Membrane Technology
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Lecture No 4
Inorganic Materials for Membrane Preparation, their Advantages and Disadvantages

Good morning students today is the lecture 4 under module 2 in this particular lecture.

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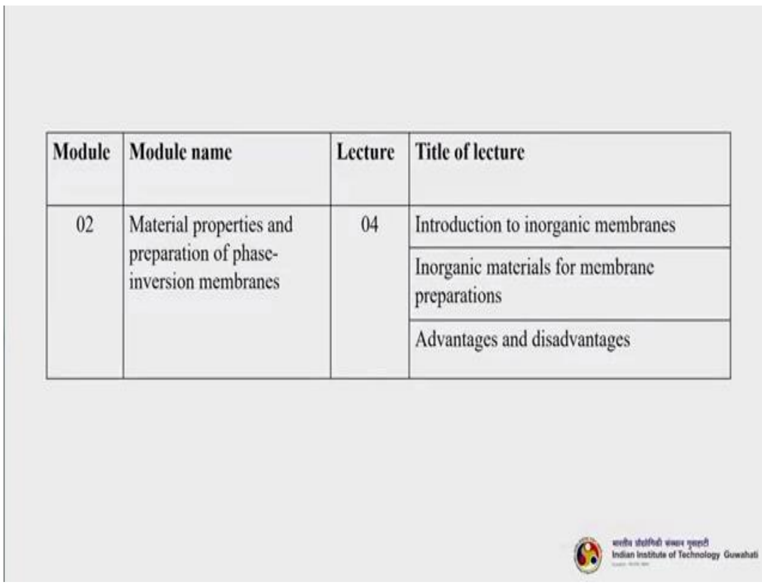

Module	Module name	Lecture	Title of lecture
02	Material properties and preparation of phase-inversion membranes	04	Introduction to inorganic membranes
			Inorganic materials for membrane preparations
			Advantages and disadvantages

We will discuss about the inorganic membranes and the materials that is required to prepare inorganic membranes, there are advantages and disadvantages. So as you know that we have been discussing the membrane materials since last class, today we will wind up this particular discussion and the next class onwards will move ahead with the module design and that merits and demerits. As you know that.

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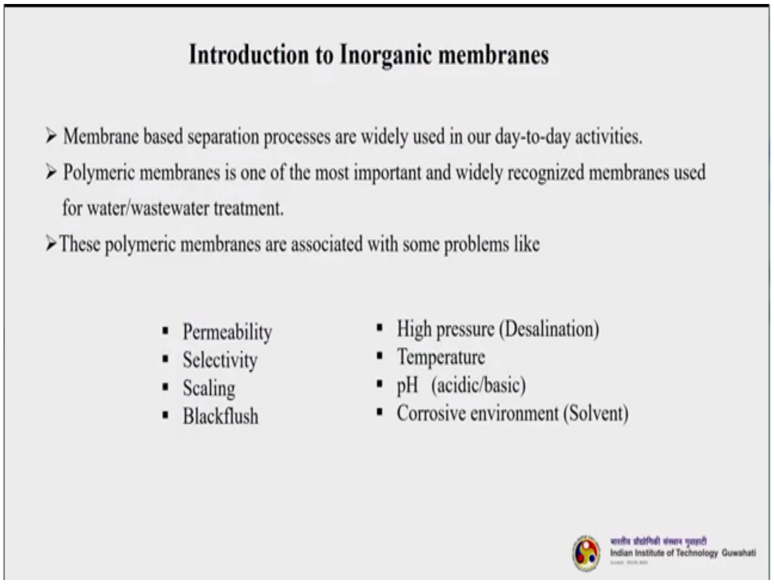

Membrane-based separation processes are widely used in our day to day activities polymeric membrane is one of the most important and widely recognized membranes used for water and wastewater treatment as well as many other applications. Now this polymeric membranes are however, associated with some problems like permeability selectivity scaling or fouling problem a backflushing then in desalination usually we need a very high pressure.

So sometimes membranes gets distorted, then it cannot withstand higher temperature applications pH whether a a very high acidic or high base pH is not good for polymeric membranes, then various corrosive environment and they are not able to withstand. And these are some of the inherent problems which are associated with polymeric membranes due to all these problems the membrane scientists have taken a keen interest to develop ceramic membranes.

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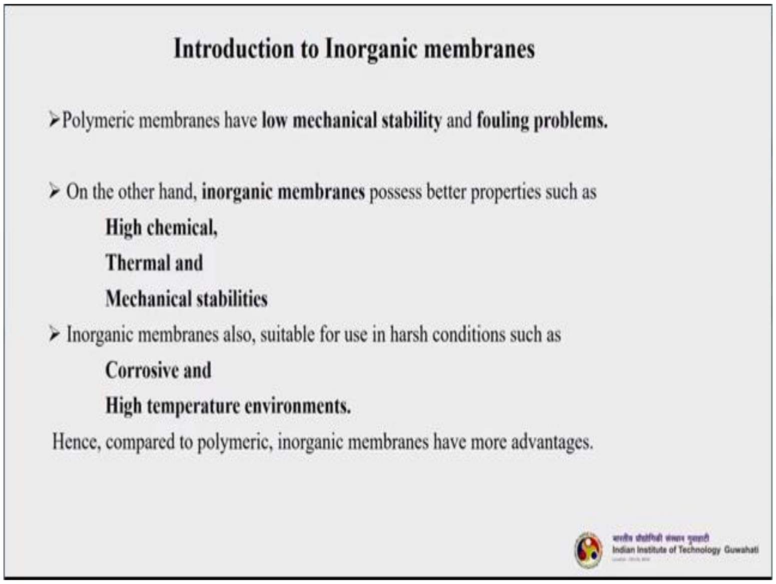

So polymeric membranes have also low mechanical stability and fouling problems, mainly to overcome these things membrane scientists have looked into inorganic membranes and inorganic materials they have very high chemical, thermal and mechanical stability. So what happens actually in many applications we need to go for higher pressure so when you go for a very high pressure application such as reverse osmosis for actually desalination purposes.

