Chemical Process Utilities
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Module No # 12
Lecture No # 58
Slag Attack & Kinds of Refractories in Uses

Welcome to this lecture of refractories in this lecture we will discuss about the slag attack and kind of refractories in use under the areas of chemical process utilities. Now again when we go into detail of the topic in question for today's lecture let us have a brief outlook that what we discussed in previous lecture? So, we discussed about the production of refractories and in the previous lecture we discussed about the firing aspect of refractories.

Then, we discussed about the thermodynamic principles including the free energy, enthalpy, entropy, chemical equilibrium, chemical stability etc. Then, we discussed about 3 stages of corrosion stage 1, stage 2, and stage 3.

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Now in this particular lecture, we are going to discuss about the various models for slag attack on refractories like Konig's model the model of Endell Fehling and Kley. And apart from this we will discuss about the various refractories including silica, alumina, aluminum, silicate, chrome, magnesite.

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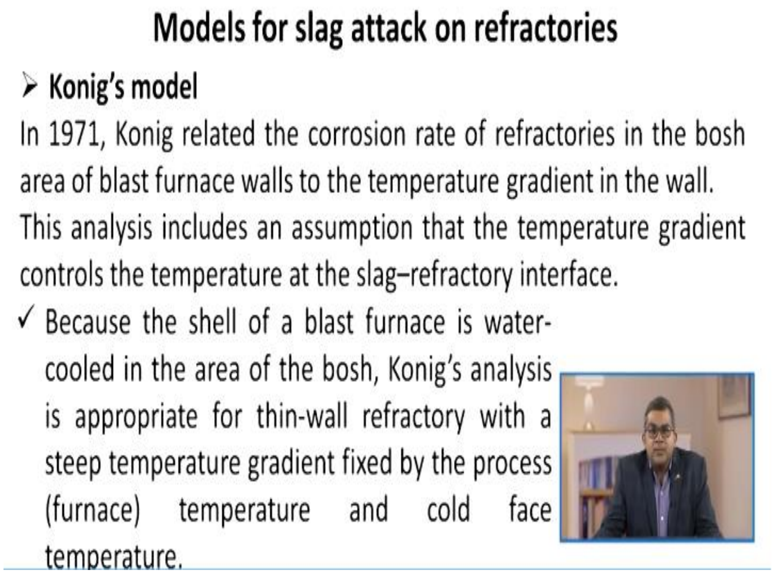

Let us discuss about the various model for slag attack on refractories. So, the first model in this aspect is Konig's model. In 1971 Konig related the corrosion rate of refractories in bosh area of blast furnace wall to the temperature gradient in the wall. Now this analysis includes an assumption that the temperature gradient controls the temperature at the slag-refractory interface.

Now because the shell of blast furnace is water cooled in the area of the bosh, Konig's analysis is appropriate for thin-wall refractory with a steep temperature gradient fixed by the process that is called furnace process temperature and cold face temperature.

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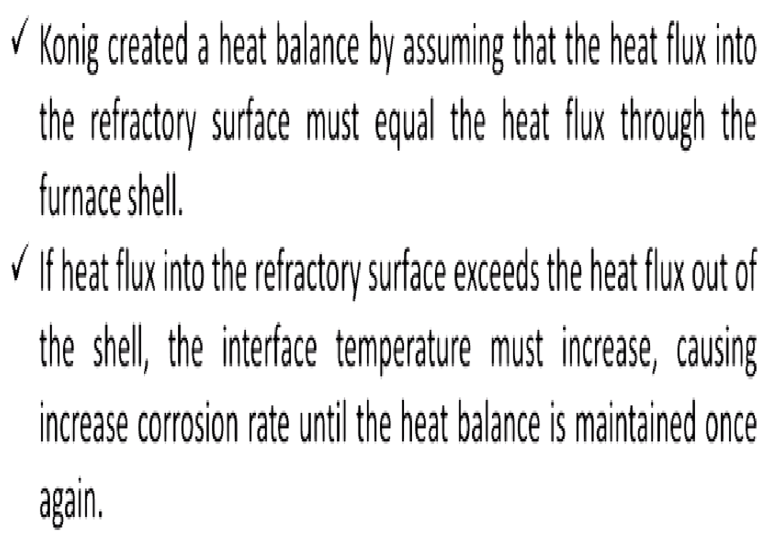

Now Konig created a heat balance by assuming that the heat flux into the refractive surface must equal the heat flux through the furnace shell. Now if heat flux into the refractory surface exceeds the heat flux out of the shell, the interface temperature must increase, causing the increased corrosion rate until the heat balance is maintained once again. Now the slag refractory interface temperature becomes Tc

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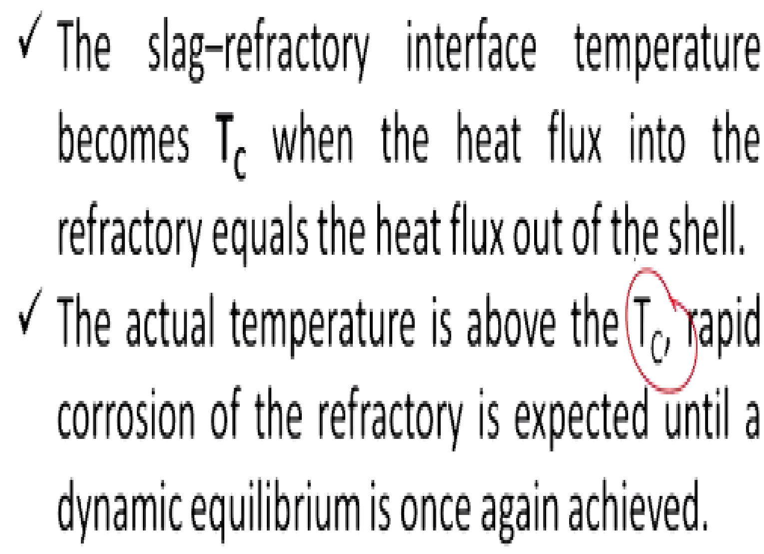

When the; heat flux into the refractory cools the heat flux out of the shell. The actual temperature is above Tc the rapid corrosion of the refractory is expected, until an above Tc the rapid corrosion of the refractory is expected until a dynamic equilibrium is once again achieved.

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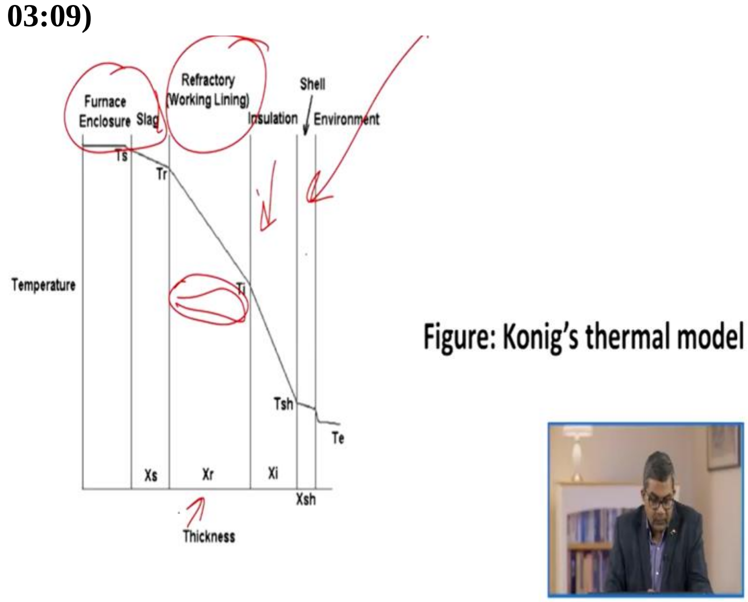

Now here you see that this figure reflects the Konig's thermal model. Here you are having the furnace enclosure then slag and refractory working line this zone and this one is the shell insulation and this is the insulation and this is the opening environment. So, if we plot the temperature versus thickness, you can see you can observe this particular behavior of the curve.

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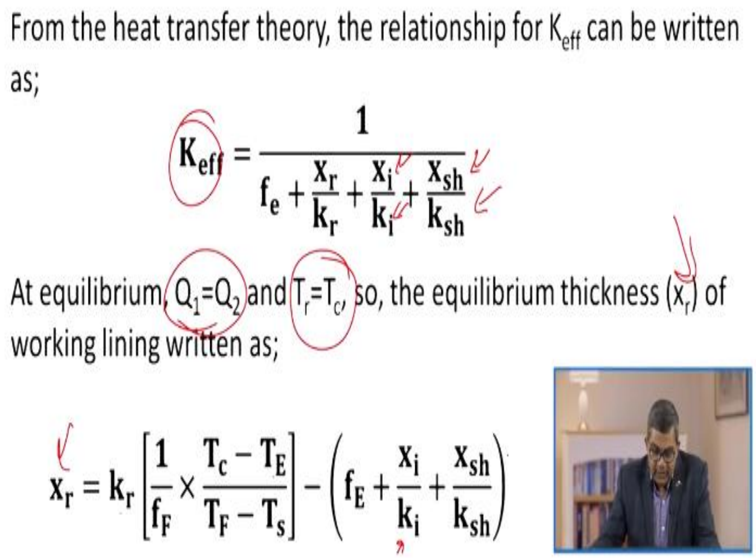

Now if we take this particular curve in cognition so the from the heat transfer theory the relationship of K effectiveness can be written as K effectiveness = 1 upon f_e + X_r over k_r + X_i upon k_i + X_{sh} over k sh. And now at equilibrium it is quite obvious that Q_1 will be equal to Q_2 and Tr would be equal to Tc. So, the equilibrium thickness that is referred as X r in this particular figure this can be represented as X_r = k_r into 1 over f_F here you see that this one into T_C – T_E over T_F – T_S – f_E + x_i over k_i + X_{sh} over k_{sh}.

