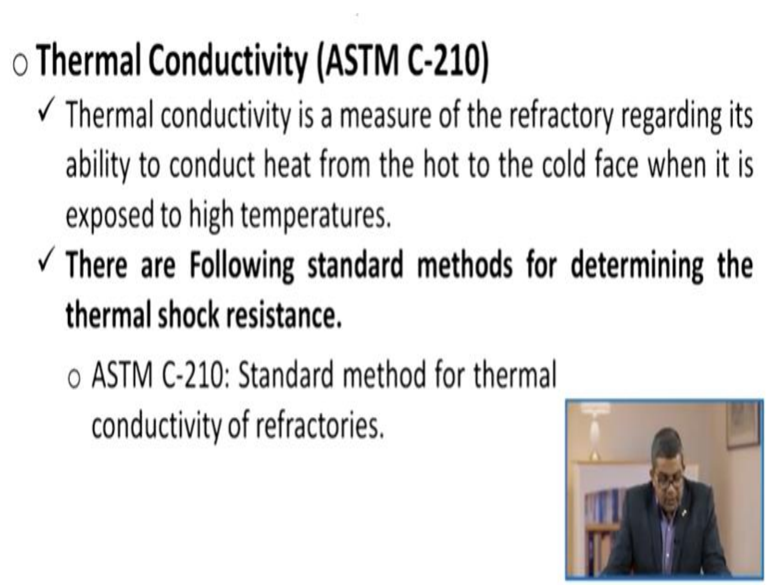

Now let us talk about the thermal conductivity, again the referring standard is ASTM C 210. Now the thermal conductivity is a measure of the refractory regarding its ability to conduct heat from the hot to the cold space when it is exposed to high temperatures. Now there are various standard methods for determining the thermal shock resistance one is the ASTM C 210 that is a standard method for thermal conductivity of refractories.

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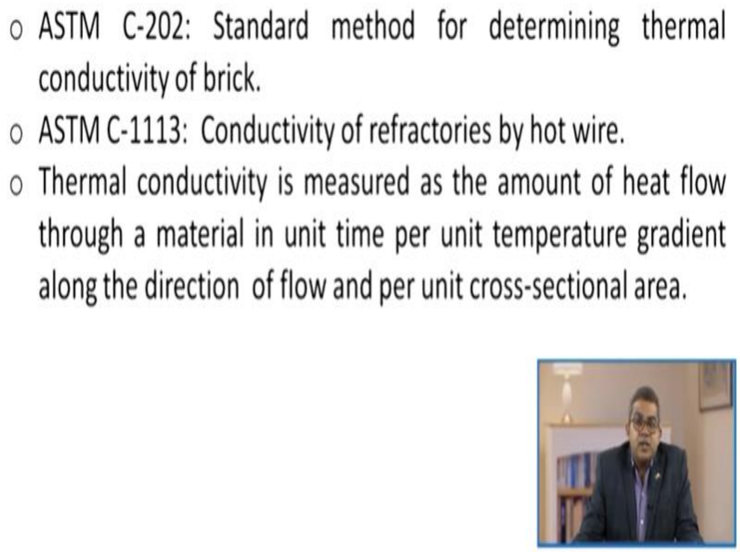

ASTM C 202 that is the standard method for determining the thermal conductivity of brick. ASTM C 1113 that is a conductivity of refractories by hot wire now the thermal conductivity is measured as the amount of heat flow through a material in unit time per unit temperature gradient along the direction of flow and per unit cross sectional area.

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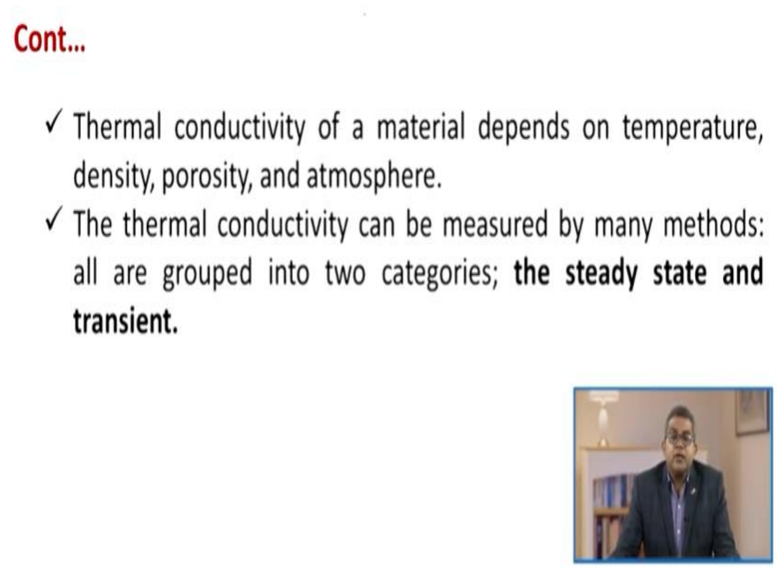

The thermal conductivity of a material depends on temperature, density porosity and atmospheric. The thermal conductivity can be measured by many methods all are grouped into 2 categories one is the study state and transient.