Then the membranes should be able to withstand that type of higher pressure, so basically mechanical and many a times we need also process certain streams, which are coming out of the let us say refineries or any other process and are at elevated temperature, that means higher temperature let us say 100 degree 200 degree even more than them. Then in such cases certain polymeric membranes are not able to withstand this higher temperature.

Actually, due to these two main things that mechanical stability and thermal stability and low flux problems also associated with the polymeric membrane, so ceramic membranes has come into picture. So inorganic membranes suitable for use in harsh condition such as corrosive and high-temperature environments. Hence compared to polymeric membranes in organic membrances more advantageous.

But it is not always true that in for any application we will use inorganic membranes, they are a high cost actually restrict the use of such membranes so polymeric membranes are also extremely good, however they have certain problems so inorganic membranes have tried to overcome these problems we will see and discuss in detail what are all these things?

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Polymeric and Inorganic Membranes Comparison

Properties	Polymeric Membranes	Inorganic Membranes
Materials	Polymers e.g., PE, PSF, PVDF, PTFE	Inorganic materials e.g., Glass, ceramic, silica, titanium
Advantages	Cost effectiveness, good selectivity, easy process ability	Withstand harsh chemicals, high temperature, ability to be sterilized and autoclaved and wear resistance. Narrow pore size distribution and higher porosity thus higher flux and better separation features, high chemical stability and long life time, higher hydrophilicity resulting in high fluxes at low pressures
Disadvantages	Fouling, chemically non resistance, limited operating temperature and pressure, short membrane life	Brittle, high cost, low membrane surface per module volume, poor reproducibility

So just a small comparison between polymeric and inorganic membranes. The materials are basically we have discussed in last lecture, a poly sulphon then PVDF, PTFE. For inorganic membranes the materials can be glass, ceramic, silica, titanium, zirconium all these things. So the advantages in polymeric membrane is that the cost is very less if you compare directly with the ceramic membranes.

The cost of polymeric membranes are much much less they have a good selectivity and easy to manufacture and the process ability is very easy in case of polymeric membrane. And the advantages of inorganic membrane that that they can withstand harsh chemicals had temperature so ability to be sterilized and autoclaved and wear resistance. So let us say I am using these membranes for certain applications in pharmaceutical or biotechnology industries.

In which once the membrane is being used I need to sterilize it so for sterilization I have to autoclave it, so autoclave means it is higher temperature and pressure, which many times polymeric membranes are not able to withstand. And narrow pore size distribution and higher porosity which exist in ceramic membranes thus they have higher flux and better separation features compared to the polymeric membranes.

And of course there the chemical stability is also very high compared to the polymeric membranes, and they have a long lifetime also so usually the higher hydrophilicity resulting in a high fluxes is at low pressures so most of the ceramic membranes have a hydrophilic. So that is why the flux is actually high at low pressure so to increase the flux we do not have to go for a very high pressure.

So the disadvantages in polymeric membrane is this fouling is a common disadvantage and then non resistance to chemicals limiting operating temperature and pressure and certain membrane life all these things have been tried to cover up by this our ceramic membranes, however they have certain disadvantages also the most important disadvantage are 2. One is high cost say the cost is of course as of now with lettuce development in ceramic membranes.

I am hopeful that the cost will come down drastically and brittleness is another membrane, you need to handle it very carefully otherwise it will break and another problem is low membrane surface per module volume. So per module the module which is housing the membrane so the surface area actually less and poor reproducibility.

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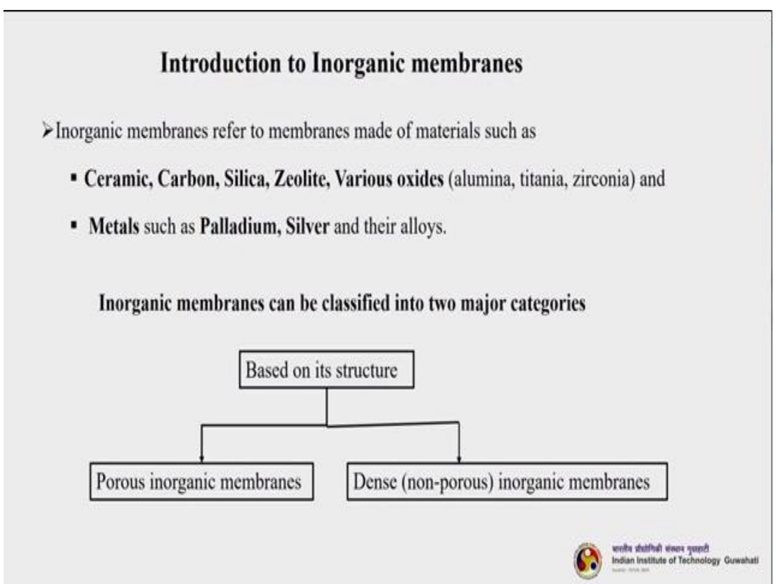

So inorganic membranes refer to membranes made up of materials such as ceramic, carbon silica, zeolite and various oxides like alumina, titania zirconia. And also metals such as palladium, silver and their alloys. So inorganic membranes can be classified into two major categories so based on structure which is in this classification is based on structure itself we can classify of course according to other things we have seen in earlier classes.