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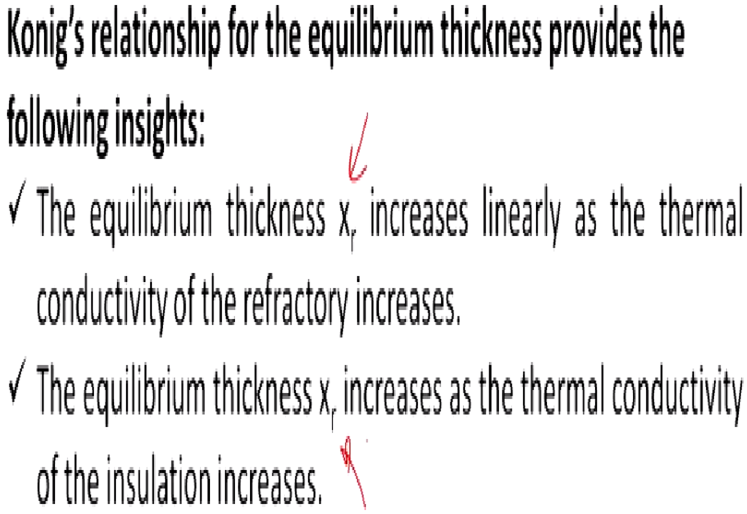
From the heat transfer theory, the relationship for K_{eff} can be written as;

$$\mathbf{K_{eff}} = \frac{\mathbf{1}}{\mathbf{f_e} + \frac{\mathbf{x_r}}{\mathbf{k_r}} + \frac{\mathbf{x_i}}{\mathbf{k_i}} + \frac{\mathbf{x_{sh}}}{\mathbf{k_{sh}}}}$$

At equilibrium, Q_1=Q_2 and T_r=T_c, so, the equilibrium thickness (x_r) of working lining written as;

$$\mathbf{x_r} = \mathbf{k_r}\left[\frac{\mathbf{1}}{\mathbf{f_F}} \times \frac{\mathbf{T_c - T_E}}{\mathbf{T_F - T_s}}\right] - \left(\mathbf{f_E} + \frac{\mathbf{x_i}}{\mathbf{k_i}} + \frac{\mathbf{x_{sh}}}{\mathbf{k_{sh}}}\right)$$



Now Konig's relationship for the equilibrium thickness this provides the different insights. Number 1 the equilibrium thickness X_r this increases linearly as the thermal conductivity of the refractory increases. Number 2 the equilibrium thickness X_r increases as the thermal conductivity of the insulation increases.

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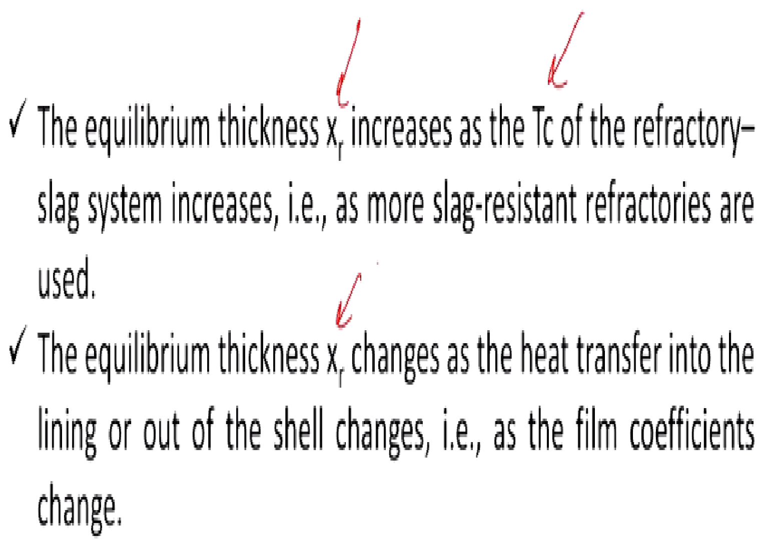

Now the equilibrium thickness X_r increases as the T_c of the refractory slag system increases. That is as more slag resistant refractories are used the equilibrium thickness X_r changes as the heat transfer into the lining or out of the shell changes that is the film coefficient changes.

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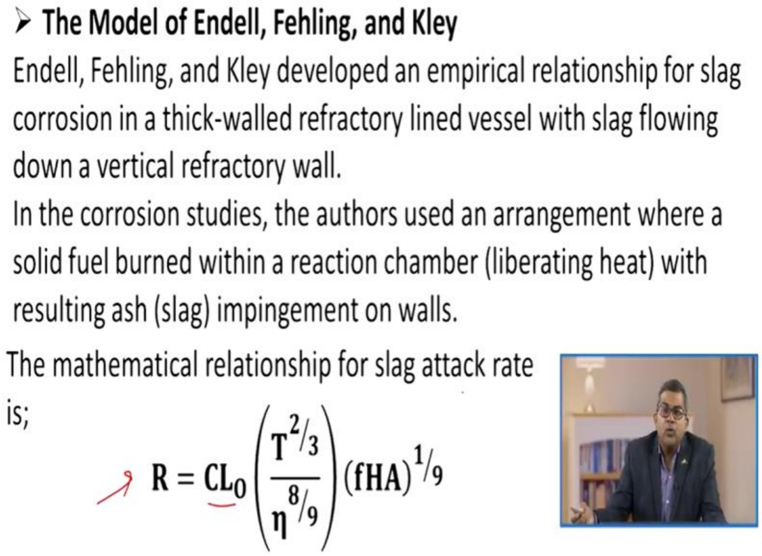

Now another; model that is called as the model of Endell, Fehling and Kley. Now the Endell, Fehling and Kley developed an empirical relationship for the slag corrosion in a thick-walled refractory lined vessel with the slag flowing down a vertical refractory wall. Now in the corrosion studies the authors they used an arrangement where a solid fuel burned within a reaction chamber that is liberating heat with resulting ash or slag impingement on walls.

So, the mathematical relationship for slag attack can be written as R = CL naught into T to the power 2 by 3 over Eta to the power 8 by 9 into f HA to the power 1 over 9.

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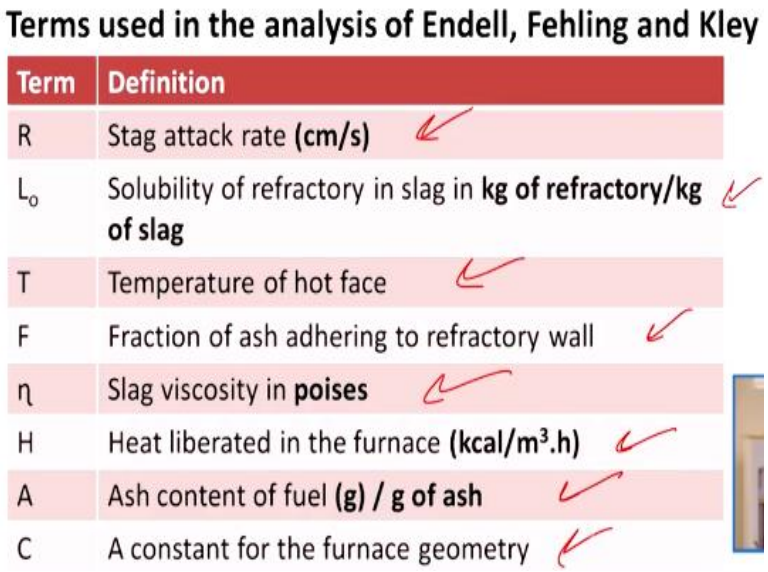
The mathematical relationship for slag attack rate is;

$$\mathbf{R = CL_0 \left(\frac{T^{2/3}}{\eta^{8/9}} \right) (fHA)^{1/9}}$$



Terms used in the analysis of Endell, Fehling and Kley

Term	Definition
R	Stag attack rate **(cm/s)**
L_o	Solubility of refractory in slag in **kg of refractory/kg of slag**
T	Temperature of hot face
F	Fraction of ash adhering to refractory wall
η	Slag viscosity in **poises**
H	Heat liberated in the furnace **(kcal/m³.h)**
A	Ash content of fuel **(g) / g of ash**
C	A constant for the furnace geometry

Now question arises that what are the different terms being used in this Endell, Fehling and Kley equation? Now there here R is the slag attack rate and usually it is represented with the units of centimeter per second. Then L naught is the solubility of refractory in slag in kilogram of refractory per kilogram of slag. Now the T is the temperature of the slag or temperature of the hot face.

Now F is the fraction of ash adhering to the refractive wall this Eta is the slag viscosity in poises. Now this H is the heat liberated in the furnace and it is represented as the kilo calorie per meter cube in hour. Now this A is the ash content of the fuel in gram per gram of ash and this is C is the constant of furnace geometry.

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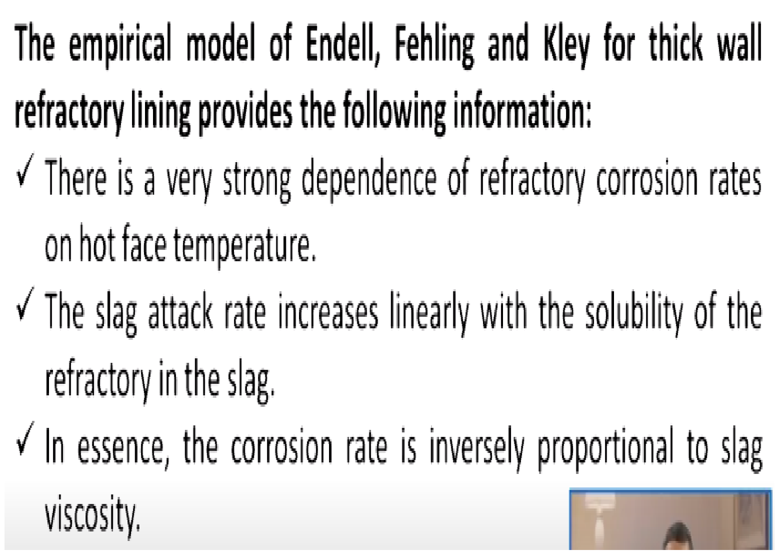

Now the empirical model of Endell, Fehling and Kley for the thick wall refractory lining provides different information. Now, one is that there is a very strong dependence of refractory corrosion rates on hot face temperature. Now second is the slag attack rate increases linearly with the solubility of the refractory in the slag. Third in the essence of the corrosion rate is inversely proportional to slag viscosity.