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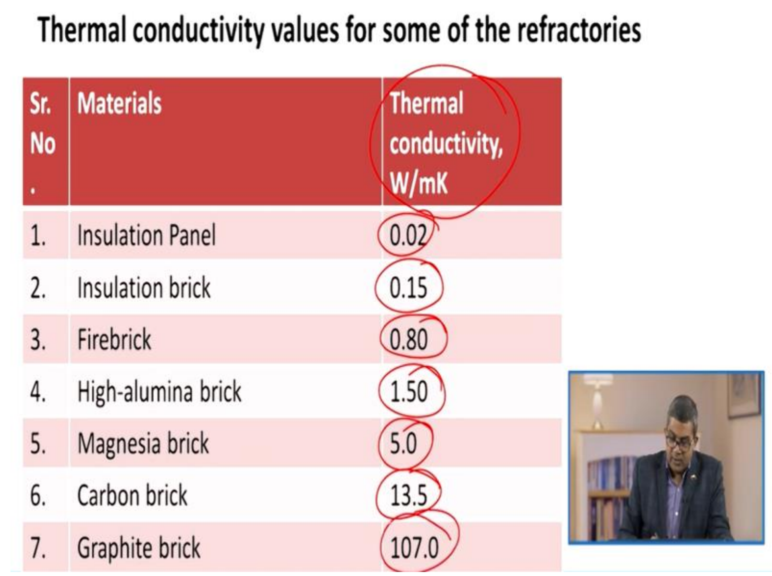
Thermal conductivity values for some of the refractories

Sr. No.	Materials	Thermal conductivity, W/mK
1.	Insulation Panel	0.02
2.	Insulation brick	0.15
3.	Firebrick	0.80
4.	High-alumina brick	1.50
5.	Magnesia brick	5.0
6.	Carbon brick	13.5
7.	Graphite brick	107.0

Now here you see that the thermal conductivity value of some of the refractories like insulation panel if we represent the thermal conductivity in watt per meter Kelvin then the insulation panel it possesses 0.02. Then insulation brick it possesses 0.15 fire brick 0.80 high aluminum brick 1.50 magnesium brick 5.0 the carbon brick 13.5 and graphite brick 107.0.

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Steady state methods

It involve the measurement of the heat flux between the hot and cold face of the sample that are each kept at constant temperatures.

Calorimeter method

- ✓ The standard procedure is illustrated in ASTM C201-98. This method is useful for materials having a conductivity of up to 20 W/mK.
- ✓ A calorimeter is fitted at the cold face of the sample. The calorimeter obtains the mass, specific heat, and temperature rise of the heat flux.

Now let us talk about the steady state method, now the steady state method it involves the measurement of the heat flux between the hot and cold phase of the sample and that are each kept at constant temperature. One is the calorie meter method the standard procedure is usually referred in the ASTM C 20198. This method is useful for material having the conductivity up to say 20 watt per meter Kelvin. The calorimeter is fitted at the cold face of the sample and the calorimeter obtains the mass specific heat and temperature rise of the heat flux.

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Split column method

This method is used for the measurement of thermal conductivity of whole brick.

- ✓ The brick is kept on a hot plate with its largest face touching the plate's surface. The brick's sides are insulated and a brass plate is kept on top of it.
- ✓ This brass plate (with copper disc which is thermally insulated, inserted in the center of the plate) distributes the temperature evenly.

Another method for determination of this is the split column method. Now this method is used for the measurement of thermal conductivity of entire brick. The brick is kept on hot plate with its large face touching the plate surface. The brick sides are insulated and a brass plate is kept on top of it. The brass plate with copper disc which is thermally insulated inserted in the center of the plate and distributes the temperature evenly. The temperature of hot plate and the copper disc are measured using thermocouples.

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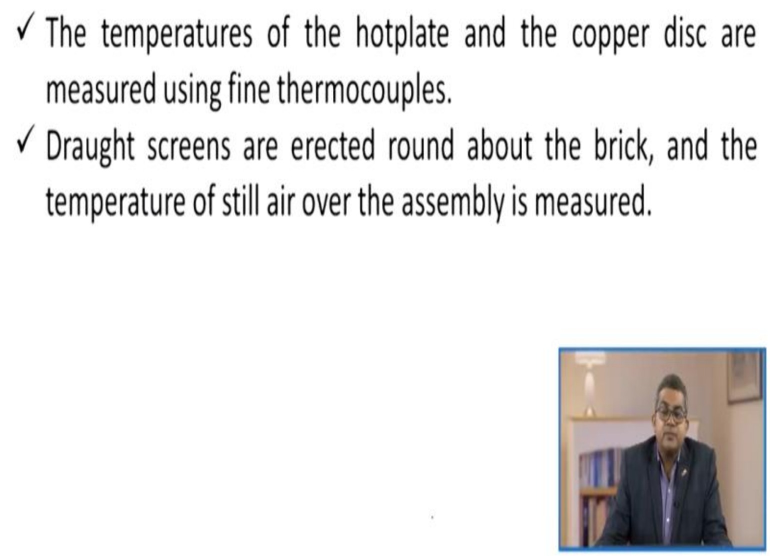

The draught screens are erected round about the brick and the temperature of still air over the assembly is usually measured.

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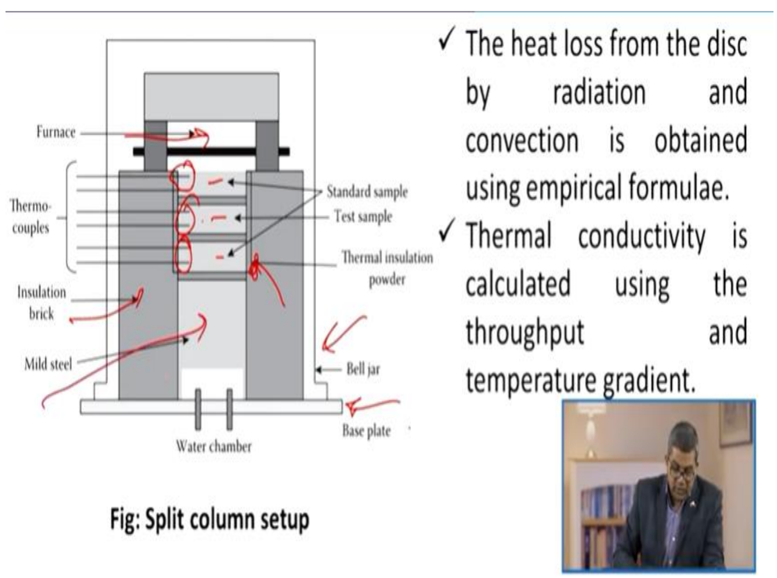

Now here you see that this is the split column setup the heat loss from the disc by radiation and convection is obtained using the empirical formula and the thermal conductivity is calculated using throughout and throughput and temperature gradient. Now here you see that this is the common way this is the bell jar and the base plate here you see that this is the template thermal insulation powder and you may keep the standard test sample in at these ports.