So based on structure it can be either porous inorganic membranes or dense that is non porous inorganic membranes.

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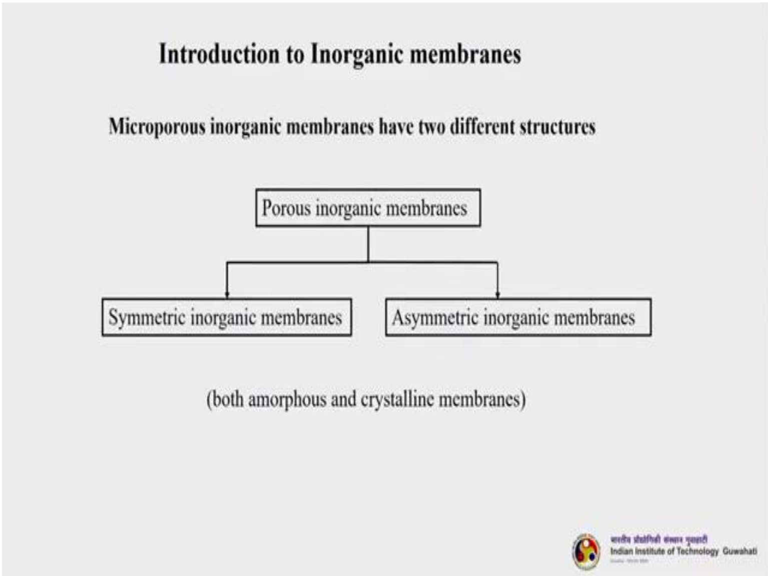

So micro porous inorganic membranes have two different structures. So porous in organic membranes either it can be symmetric in organic membranes or asymmetric and inorganic membranes so this is true for both amorphous and crystalline membranes.

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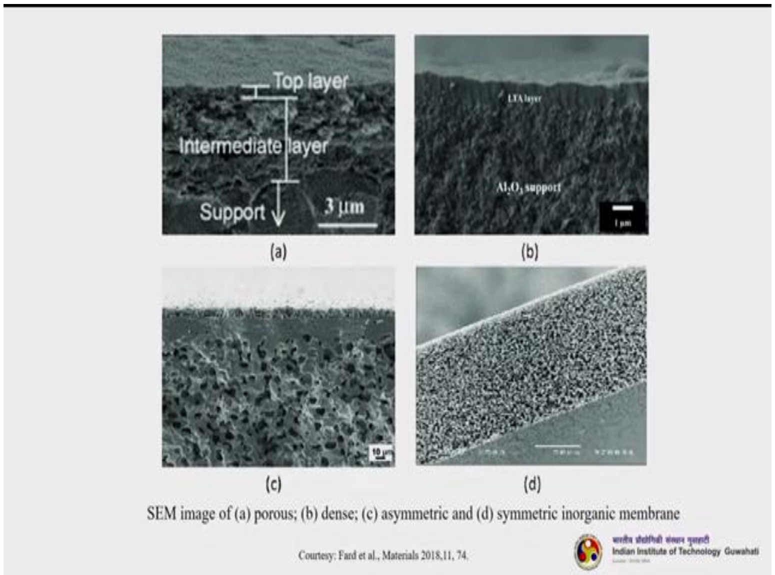

SEM image of (a) porous; (b) dense; (c) asymmetric and (d) symmetric inorganic membrane

So please closely look at this particular slide, so you see that the top one the a1 and these are all micrographs of a scanning electron microscope. So the first one is a porous membrane so we have a top layer there there is an intermediate layer so we have a top layer here okay we have been intermediate layer this is the intermediate layer and we have a support which starts from here.

So you can see there are three distinct layers here, it is a porous membrane so the B is a dense membrane this is a dense membrane, in which we have a alumina support and the top layer is a LTA layer it is a zeolite basically. Then the third is asymmetric membrane it is a clear structure where you can say the distinct pores can be seen here and it is a double layer of membrane so it is asymmetric membrane actually c1.

So in which we can see there are two distinct layers here one is here and one is here so this is a symmetric membrane and the pores are clearly visible and the last one is symmetric inorganic membrane in which there is only one layer of membrane okay and the pores are also very clearly visible. And so we just understand that from this particular slide that we can make porous or non porous membranes of different configurations either symmetric or asymmetric using the various ceramic membranes.