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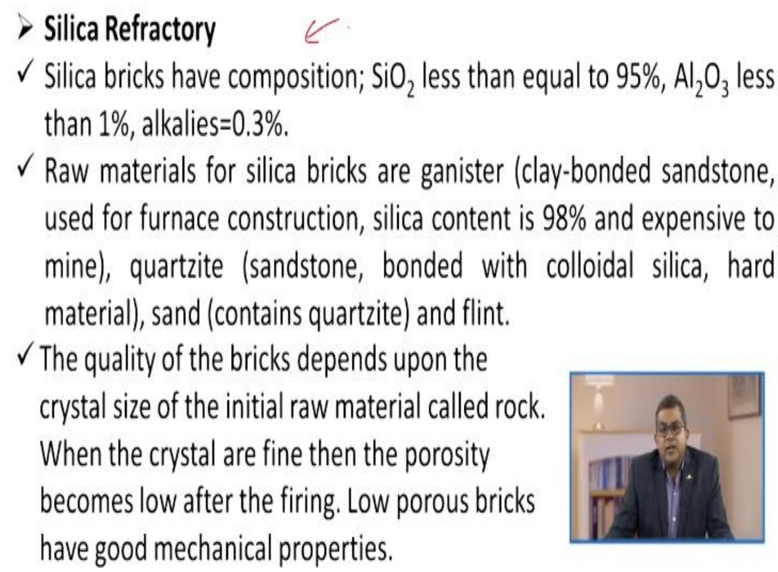

Now let us talk about the silica refractory now silica bricks have composition of SiO_2 less than equal to 95% and Al_2O_3 less than 1% and alkalies 0.3% approximately. Raw material for the silica bricks are ganister that is clay bonded sandstone used for the furnace construction silica content is 98% and expensive to mine quartzite sandstone bonded with the colloidal silica hard material and sand contains the quartzite and flint.

The quantity of the bricks depends upon the crystal size of the initial raw material that is called rock. When the crystals are fine then the porosity becomes low after the firing and low porous bricks have good mechanical properties. Yellow tops of silica now there are 15 allotropes exist of silica and most of them are meta stable transformation do not change their volume too much. The alpha quartz is the natural occurring form of silica and on heating this at say 503 degree Celsius transformed into beta quartz with rapid and reverse section.

Now beta quartz is stable up to 867 degree Celsius and if heating rate is faster than it may remain for few 100 degree more. You can further convert into tridymite in slow process this conversion can be enhanced by using a mineralizer such as calcium tungstate as catalyst. Now tridymite transforms to cristobalite at 1470 Celsius temperature in a slow process and there is a contraction of say 1.95%. The transformed cryotobalite becomes stable up to melting point of say 7720 degree Celsius.

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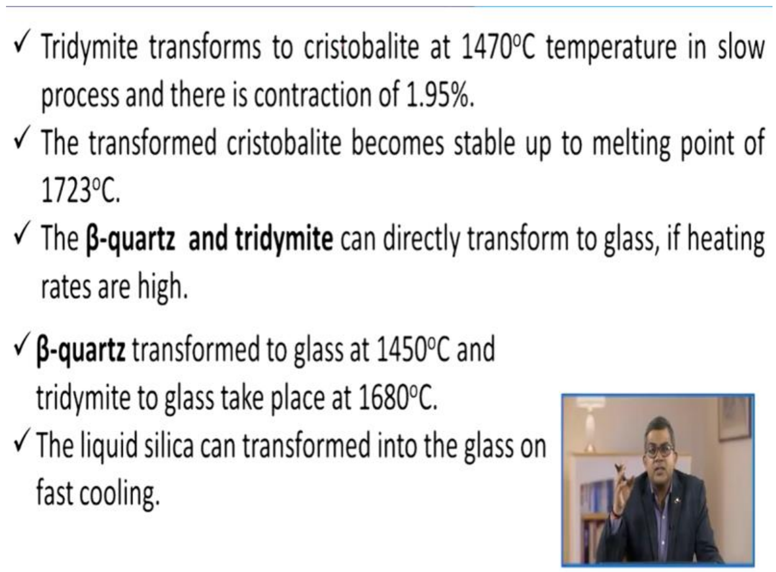

The beta quartz and tridymite can directly transform to glass if it take rates is a bit high. Beta quartz transform to a glass at 1450 degree Celsius and tridymite to glass takes place at 1680 degree Celsius the liquid silica can transformed into a glass on fast cooling.

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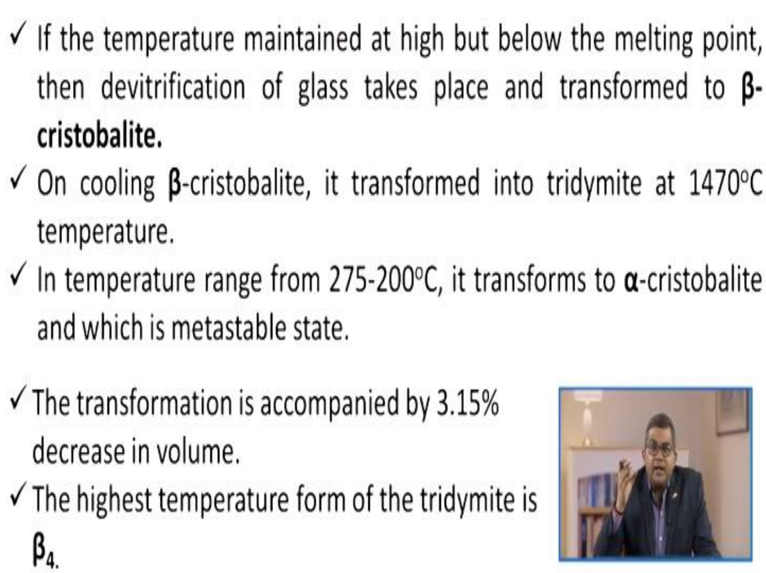

Now if temperature maintained at high but below the melting point then devitrification of the glass takes place and transformed to beta cristobalite on cooling the beta cristobalite is transformed into tridymite at 1470-degree Celsius temperature. Now in temperature range from 275 to 200 degree Celsius it transforms to alpha cristobalite and which is a metastable state. The transformation is accompanied by 3.15% decrease in volume the highest temperature form of tridymite is beta 4.

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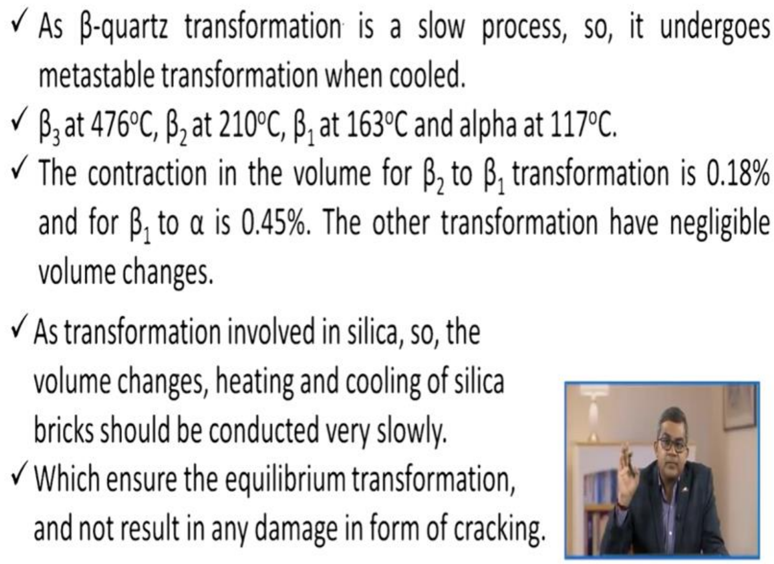

Now as beta quartz transformation is a slow process so it undergoes meta stable transformation when cooled. Now beta 3 at says 476 degree Celsius and beta 2 at 210 degree Celsius and beta one at 163 degree Celsius and alpha at 117 degree Celsius. The contraction in the volume for beta 2 to beta 1 transformation is 0.18% and for beta for one to alpha is 0.45 the other transformation have negligible volume changes.

Now as a transformation involved in silica so the volume changes heating and cooling of silica brick should be conducted very slowly. Which; ensures equilibrium transformation and not result in any damage in the form of cracking. Let us talk about the manufacturing of silica bricks now there are the general steps involved in the manufacturing of silica bricks. They are the raw materials are crushed to angular particles which helps in better packing during the compaction.

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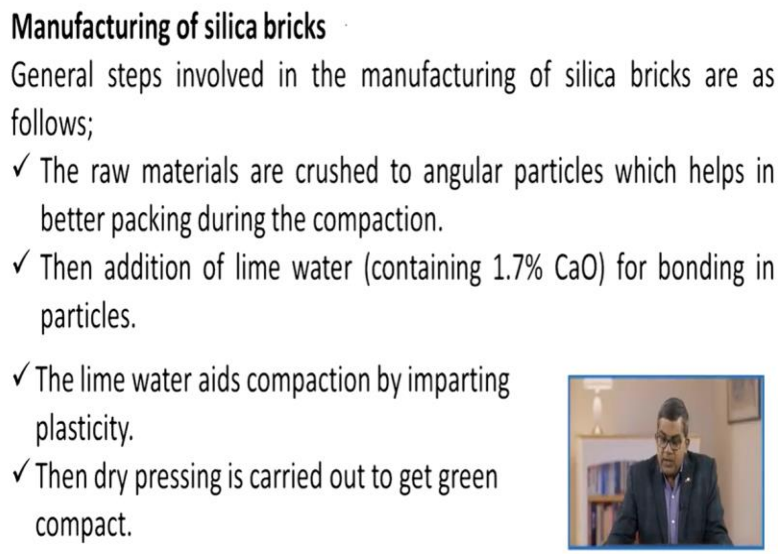

Now then addition of lime water that containing 1.7% of CaO for bonding in particles. The lime water aids compaction by imparting plasticity and then dry pressing is carried out to get green compact. Then firing at 1500 degree Celsius for at least 2 weeks here the various volume changes takes place during the transformation. The slow process of firing ensures that the brick obtained are undamaged.