And these ports are attached with the thermocouples here you see these are the thermocouples and the furnace is situated over here and everything is aligned with the insulation brick under the edges of this mild steel.

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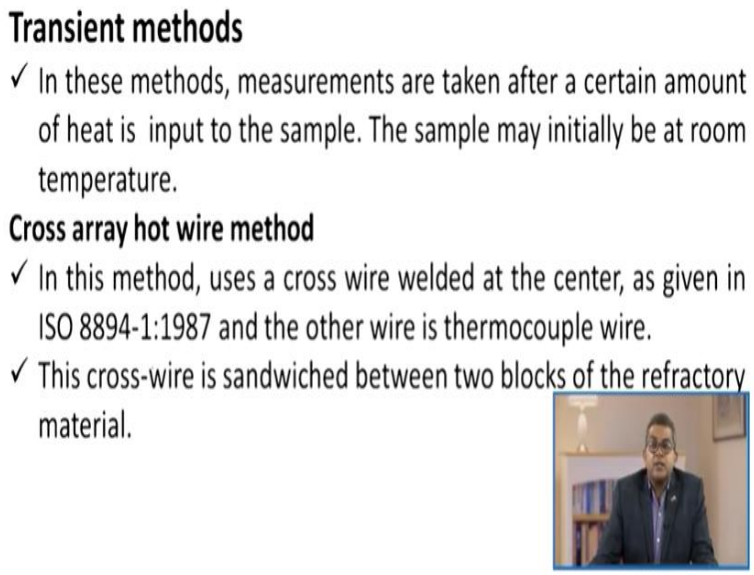

Transient method, now in this method the measurements are taken after a certain amount of heat is input to the sample and the sample may initially be at room temperature then there is a cross array hot wire method. In this method uses a cross wire welded at the center as per the given standard in ISO 8894 dash 1 1987 and the other wire is the thermocouple wire. The cross wire is sandwiched between the 2 blocks of the refractory material.

The powder is fed into the heating element for a short time and the temperature rise in the block is measured. The temperature rises related to thermal conductivity of the material and thermal conductivity up to 2 watt per meter Kelvin can be measured by this particular method. Now let us talk about the parallel hot wire method.

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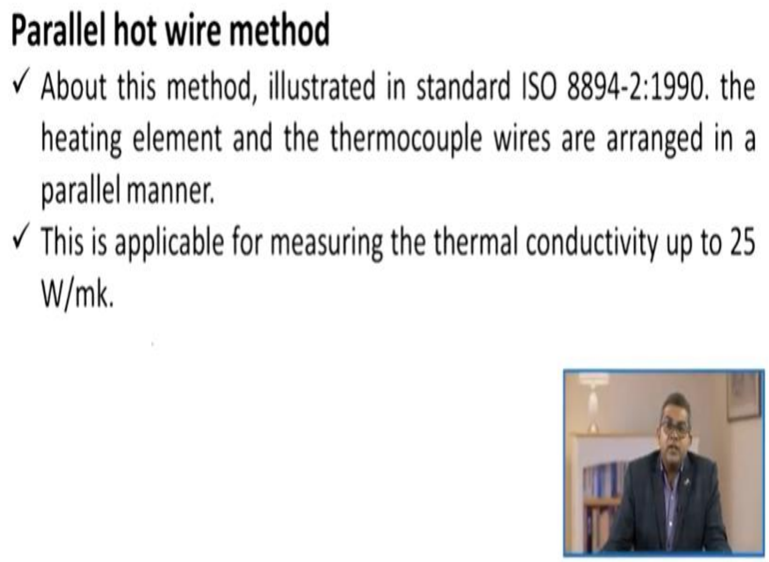

Now this particular method is well illustrated in the standard ISO 8894 dash 2 1990 the heating element and thermocouple wires are arranged in a parallel manner. Now this is applicable for measuring the thermal conductivity say up to 25 watt per meter Kelvin.

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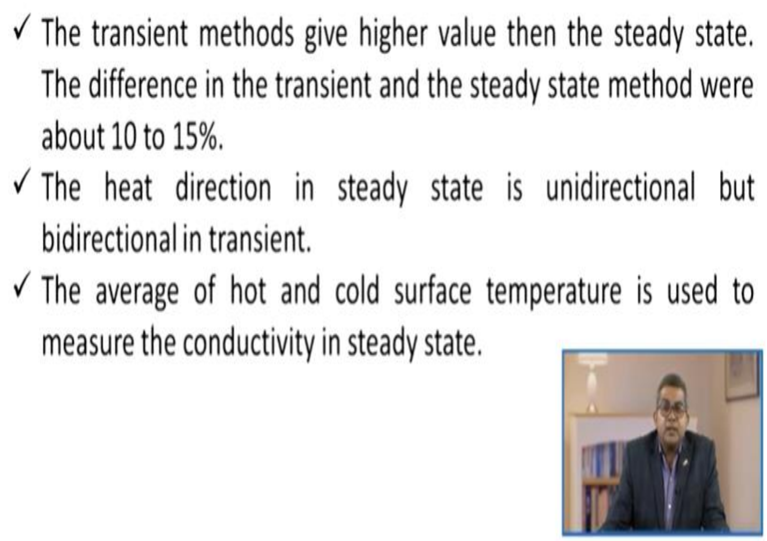

The transient method gives high value then the steady state and the difference in the transient and the steady state method this is usually about 10 to 15%. The heat direction in a steady state is unidirectional but bidirectional in transient. The average of hot and cold surface temperature is used to measure the conductivity in steady state.