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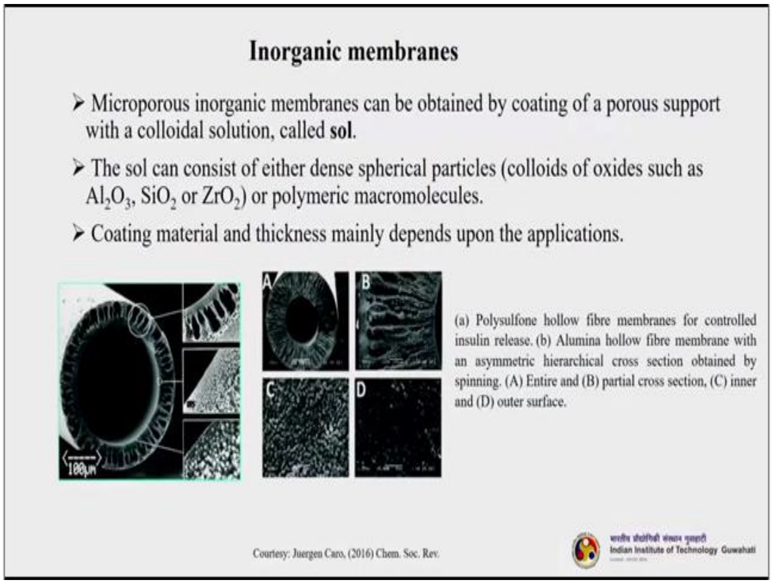

So micro porous inorganic membranes can be obtained by coating of a porous support with a colloidal solution it is called actually Sol so the there is a process called Sol gel process which is one of the most important breakthrough in preparing this ceramic membranes, in organic membranes this process we will discuss in detail, when we will discuss the different methods to prepare membranes.

So as of now let us understand that the sol can consist up either dense spherical particles that is basically colloids of oxides such as alumina silicon dioxide or zirconium oxide or polymeric macromolecules. So coating material and thickness mainly depends upon the application it is your intended application or targeted applications based on that only you can decide what is the type of coating material you want to use.

And what thickness you want to keep. So as you understand that more the thickness more will be the member resistance or resistance to flow so that will create problem. So please look into this particular figure, this figure is a polysulfone hollow fiber membrane for control insulin release, now this is taken from a manuscript okay and the next figure is all about alumina hollow fiber membrane with an asymmetric hierarchical cross section obtained by spinning.

So by spinning method this particular membrane was manufactured here you can see the entire membrane how it looks like, as a hollow fiber membrane and a B is the partial cross section here the cross section so that means this is what you are seeing here, okay is being projected here and higher resolution then C is the inner surface okay, so inner surface means this surface okay and then D is the outer surface.

The outer surface means this surface so these are the scanning electron microscope images which tells us about how the particular membranes have been prepared and how they look like when you go for a electron microscopic image.

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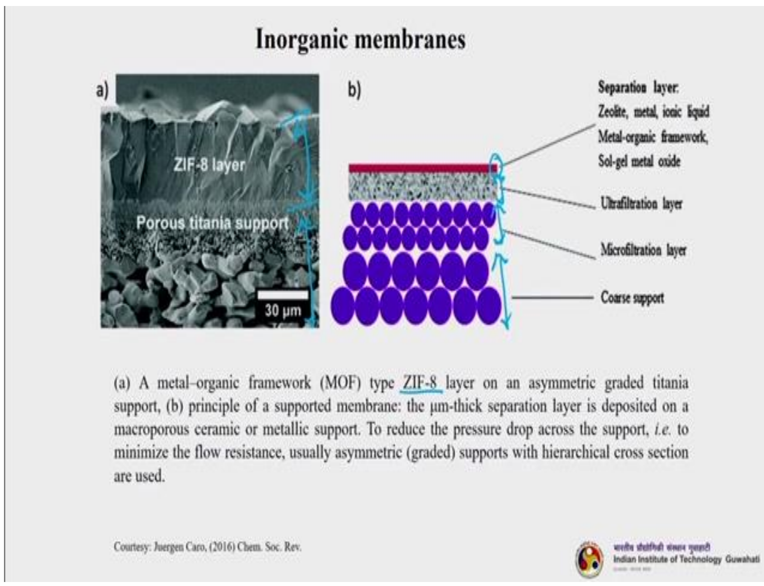

So another example where you can clearly see this is actually MOF framework, MOFstands for a metal organic frameworks of type ZIF8 layer on asymmetric graded titania support. So this support you can see okay so this is made up of titania support and this particular layer from here to here okay so this is ZIF8 layer and you can see this side under B image so it tells about the principle of a supported membrane.

And you can see that the micron thick separation layer is deposited on a micro porous para ceramic or metallic support so this is the separation layer. So this red one you can see so this is the separation layer actually this will do the separation and this is made up of either zeolite, metal ionic liquid or MOF by sol-gel method usually. Then the second layer where we can see here its it true it is a ultra filtration layer third layer again here.

So this is a micro filtration layer then we have a course support so basically it can be a more micro porous layer. So this particular structure is a hierarchical asymmetric inorganic membrane which tells us that we can have more than three or two for different types of distinct layers a fuse together to prepare a particular inorganic membrane for a particular applications.

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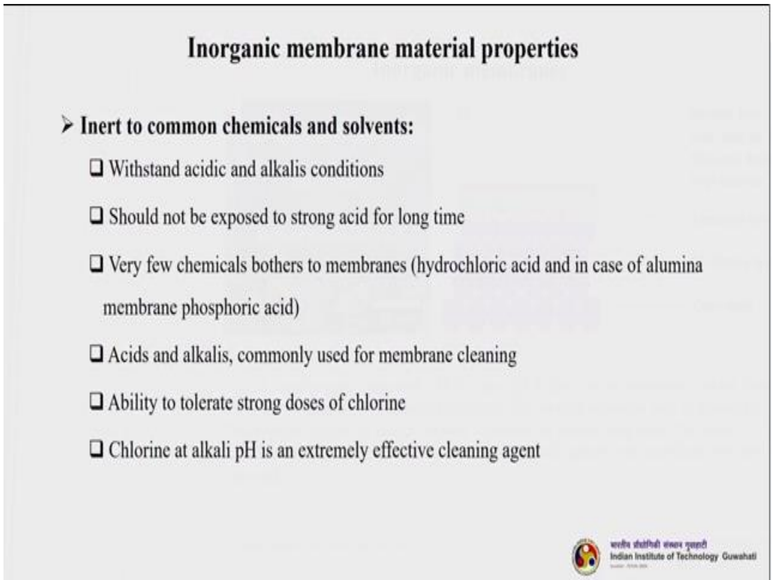