The transformation of alpha to beta quartz is a fast process so heating beyond 573-degree Celsius temperature must be slow. The cooling from 300 to 100 degree Celsius is also slow for metastable transformation of cristobalite to tridymite. The firing at high temperature for long time is called hard firing.

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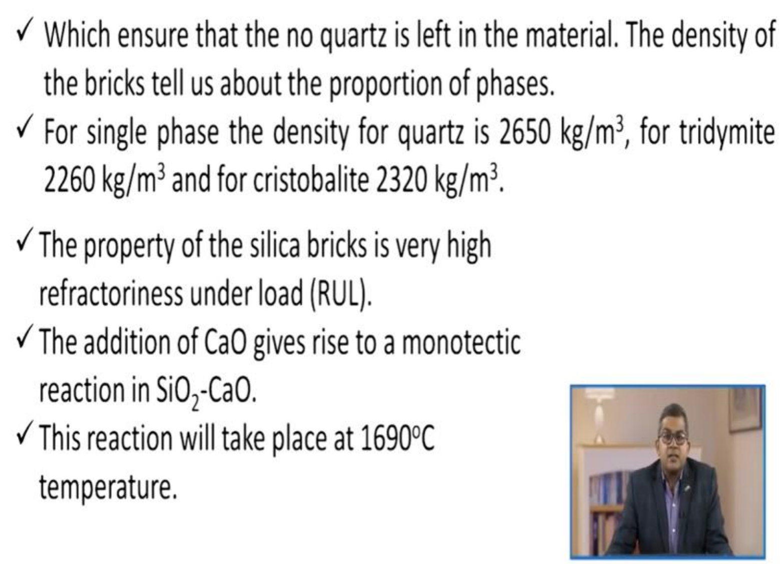

This ensures that no quartz is left in the material and the density of the bricks tells us about the proportion of phases. For single phase the density of quartz is 2650 kilogram per meter cube for tridymite 2260 kilogram per meter cube and for cristobalite 2320 kilogram per meter cube. The property of the silica brick is very high refractoriness under load. The addition of CaO gives rise to monotectic reaction in SiO_2 CaO this reaction will take place at around 1690 degree Celsius temperature.

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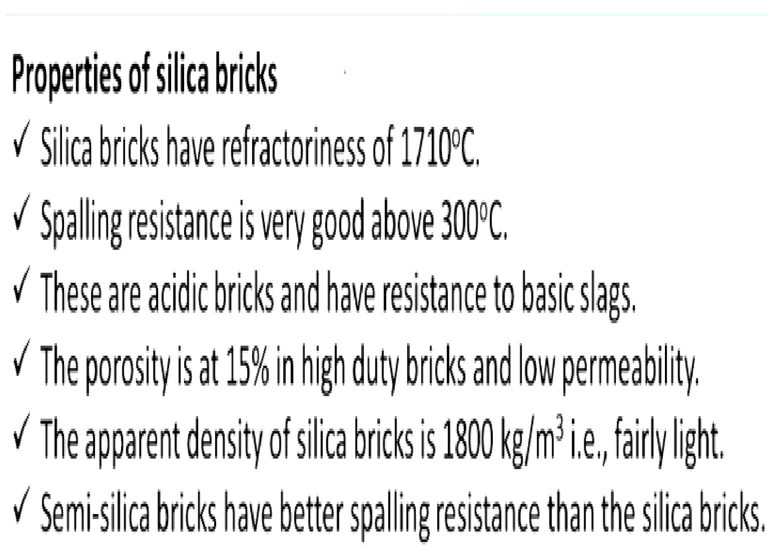

There are various properties attributed to the silica bricks now the silica brick have the refractiveness of 1710 degree Celsius spalling resistance is very good above 3000 degree Celsius. Now these are acidic bricks and have the resistance to the basic slag the porosity is around 15% in high duty bricks and low permeability. The apparent density of silica brick is 1800 kilogram per meter cube that is fairly light and the semi silica bricks have better spalling resistance than the silica bricks

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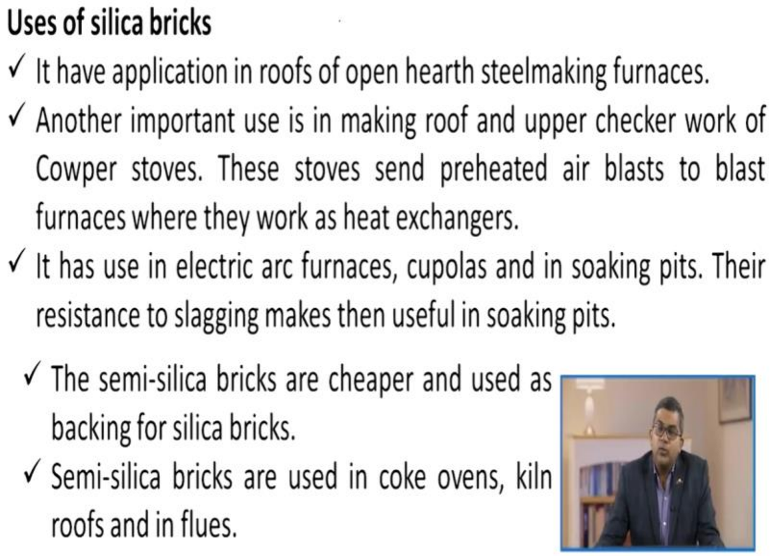

Now uses of silica bricks it has application in roof of open-hearth steel making furnace. Another important use is in the making of roof and upper checker wall work of copper stoves. Now these stoves and pre-heat air blast to the blast furnace where they work as a heat exchanger. It has a use in electric arc furnaces Q plus and soaking pits their resistance to stagging makes them useful in soaking pits.

The semi silica bricks are cheaper and used as a backing for silica bricks. The semi silica bricks are used in coke oven kiln roofs and flues. Let us talk about the alumina it is useful abundant and a simple oxide refractory. It is ionic in bond corrector.

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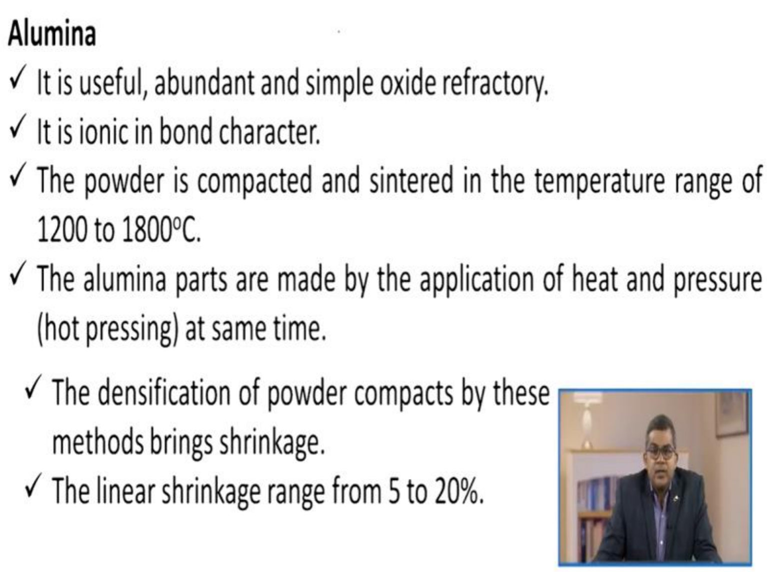

The powder is the compactness and centered in the temperature range of 1200 to 1800 degree Celsius. The alumina parts are made by the application of heat and pressure at the same time. The densification of powder compacts by these methods brings shrinkage the linear shrinkage range from 5 to 20%.

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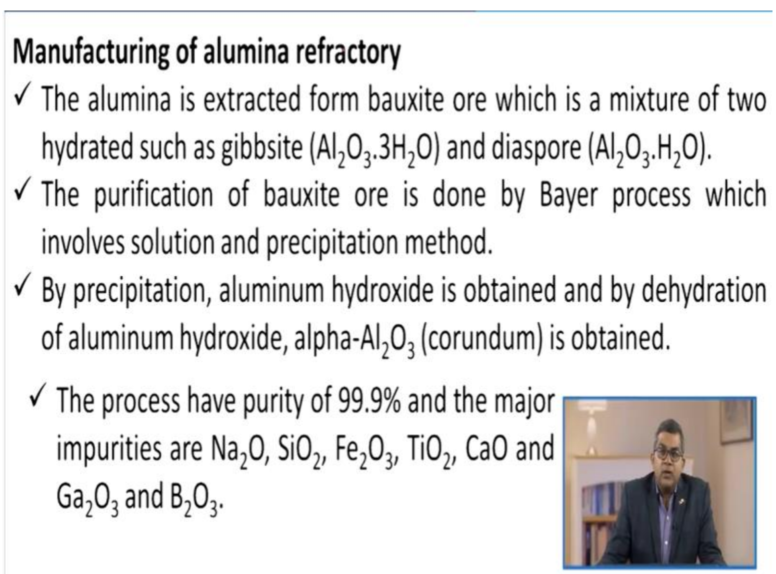

Let us talk about the manufacturing of alumina refractory; the alumina is extracted from bauxite ore which is a mixture of 2 hydrated such as gibbsite $Al_2O_3.3H_2O$ and diaspore $Al_2O_3.3H_2O$.The purification of bauxite ore is done by Bayer's process which involve the solution and precipitation method. Now by precipitation aluminum hydroxide is obtained and by dehydration the aluminum hydroxide alpha Al_2O_3or corundum is obtained. The processes have purity of 99.9% and the major impurities are Na_2O, SiO_2, Fe_2O_3, TiO_2, CaO and Ga_2O_3 and B_2O_3.