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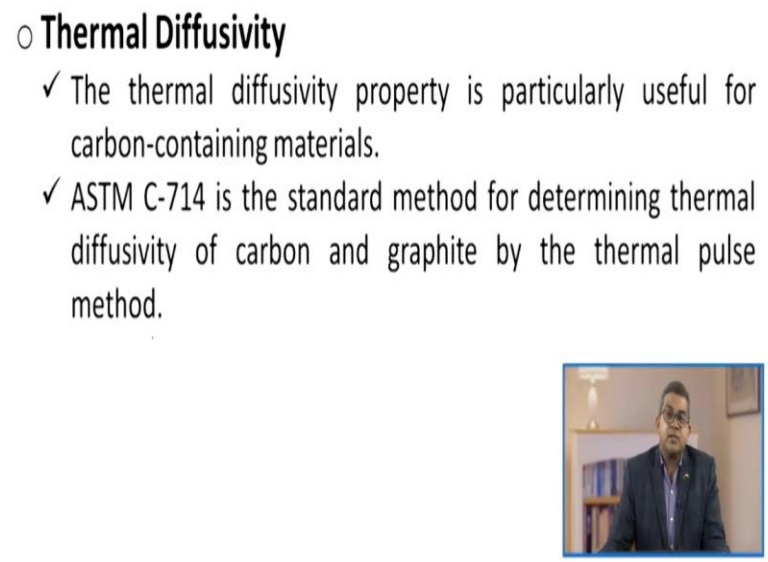

Thermal diffusivity the thermal diffusivity property is particularly useful for carbon containing materials and for this ASTM C-714 is the standard method this is used for the determining the thermal diffusivity of carbon and graphite by the thermal pulse method. Now let us talk about the chemical properties the chemical properties of a refractory are defined by the chemical analysis of refractory grains.

By the nature of bonding by the ability of the refractory to resist the action of liquid when exposed to higher temperature with respect to the corrosion or erosion.

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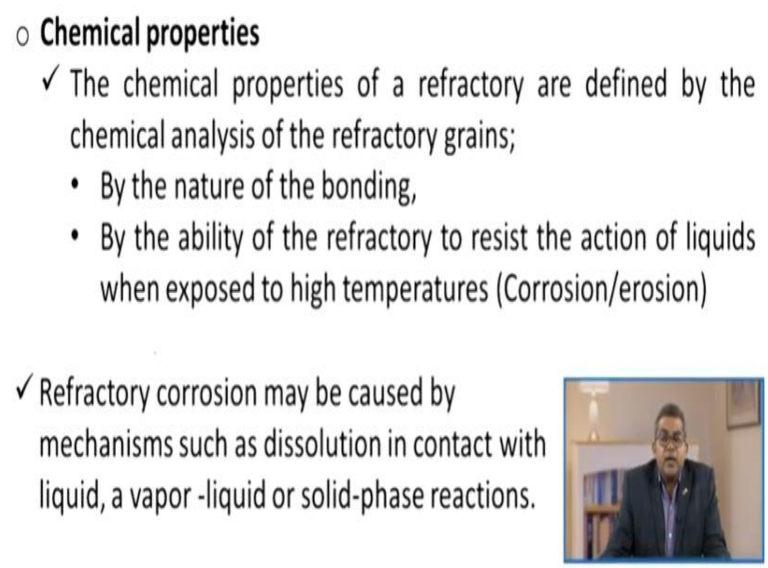

The refractory corrosion may be caused by the mechanisms such as dissolution in contact with the liquid, a vapor liquid or a solid phase reaction. It may occur due to the penetration of water vapor or liquid in pores the nature and rate of dissolution of a refractory in a liquid can be calculated from a phase equilibrium diagram. A concentration gradient occurs in refractory composition at the boundary region.

When the refractory comes in contact with the molten slag the larger the concentration gradient the faster the dissolution rate and thus the refractory dissolves more readily. For steel making refractories rotary slag test ASTM C-874 provides close simulation of the condition in steel making refractories.

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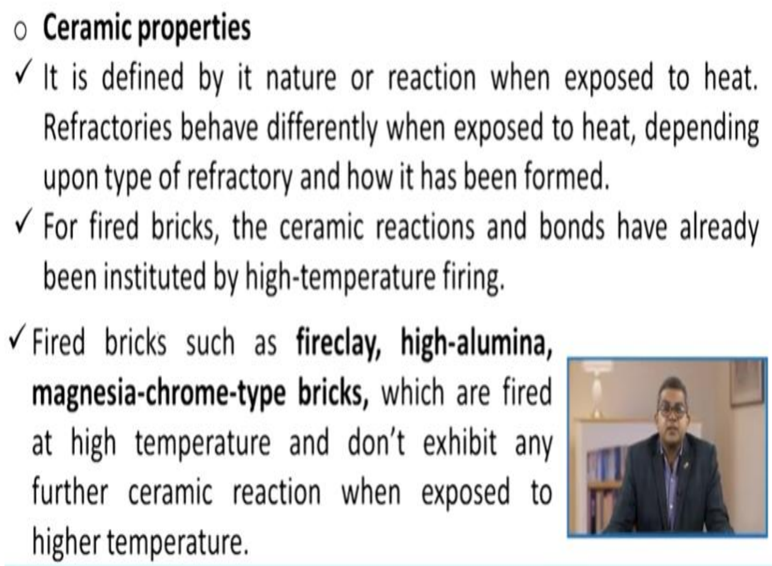

Now let us talk about the ceramic properties now it is defined by its nature or reaction when exposed to heat refractories behave differently when exposed to heat depending upon the type of refractory and how it has been formed. For the fire bricks the ceramic reaction and bond have already been instituted by high temperature firing. Fire bricks such as fire clay high alumina, magnesia chrome, type bricks which are fired at high temperature and do not exhibit any further ceramic reaction when exposed to high temperature.