So the next slide is basically tells us about the inorganic materials okay and their properties. So most of the inorganic membranes are inert to common chemicals and solvents. So what is the inherent meaning of this particular sentence is that so it can withstand acidic and alkaline conditions it should not be exposed to strong acid for a long time, though it can withstand acids and alkalis.

But if you are exposing the ceramic materials for a long time then they will start corroding so very few chemicals actually bothers two membranes. So hydrochloric acid and in case of aluminium membrane it is phosphoric acid that is they simply no no for this type two types of membranes. So acids alkali are usually used for membrane cleaning however they are used in a dilute form no concentrated acids or alkali are ever used to clean the membranes.

So there is no question of any resistance when you are dealing with a dilute acid or dilute base. So the ability to tolerate strong disease of chlorine that is another important features of this ceramic materials a chlorine ethically pH is an extremely effective as a cleaning agent so all these properties also makes them ceramic membrane more interesting and for applications to harsh conditions.

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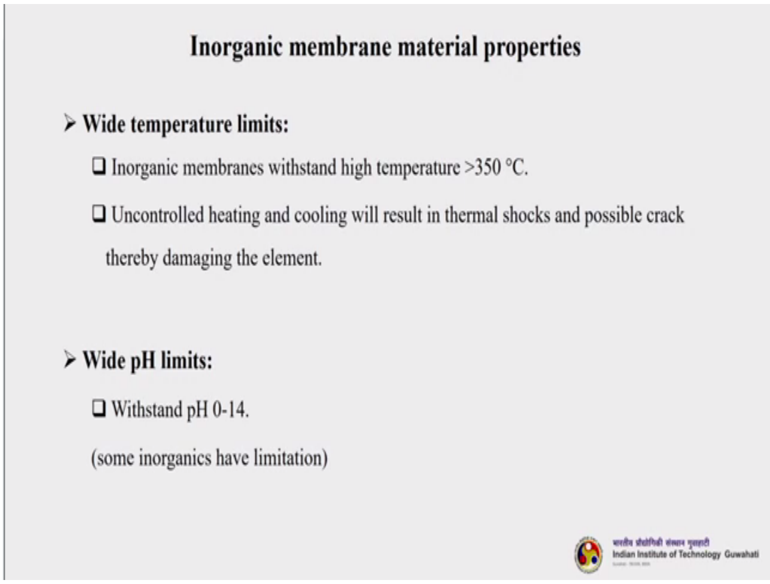

Then the next properties it wide temperature limits. So inorganic membranes can withstand up to more than 350 degree centigrade temperature for 500-600 also so uncontrolled heating and cooling will result in thermal shocks and possible clogged thereby damaging the element. If you are not doing the thermal treatment or thermal procedure either it you are cooling it or you are heating it in a proper or controlled manner.

Then there will be shocks for the membrane and they will actually develop cracks under this thermal shock which is not good for the membrane life. Then these materials can withstand white pH limits so it can withstand a pH of 0 to 14 however some inorganic materials have some limitations.

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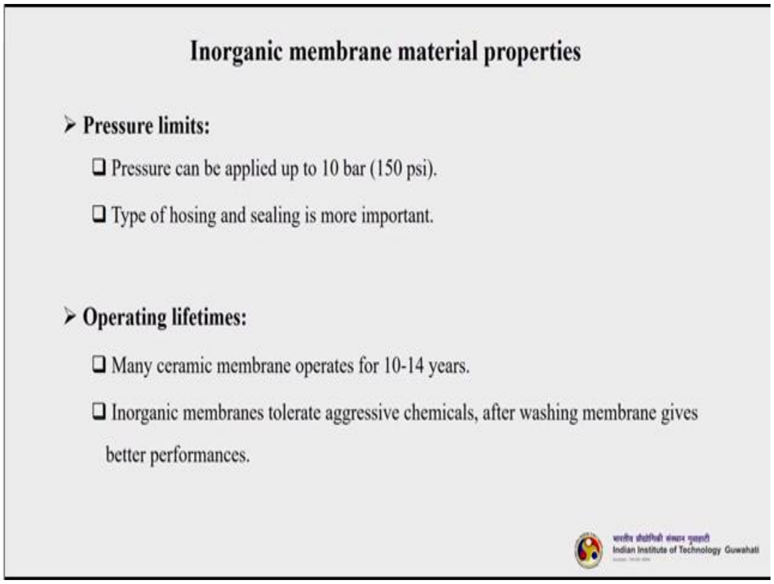

The next one is the pressure limits, so pressure can be applied almost up to 100 psi even little more than that also and how about the type of housing and sealing that is actually used to hold this membrane inside a membrane module plays a very important role in deciding what type of membrane pressure can be applied for a particular membrane system and a module so operating lifetimes.