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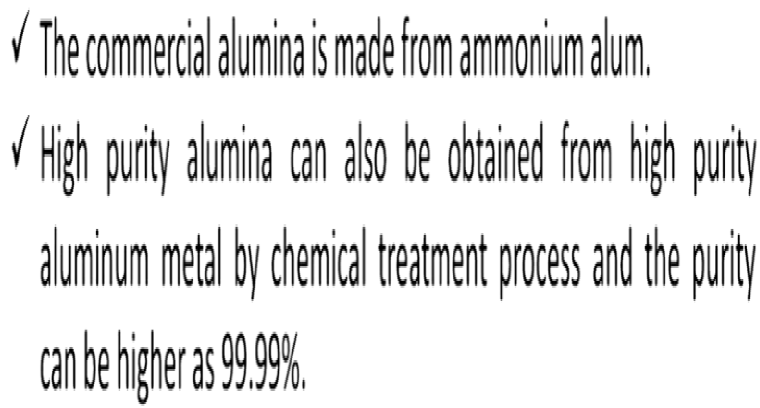

The commercial alumina is made from aluminum alum high purity alumina can also be obtained from high purity aluminium metal by chemical treatment process and the purity can be higher as 99.99%.

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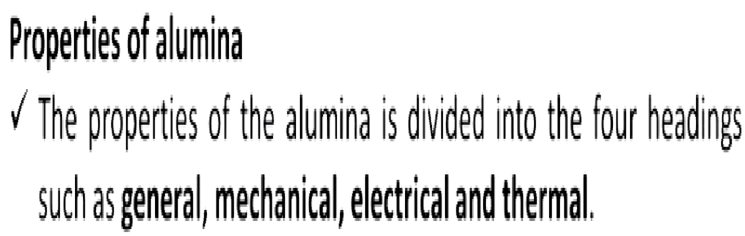

Now when we talk about the alumina the properties of alumina is divided into 4 different headings like general, mechanical, electrical and thermal.

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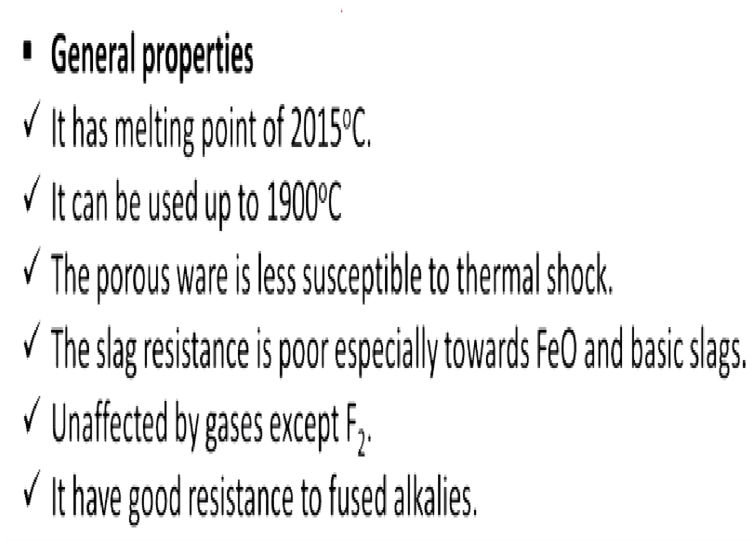

The general property the alumina possess that it has the melting point of 2015 degree Celsius it can be used up to 1900 degree Celsius. The process is less susceptible to thermal shock the slag resistance is poor especially towards the FeO and basic slag unaffected by gas except F 2 and it has the good resistance towards the fused alkalies. Let us talk about the mechanical properties the strength of alumina depends on the density and that is higher the density greater will be the strength.

The high strength of the material causing failure by brittle fracture as dislocation movement becomes difficult the theoretical strength of the alumina should be greater than 7000 mega Pascal

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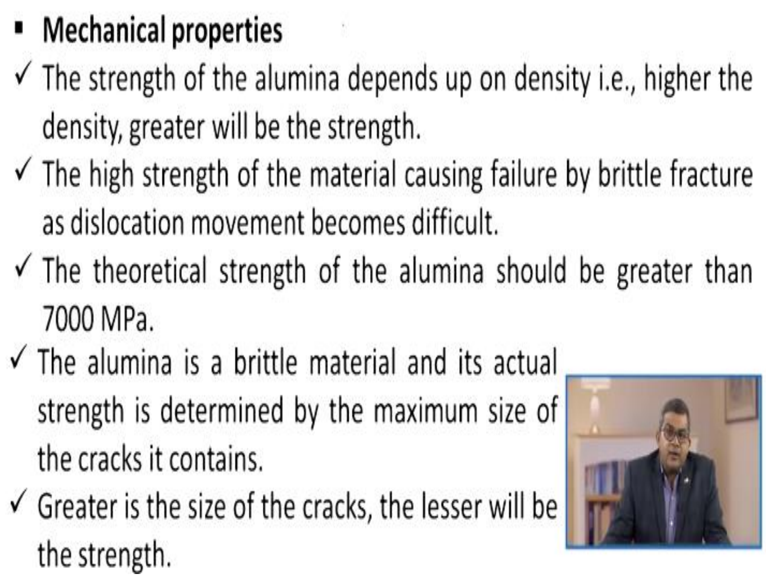

The alumina is brittle material and its actual strength is determined by the maximum size of the cracks it contains greater is the size of the cracks the lesser will be the strength.

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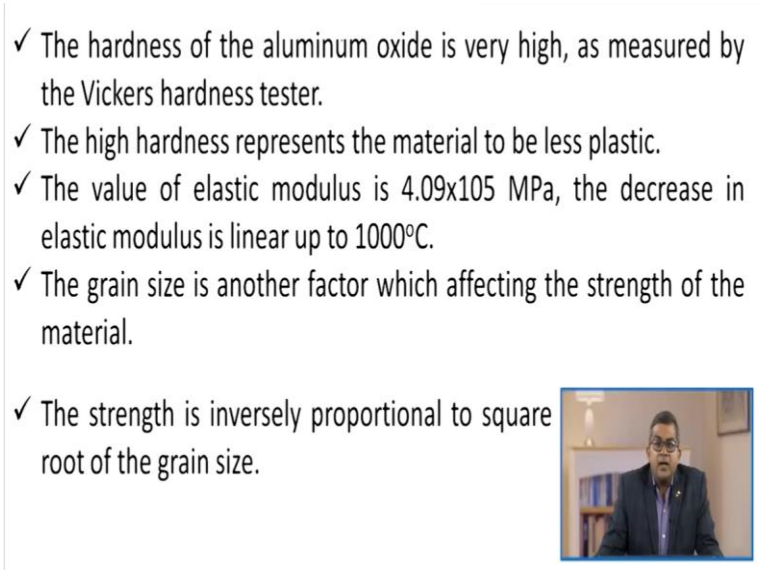

The hardness of aluminum oxide is very high as measured by the Vickers hardness tester. The high hardness represents the material to be less plastic. The value of elastic modulus is around 4.09 into 10 to the power 5 mega Pascal and decrease in the elastic modulus is linear up to 1000 degree Celsius. The grain size is another factor which affecting the strength of the material the strength is inversely proportional to the square root of grain size.

Let us talk about the electric properties the sintered alumina provided excellent insulating properties so it is used as insulator in electrical and electronic industries the electric conductivity of alumina is of 20 orders of the magnitude smaller than the metallic conductor it is also doped to use as a semiconductor at temperature greater than 1500 degree Celsius it behaves like an intrinsic semiconductor.

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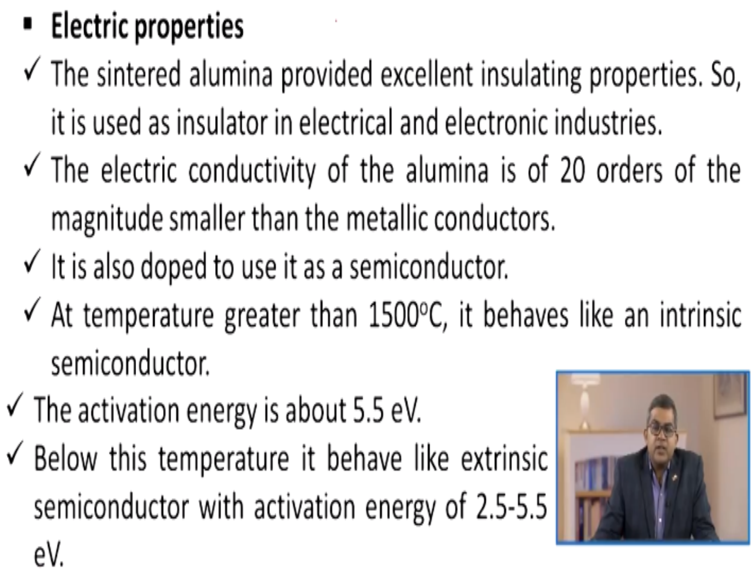

The activation energy is about 5.5 electron volt below this temperature it behaves like extrinsic semiconductor with an activation energy of 2.5 to 5.5 electronic volt.