For unfired refractories the formulations are designed so that the ceramic reactions are supposed to take place at those temperatures.

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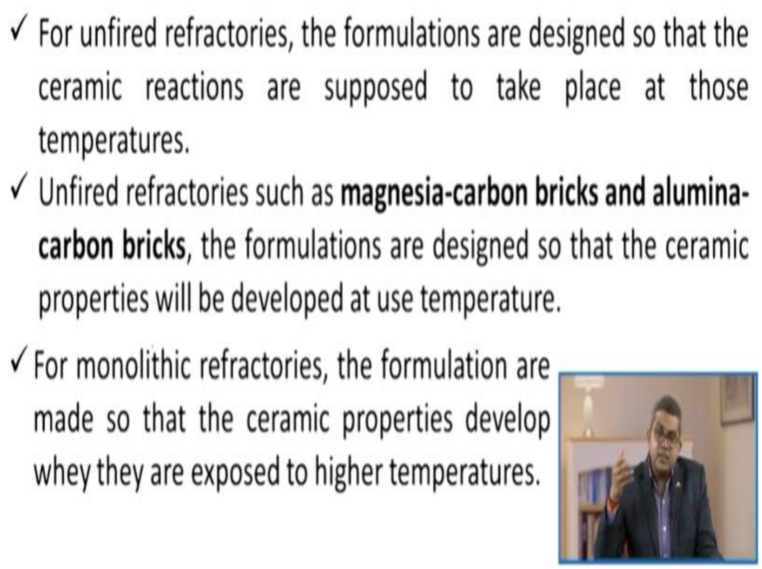

And unfired refractories such as magnesia carbon bricks, alumina carbon bricks the formulation are designed so that the ceramic properties can be developed to use temperature. For monolithic refractories the formulation are made so that the ceramic properties develop when they are exposed to higher temperature.

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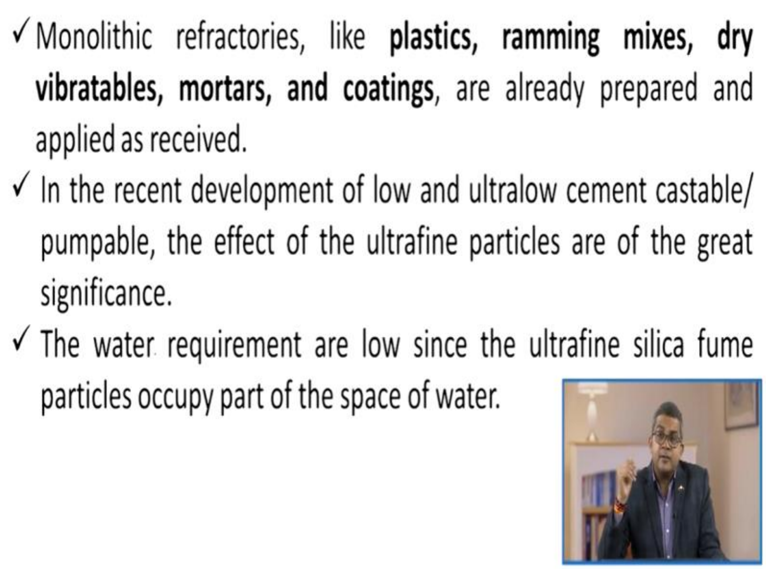

The monolithic refractories like plastic ramming mixtures dry vibratables motors coatings. They are already prepared and applied as received in the recent development of low and ultra low cement castable, pumpable the effect of ultra fine particles are of the great significance. The water requirements are low since the ultra fine silica fume particles occupy part of the space of the water.

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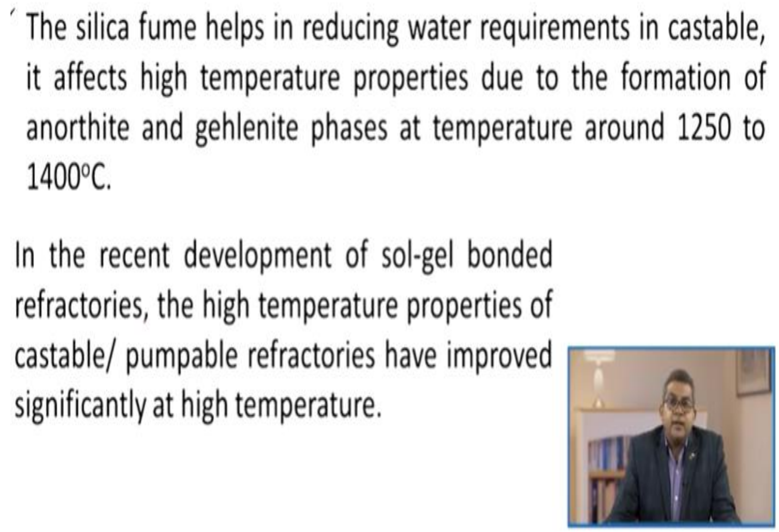

The silica fume helped in reducing the water requirement in castabel it affects the high temperature properties due to the formation of an arthritic and galanite phases at temperature around 1250 to 1400 degree Celsius. In the recent development of solid gel bonded refractories, the high temperature properties of the castable and pumpable refractories have improved significantly at high temperature.