So many ceramic membranes actually operate for 10 to 14 years it is a pretty pretty long time, you cannot imagine this for any polymeric membrane whatever polymeric membrane you can talk of no polymeric membrane will give such a long lifetime. And inorganic membranes tolerate aggressive chemicals after washing membrane gives better performance so obviously any membrane whether it is polymeric or inorganic ceramic membrane.

We need to wash the membrane because of the concentration, polarization, fouling both external fouling and internal fouling so you need to wash it okay so once he was the performance of membranes actually increases. So washing is very easy in case of ceramic membrane that is what is the message actually. And polymeric membrane the washing is the little has to be done in a very carefully or controlled manner whereas ceramic membranes it is easy

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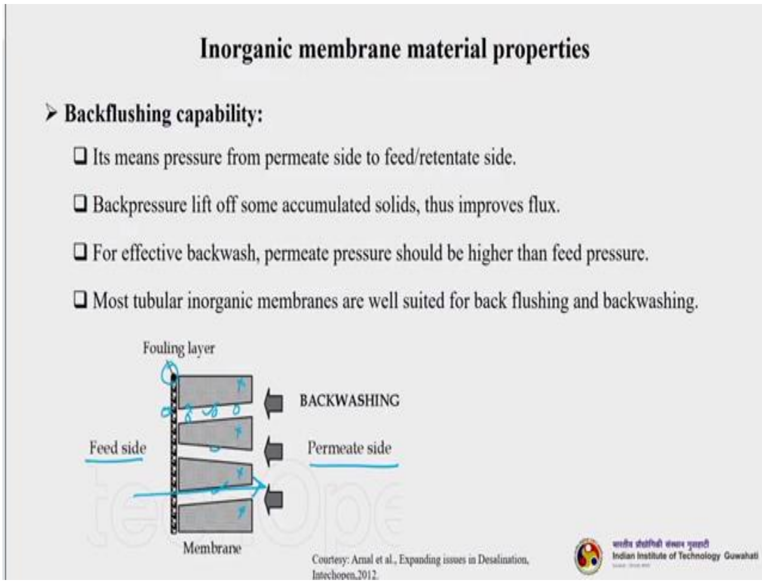

Then backflushing capability this is what I was talking about actual washing so it means pressure from the permeate side to feed oriented side you can see actually this is the fouling layer which is getting deposited on the surface of the membrane and these are the pores, these are the pores and this is actually membrane material okay, so this is feed side and and this is permeate side so here when the process is getting carried out the feed is here.

So feed will get better will be transfer the feed the solute will be separated and then the separation takes place in this way and we get a permeate in permeate side so when we are doing actually back flushing or back washing so the name indicates the name itself indicate that we are washing from the back side of the membrane that pit from the permeate side of the membrane so this back pressure lifts up some of the accumulated solids thus improve the flux.

So, many times as I told, the solids are getting deposited on the sol of the membrane as well as here also is there so any air dry and doing back flushing usually water is being used at a certain pressure. So under this pressurized condition water would wash away this solutes which are deposited inside the pores is realized on the surface of the membrane and for effective back was permeate pressures would be higher than the pre-pressure.

So the permeate side presence would be higher than the feed side pressure then only back washer will be effective, and most tubular inorganic membranes are well suited for black power back pressing and back washing. So most of the inorganic membranes whether it is a flat sheet membrane or whether it is a tubular membrane it will most of the ceramic membranes and their tubular so it is very easy to do back flushing as they can with stand higher pressure.

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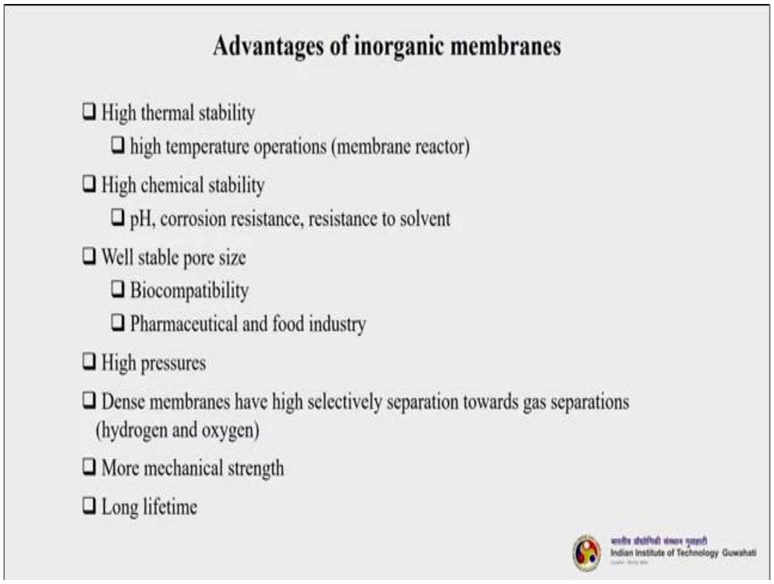

So again let us just quickly go through the advantages and disadvantages of the inorganic membranes just in a nutshell again try to recapture what we discussed, so it has high thermal stability that is it can we can go for high temperature operations such as membrane reactors and in certain situations then it can withstand high chemical stability, pH corrosion resistance, resistance to most of the organic solvents then well stable pour sizes.

So biocompatibility and pharmaceutical and food food industry then high pressures it can withstand. A dense membranes have high selectivity separation towards gas separation so like ceramic membranes are very good for the gas separation applications as well as for pervaporation. So selective separation of gases can be done by this by such membranes and they have more mechanical strength as well as long lifetime.