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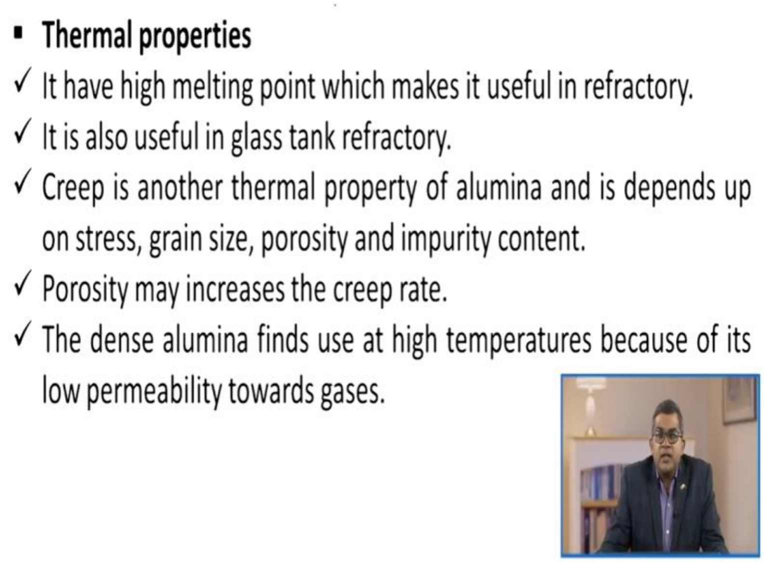

Let us talk about the thermal properties it have the high melting point which makes it useful in refractory. It is also useful in glass tank refractory. Now creep is another thermal property of aluminum and it depends upon the stress grain size porosity and impurity content. The porosity may increase the creep rate. Dense aluminum finds used at high temperature because of its low permeability towards gases.

Uses of alumina refractory it used commonly in the form of tubes and crucibles the fused aluminum mixed with clay and produces abundant cement. Now it is used in the laboratories and it is useful in the range of 1500 to 1700 temperature degree Celsius temperature application.

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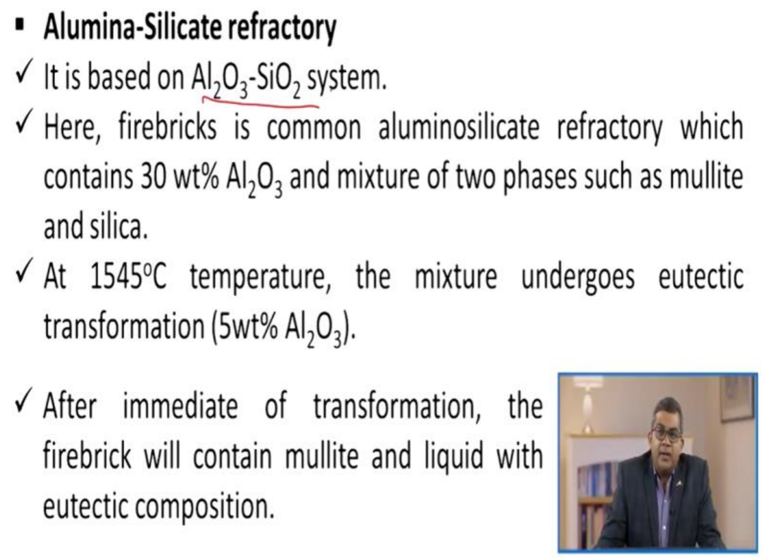

Let us talk about the alumina silicate refractory now it is based on Al_2O_3-SiO_2 system. Here the firebricks is common aluminum silicate refractory which contains 30 weight percent of Al_2O_3 mixture of 2 phases such as mullet and silica. At 1545-degree Celsius temperature the mixture undergoes eutectic transformation that is 5 weight percent of Al_2O_3. After immediate of the transformation the fire break contains mullite and liquid with eutectic composition.

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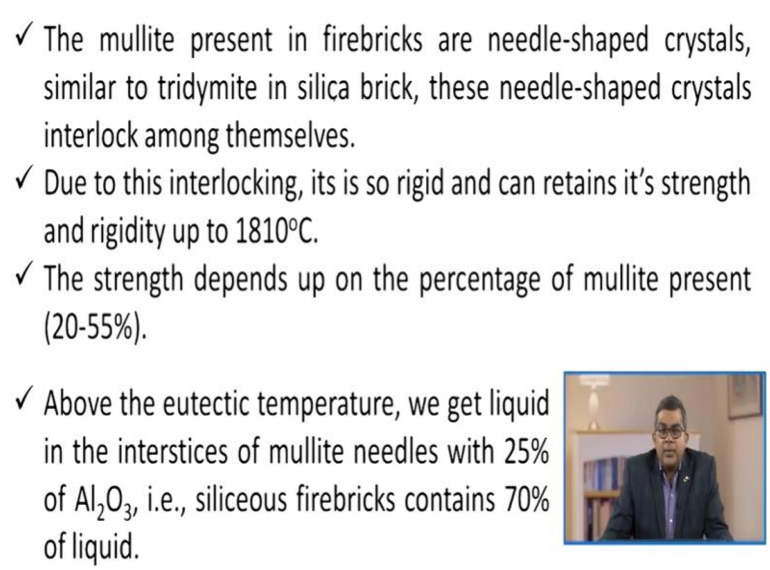

The mullite present in the fire bricks are needle shaped crystals similar to tridymite in silica brick these needle shaped crystals interlock among themselves. Due to this interlocking, it is so rigid and it can retain its strength and rigidity up to 1810 degree Celsius. The strength depends on the percentage of mullite present and that is 20 to 55% above the eutectic temperature we get liquid in interstices with mullite needles with 25% of Al_2O_3 and that is siliceous firebreaks contains 70% of liquid.

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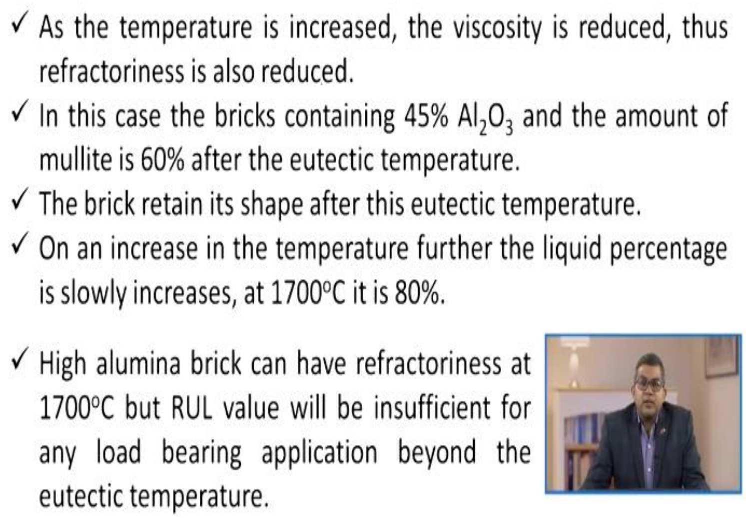

Now as the temperature is increased the viscosity is reduced thus the refractoriness is also reduced. In this case the bricks containing 45% Al_2O_3 and the amount of malate are 60 after the eutectic temperature. The brick retain its shape after this eutectic temperature now an increase in the temperature further the liquid percentage is slowly increases at around 1700 degree Celsius and it is about 80%. High alumina brick can have refractoriness at 1700 degree Celsius but RUL value will be insufficient for any load bearing application beyond the eutectic temperature.

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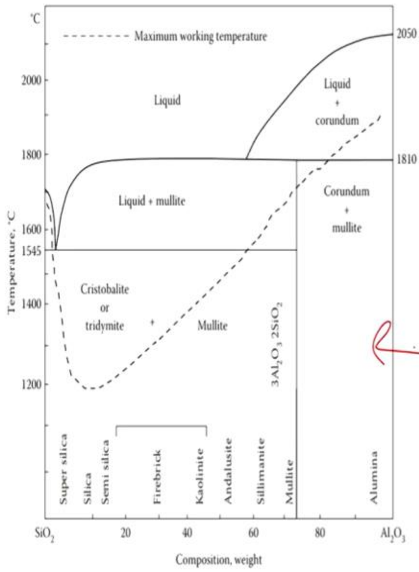

Figure showing equilibrium diagram of Al_2O_3-SiO_2 system wherein the composition of various alumino-silicate refractories marked including the composition of semi-silica.

Now here you see that the equilibrium diagram of Al_2O_3-SiO_2 system where in the composition of various aluminum silicate refractories marked including the composition of semi-silica.

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Firebricks

- ✓ It is regular brick of a furnace designer and most common refractory, which is made up of fireclay.
- ✓ China clay is also used to make bricks, and these bricks have enhanced properties than the firebricks.
- ✓ If we talk about the fireclay it forms from the decomposition of the igneous rocks.
- ✓ The decomposition is caused by the geological processes which take place over many years.
- ✓ The types of fireclay formed are based up on the rock type and the geological process.

Let us talk about the fire bricks; it is the regular brick of furnace designer and most common refractory which is made up of fire clay. China clay is also used to make the bricks and these bricks have enhanced properties than the fire bricks. If you talk about the fire clay forms with the decomposition of the ingenious rock. Now decomposition is caused by the geological processes which take place over many years.

The type of fire clay formed based upon the rock type and geological process. Now this fire clay comes from granite which is acid rock and that contains feldspar the feldspar is a group of minerals such as aluminum silicate of potassium sodium and calcium.