Now let us talk about the production of refractories the production of refractory. The products start with the raw material and each kind of brick is made from different raw material and treatment.

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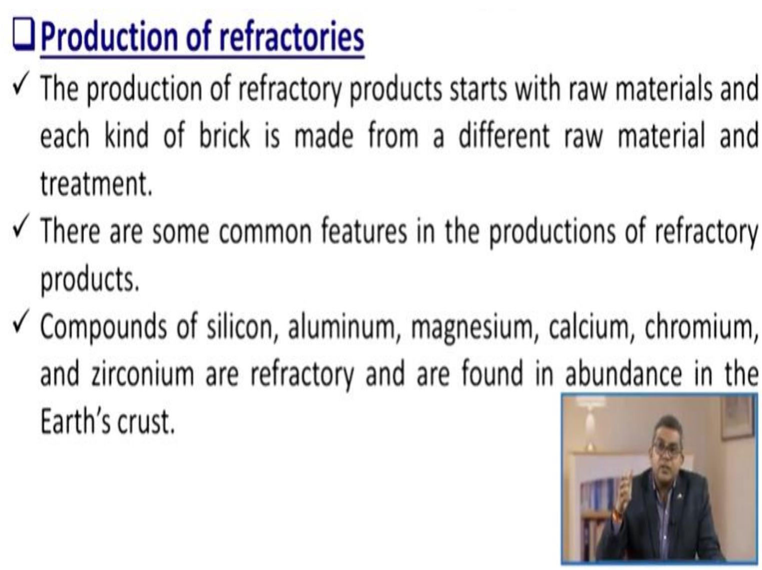

There are some common features of the in the production of refractories product the compounds of silicon, aluminum, magnesium, calcium, chromium and zirconium are refractories and are found in abundance in the hearth's crust.

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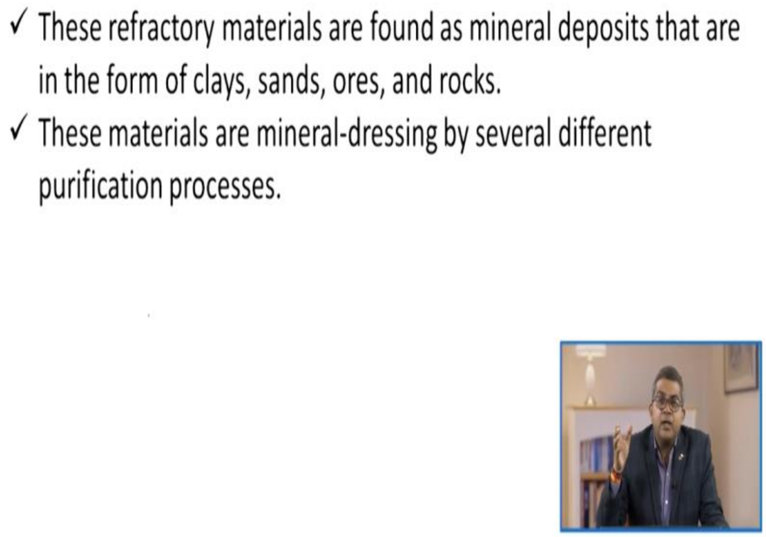

These refractory materials are found as mineral deposits that are in the form of clay sand oars and rocks. These materials are mineral dressings by several different purification processes. Let us talk about the blending now it is the process in which the fine particles they fill the interstices between the coarse particles. The porosity of the product is determined by controlling the fractional proportion of the different sized particles.

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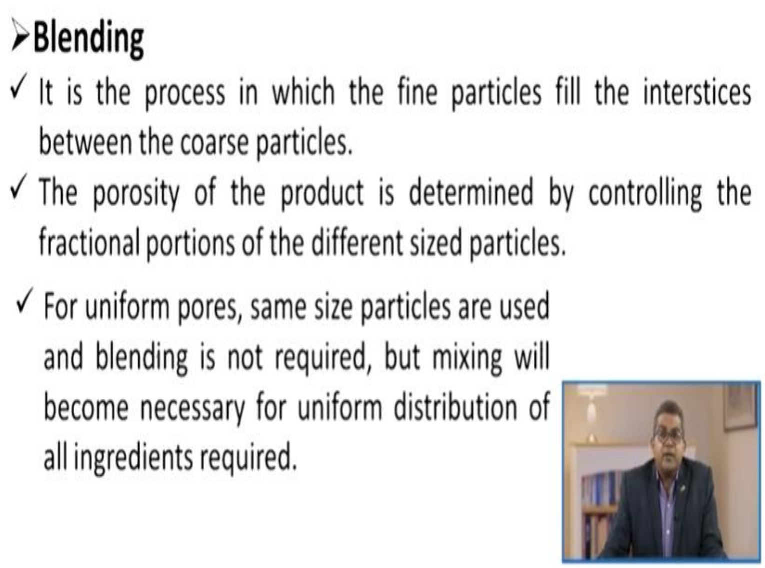

For uniform pores same size particles are used and blending is not at all required but mixing will become necessary for uniform distribution of all ingredients required. The ingredients are other than the refractory powder and also called flux such as bond material and grog. The flux material reduces the melting point of refractory and needed in melting glass as well as to form a glass phase in the refractory brick. Bonding materials they bind the hard refractory particles and gives strength to the fire product.