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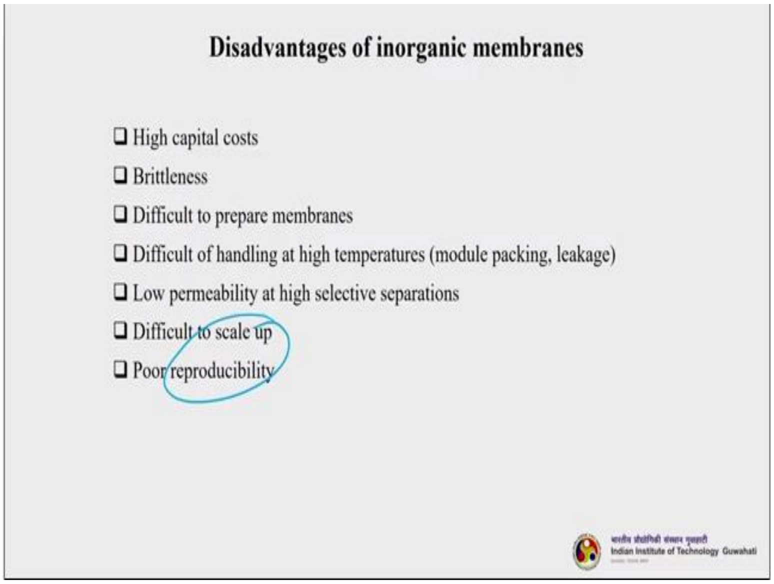

But again they have some disadvantages it is not that they are ceramic membranes have we mean for all cases are all situations. So the most important disadvantages as to the two which I told you one is high capital cost second is brittleness, and then it is difficult to prepare membranes it is no saw easy polymeric membrane are easy to prepare and it is difficult to handling at high temperatures.

So when you go for this module packing and then leakages will be their probabilities always remain for such ceramic membranes, then low permeability at high selective separations then difficult to scale up and poor reproducibility. So these two are limiting their application in certain areas actually scale up is very important when you go per and designing of such systems for a large scale applications.

And reproducibility also very important because unless until the membranes and their composition is reproducible and at giving more or less the same performance then commercial it is not feasible to manufacture them.

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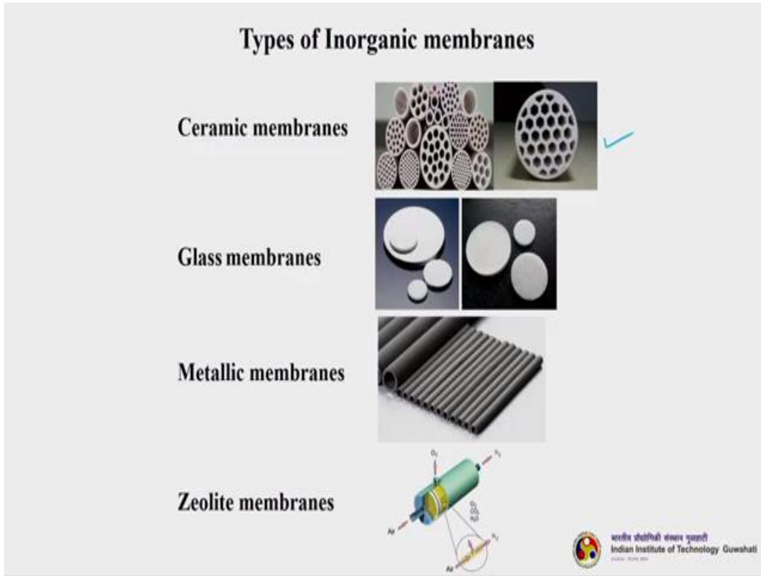

So let us look at some of the inorganic membranes and the various types of inorganic pigments that are available commercially. The first one is ceramic membranes this you can see from the image so these are actually tubular ceramic membranes okay, then we have glass membranes glass membranes are having lot of applications also we will see in our subsequent discussion then we have metallic membranes like stainlees steel membranes.

And other metallic membranes and we have zeolite membrane cells, zeolite membrane so zeolites are very interesting class of materials and have wide range applications from catalyst and adsorbents and as well as membranes

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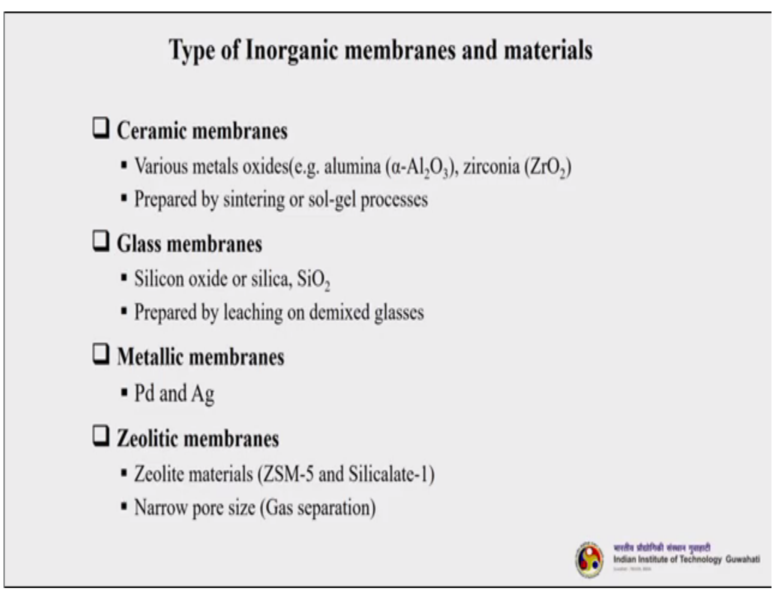

So there are different types of materials we will see one by one the first one is ceramic membranes so various types of metal oxides like alumina and zirconia are used there are many others also, they are not limited to these two there are many others just I have shown two. And they are prepared by sintering or sol-gel process then we have glass membranes so silicon oxide or silica which is silicon dioxide is essentially used to prepare glass membranes.