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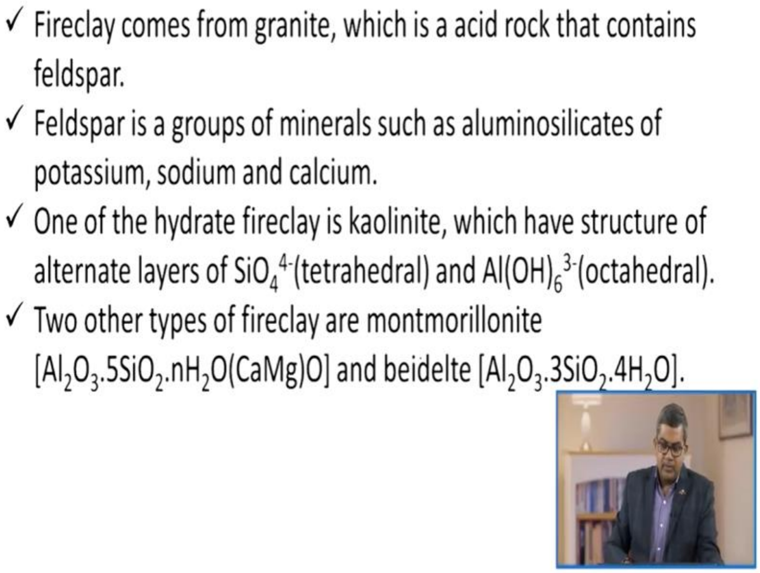

One of the hydrate fireclay is a kaolinite, which have structure of alternate layers of SiO_4 tetrahedral and $Al(OH)_6^{3-}$ octahedral. Now 2 other type of fire clay they are montmorillonite that is $Al_2O_3.5SiO_2.nH_2O$ (CaMg)O] and beidelte that is $Al_2O_3.3SiO_2.4H_2O$.

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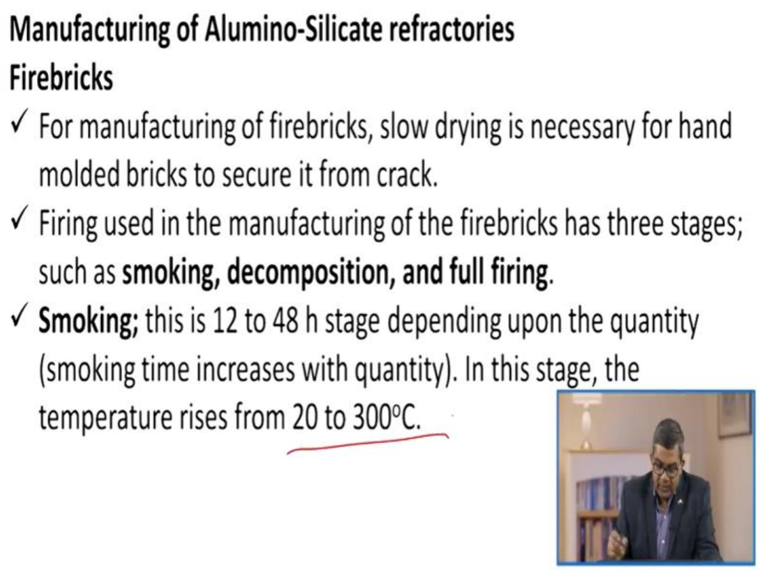

Now let us talk about the manufacturing aspect of aluminum silicate refractory firebricks. For manufacturing of firebricks slow drying is necessary for hand molded bricks to secure it from crack. Now firing used in manufacturing of the fire break has 3 stages smoking, decomposition and full firing. Now smoking this is 12 to 48 hour stage depending upon the quantity and smoking time increases with quantity. Now in this stage the temperature rises from 20 to 300 degree Celsius.

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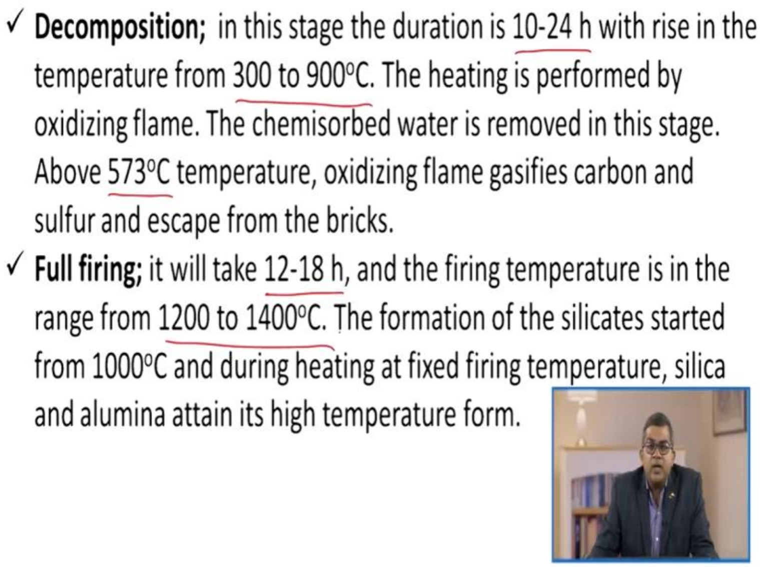

Decomposition in this stage the duration is around 10 to 24 hours with the rise in temperature from 300 to 900 degree Celsius. The heating is performed by the oxidizing flame and the chemisorbed water is removed in this stage above 573 degree Celsius temperature oxidizing flame gasifies carbon and sulfur and escape from the bricks. Full firing it will take around 12 to 18 hours and the firing temperature is in the range from 1200 to 1400 degree Celsius.

The formation of silicate is started from 1000 degree Celsius and during heating at fixed firing temperature silica and alumina attain its high temperature form.

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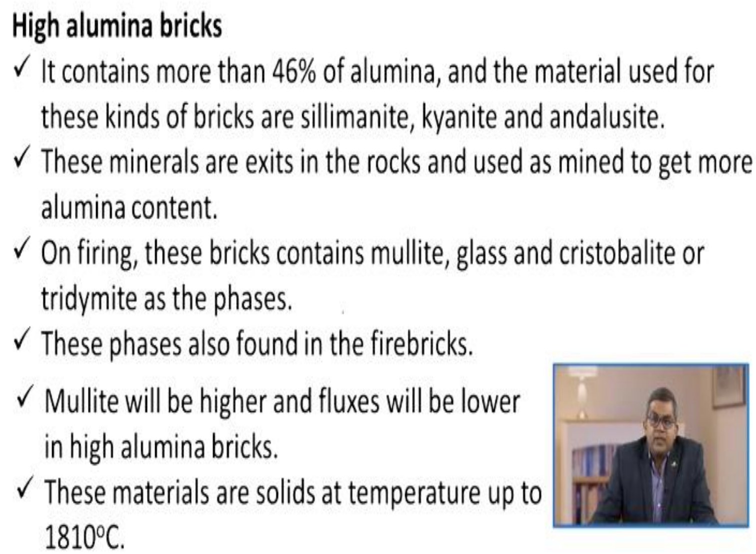

High alumina bricks now it contains more than 46% of alumina and the material used for these kinds of bricks are sillimanite kyanite and leucite. Now these minerals are existing in the rocks and used as mine to get more alumina content. On firing these bricks contain mullite glass and cristobalite or tridymite as the phases. Now these phases also found in fire bricks. Mullite will be higher and fluxes will be lower in the high aluminum bricks.

Now these materials are solid at temperature up to 1810 degree Celsius. Let us talk about the properties of alumina silicate refractories fire bricks.

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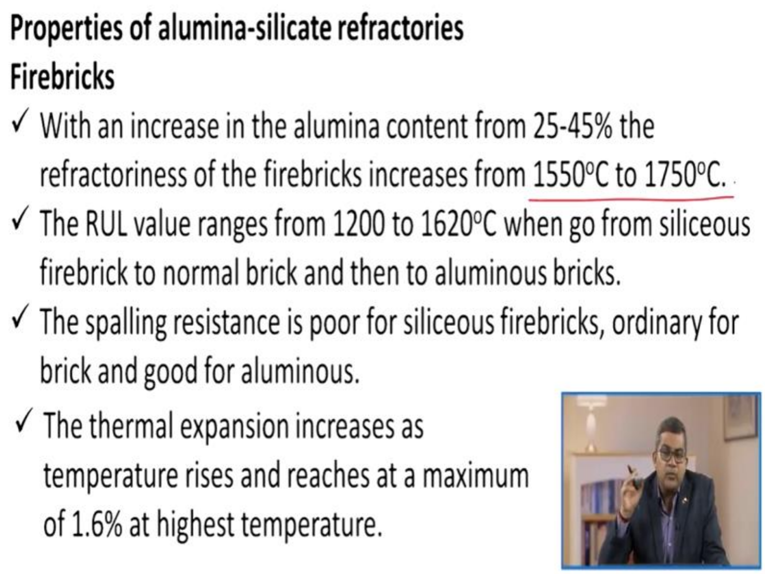

Now with an increase in the alumina content from 25 to 45% the refractoriness of the fire break increases from 1550 degree Celsius to 1750 degree Celsius. The RUL value ranges from 12000 to

1620 degree Celsius when grow from siliceous fire break to normal brick and then to aluminous brick. The spalling resistance is poor for siliceous fire bricks ordinary for brick and good for aluminous.

The thermal expansion increases as temperature rises and reaches at a maximum of 1.6% of highest temperature. The acid slag resistance is good for all type of fire bricks but the basic slag resistance is poor for siliceous and ordinary fire bricks but good for aluminous one. Now to increase the abrasion resistance the fire brick are hard fired and which causes the partial vitrification.

The vitrification reduces the porosity so the brick will become harder and more compact but spelling resistance is reduced grog particles present in the structure also make it harder.