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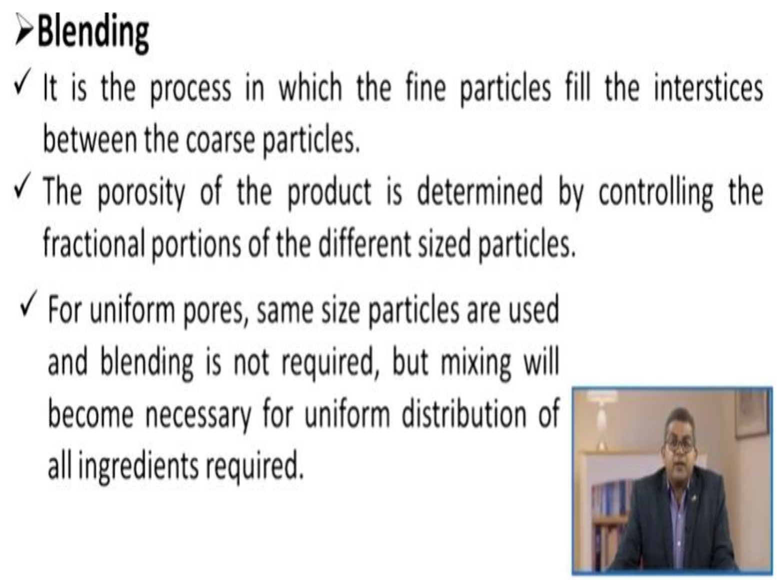

Grog is a pre fired material generally scrap brick is crushed and used as grog. Sometimes grog is separately made by hard firing the refractory material to produce mullite grog firing at 1750 degree Celsius this type of refractory possesses high abrasion resistance and low gas per inability. The blending is carried out in a in a paddle mill with kneading action along with raw material water and additives.

The process brings plasticity to the product as bonding agent clay absorbs water and become plastic. The particle of the refractory raw material becomes embedded in the plastic clay.

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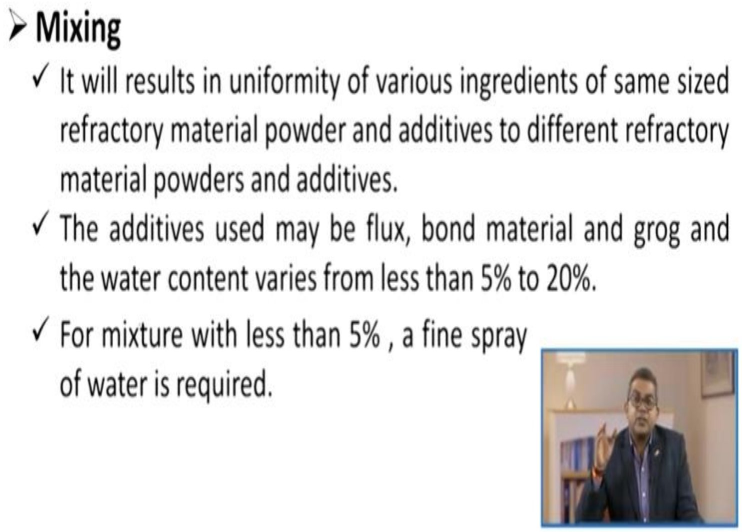

Now let us talk about the mixing it will result in the uniformity of the various ingredients of same size refractory material powder and additive to different refractory material powder and additives. The additives used may be flux bond material and grog and the water content varies from less than say 7% to 20% for mixture with less than 5% a fine spray of water is required.

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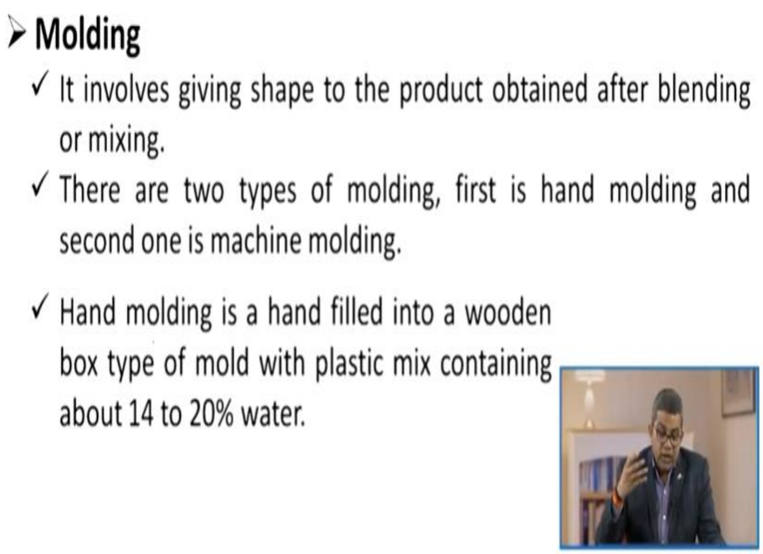

Molding because the shape is again very crucial in the refractory aspect so it involves giving the shape to the product obtained after blending or mixing. Now there are 2 type of molding first is the hand molding and second one is the machine molding. Now hand molding is the hand filled into a wooden box type of a mold with plastic mix containing about 14 to 20% of water. Now this is low-cost method but very slow it is not used for the mass production and requirement of pressure is moderate and it involves the 2-stage process.

For non plastic mixture and a clay containing less than say 5% of water they are molded in a dry pressing with the pressure up to say 35 to 140 mega Pascal. Another important process is the slip casting the suspension of fine refractory particle in water is poured into the mould of plaster of Paris. The slip casting is advantageous for making complicated shapes but the product obtained is highly porous in nature.