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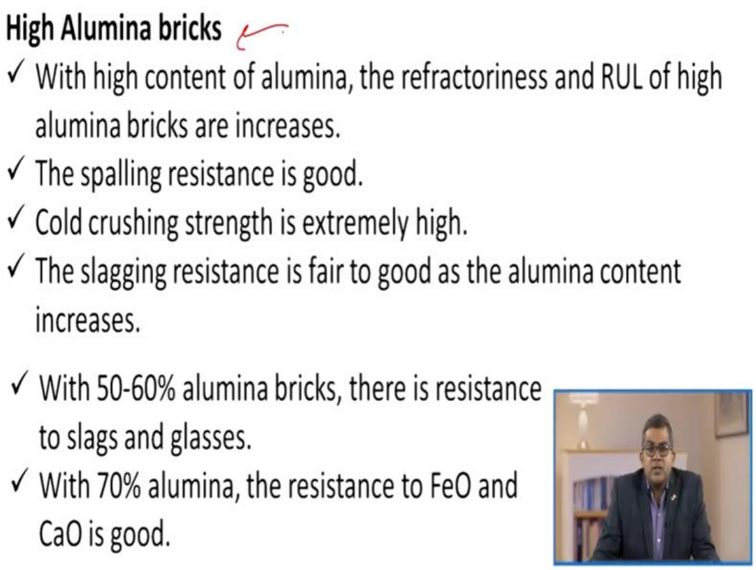

Let us talk about the high alumina brick with the high content of alumina the refractiveness and RUL of high alumina bricks are increases. The spalling resistance is good the cold crushing strength is extremely high. The slagging resistance is fair to good as the alumina content increases with 50 to 60% alumina bricks there is a resistance to slag and glasses. With 70% of alumina the resistance to FeO and CaO is good.

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Now the uses of alumina silicate refractories the fire brick are used in furnace construction and also in the domestic fireplace and store. In iron making industries the fire bricks are found in blast furnace stuck bosh hearth and ladles. Copper stoves and blast duct connecting copper stoves and blast furnaces are also constructed of fire bricks. It has application in the open-hearth steel making in the area where the bricks are not exposed to steel making temperature such as checkers of regenerators.

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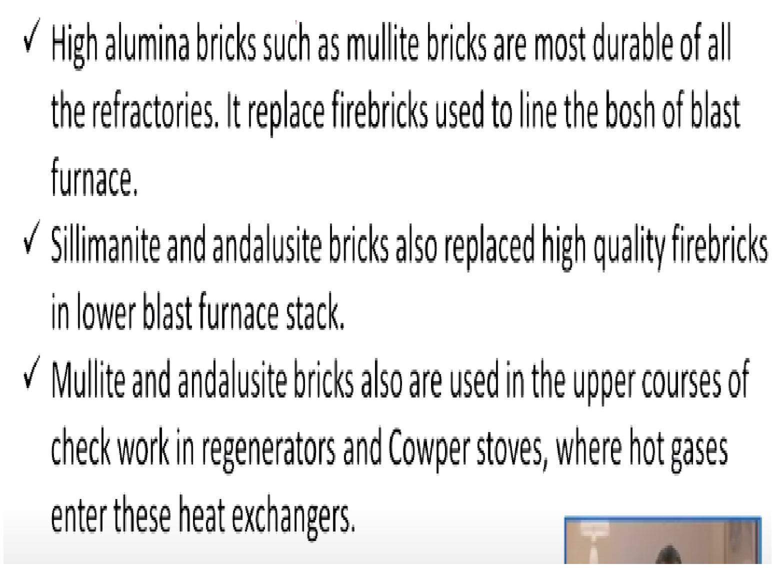

The high alumina bricks such as mullite bricks are most durable for all refractories it replaces the fabrics used in to line the bosh of blast furnace. Sillimanite and andalusite bricks also replaced high quality fire bricks in the lower blast furnaces stack. Mullite and andalusite bricks also are used in the upper courses of a check work in the regenerators and copper stoves where hot gases enter these heat exchangers.

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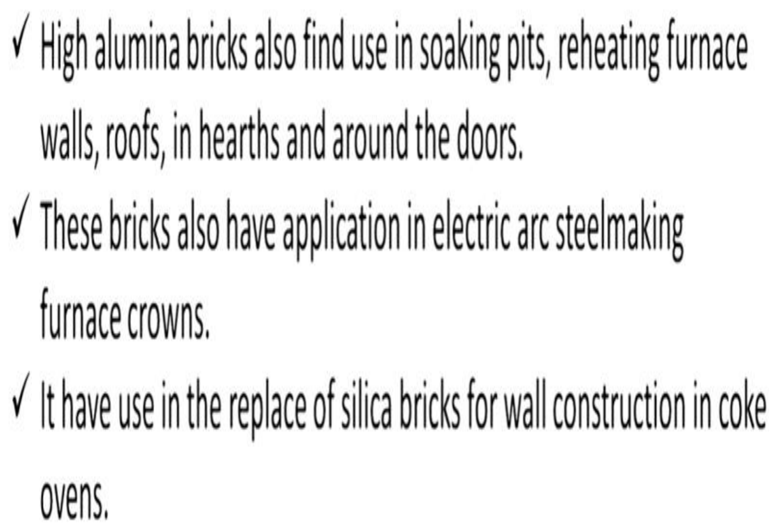

The high alumina brick also find use in the soaking pits re-eating furnace walls roofs in hearths and around the doors. These bricks also have application in electric arc steel making furnace crowns. It has the use in the replacement of the silica bricks for wall construction in coke ovens.

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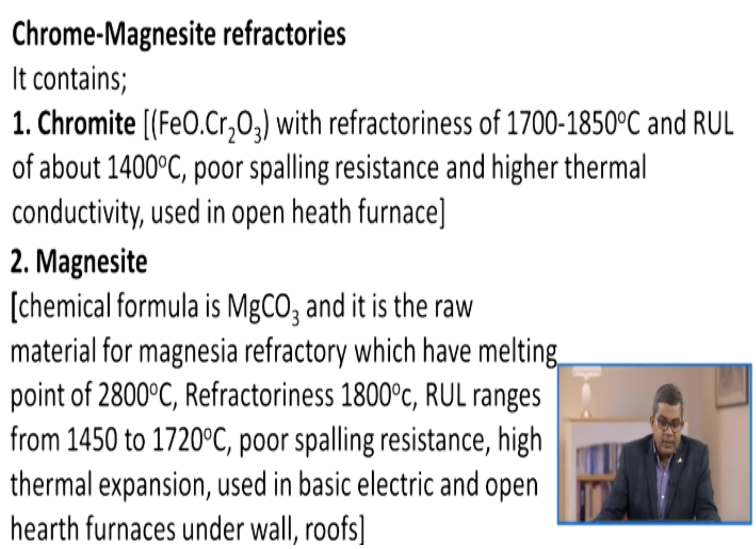

Let us talk about the chrome magnesite refractories now it contains chromite that is $FeO.Cr_2O_3$ with the refractiveness of 1700 to 1850 degree Celsius and RUL is about 1400 degree Celsius. Poor spalling resistance and higher thermal conductivity used in the open heart furnace. Magnesite that is having the chemical formula of $MgCO_3$ and it is the raw material for magnesia refractory which have the melting point of 2800 degree Celsius.

Refractiveness is about one thousand eight hundred degree Celsius RUL ranges from 1450 to 1720 degree Celsius. Poor spalling resistance, high thermal expansion is used in the basic electric and open earth furnace under wall roofs.

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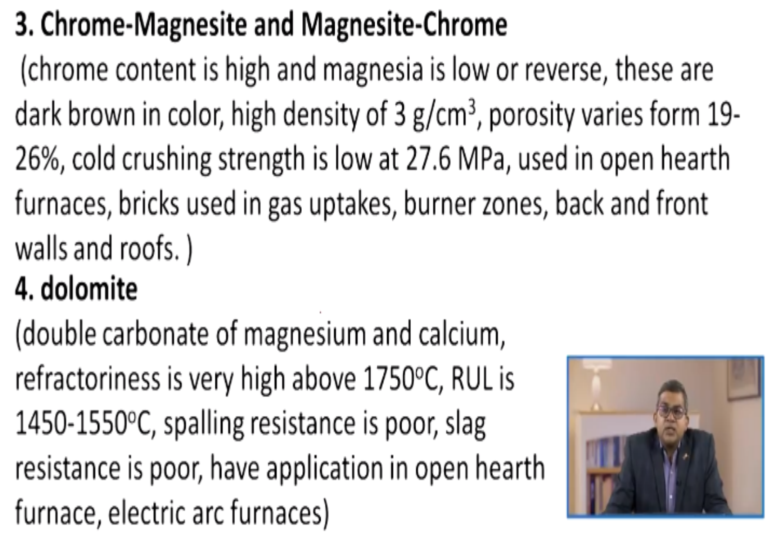

The chrome magnesite and magnet magnesite chrome this chrome content is high and magnesia is low or reverse these are the dark brown in color and high density of 3 gram per centimeter cube. Porosity varies from 19 to 26% cold crushing strength is low at 27.6 mega Pascal used in the open hearth furnace bricks used in the glass uptakes burner zone back and front walls and roofs.

Dolomite, this is the double carbonate of magnesium and calcium refractories and it is having a very high refractiveness is very high that is above 1750 degree Celsius RUL is 1450 to 1550 degree Celsius. Spalling resistance is poor slag resistance is poor have application in open hearth furnace electric arc furnace.

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5. Fosterite

(double oxide and mixture of magnesia and silica, refractoriness of 1750ºC, RUL minimum value is 1550ºC, thermal expansion is low, good spalling resistance, have resistance to both acid and basic slags, have application in open hearth back wall, downtakes and top courses for furnaces).

Fosterite this is a double oxide and mixture of magnesium and silica refractiveness around 1750 degree Celsius RUL minimum value is 1550 degree Celsius thermal expansion is low. Good spalling resistance have resistance to both acid and basic slags have application in the open hearth back wall down takes and top courses of furnaces. So, in this particular chapter we had a discussion about the different bricks and different bricks materials.

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References

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- Refractories Handbook:, Edited by Charles A. Schacht, Marcel Dekker, Inc., New York, Basel, (2014), ISBN: 0-8247-5654-1.

And if you have any doubt or if you have wish to have further study we have enlisted couple of references for your convenience. You can have a look of all these references for your convenience and as per your ease thank you very much.