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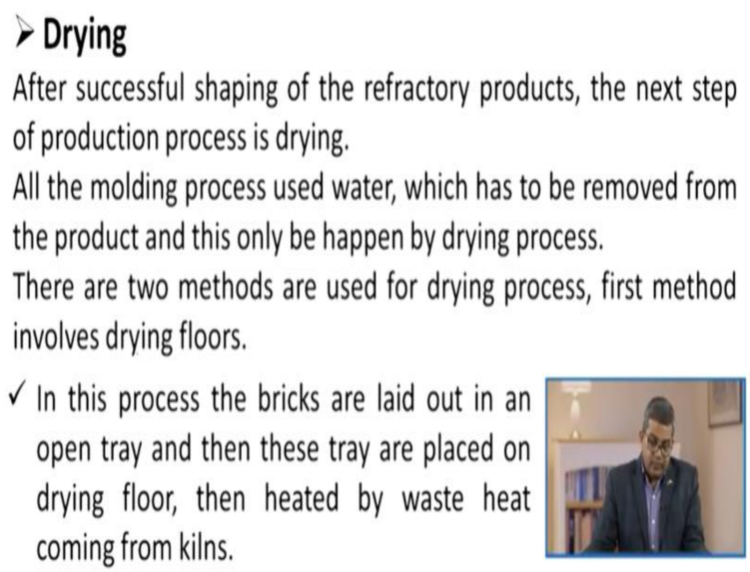

Drying once you have formed this shape through mold then next aspect is the drying. So, after successful shaping of the refractory product the next step is the production process is drying. All the molding process used water which has to be removed from the product and this, only be happened by the drying process. Now there are 2 methods are being used for the drying process first method involves the drying floors in this particular process.

The bricks are laid down in an open tray and these trays are placed in the drying floor then heated by the waste heat coming from kiln.

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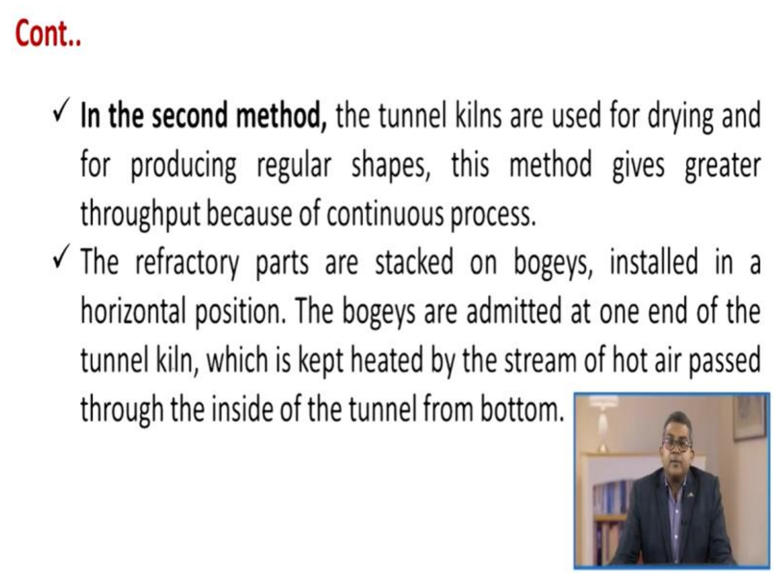

The second method that is a tunnel kill, the tunnel kiln are used for drying and producing regular shapes. This method gives a greater throw out because continuous process. The refractory parts are stacked on boggies and installed in a horizontal position. And these bogeys are admitted at one end of the tunnel kill which is kept heated by the stream of hot air passed through the inside of the tunnel from bottom.

As the bogies they come down the kiln counter current to the hot air and a drying takes place. The speeds of these bogeys are adjusted in such a way that when they exit the kiln the drying is completed.

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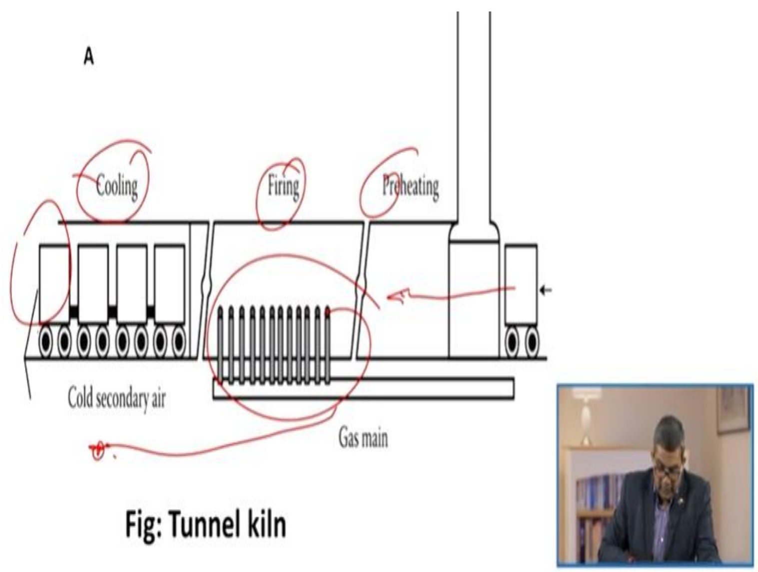

Now this is the typical shape of tunnel kiln. Now here you see that the different stages the cooling firing preheating now this is the gas main. So, they are coming from like this and after the cooling you can discharge all these refractory bricks. So, in this particular chapter we have discussed about the different aspect of refractories what are the ingredients? How we can classify them? What are the different properties with respect to the physical thermal and chemical we can look into for the appropriate use?

How we can manufacture all these refractory bricks in the different shapes? We discussed all the steps which are involved in this particular manufacturing aspect.

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References

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And for your convenience we have listed couple of references and if you wish to have a further reading or further knowledge about the subject in question you can utilize these references thank you very much.