So they are prepared by leaching on demixed to get glasses then we have metallic membranes like palladium and silver coated metal encumbrance we have stainless steel metal encumbrance membranes and then we have zeolite membranes so zeolite membranes ZSM-5 and Silicalate 1 or narrow pore size and they are used actually put the gas separation applications.

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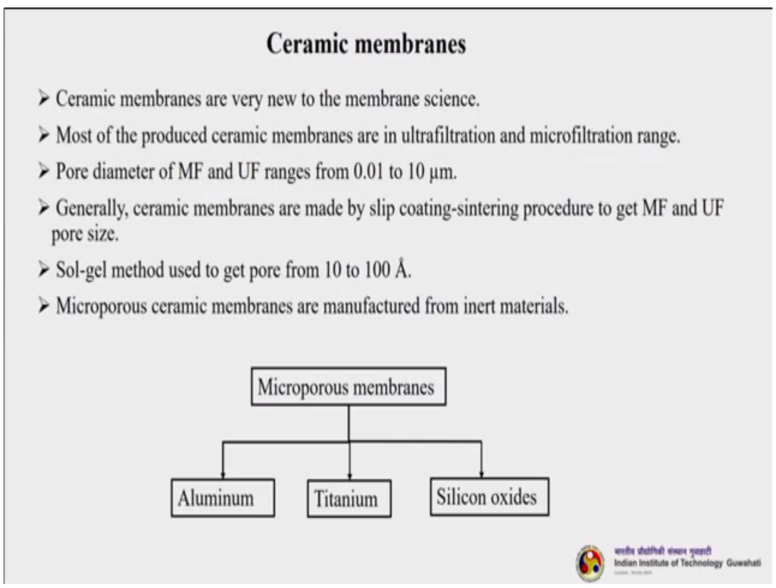

Ceramic membranes are very new to the membrane sense actually and since last a decade or so they have been commercialized and now they have wide range applications, whether it is the water, wastewater treatment or they are using membrane reactors for carrying out certain chemical reactions under controlled conditions and even pharmaceutical and biopharmaceutical industries also.

So most of the produced ceramic membranes are usually in the ultra filtration and micro filtration range this is another limiting application sexually so we hardly can produce nano filtration or RO membranes using ceramic materials support diameter of microfiltration and ultrafiltration ranges from 0.1 to 10 micron generally ceramic membranes are made by slip coating sintering procedure to get usually MF & UF pore sizes.

Sol gel is used method is used to get pour from 10 angstrom to 100 angstrom so micro porous ceramic membranes are manufactured from inert materials. So we can have aluminium membrane ceramic membrane and we can have either titanium based where we can have silicone oxides based.

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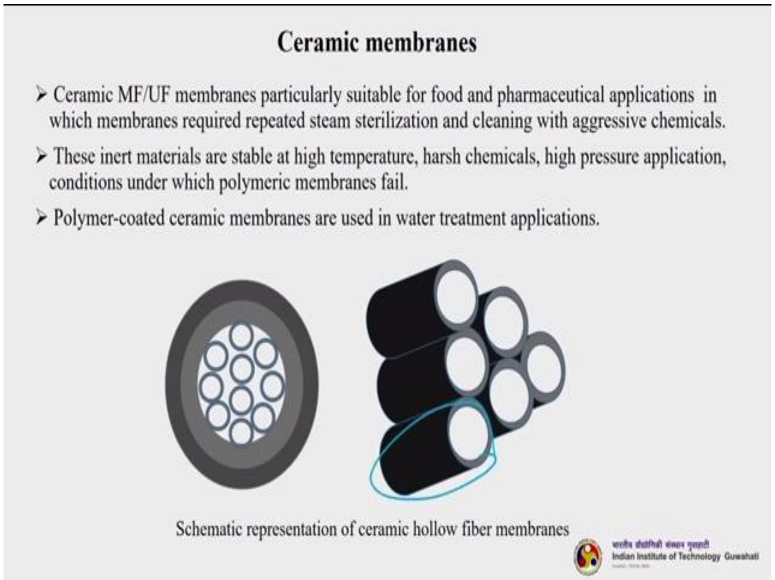

So ceramic microfiltration and ultrafiltration membranes particularly suitable for food and pharmaceutical applications, in which membranes require repeated steam sterilization and cleaning with aggressive chemicals. Because they are for human consumption anyway so you have to be very careful about the sterilization processes which is basically done using Auto clamps so these inert materials are stable at high temperature.

And has chemicals high pressure application and conditions under which polymeric membranes usually fill. So polymer coated ceramic membranes are also used and developed and they are especially used in water and wastewater treatment applications so this you can see this particular scheme tells us about it is a ceramic membrane hollow fiber membranes so this is a single unit of a hollow fiber membrane.

So you can fuse together many such membranes and housed in a particular module so then this looks something like this.

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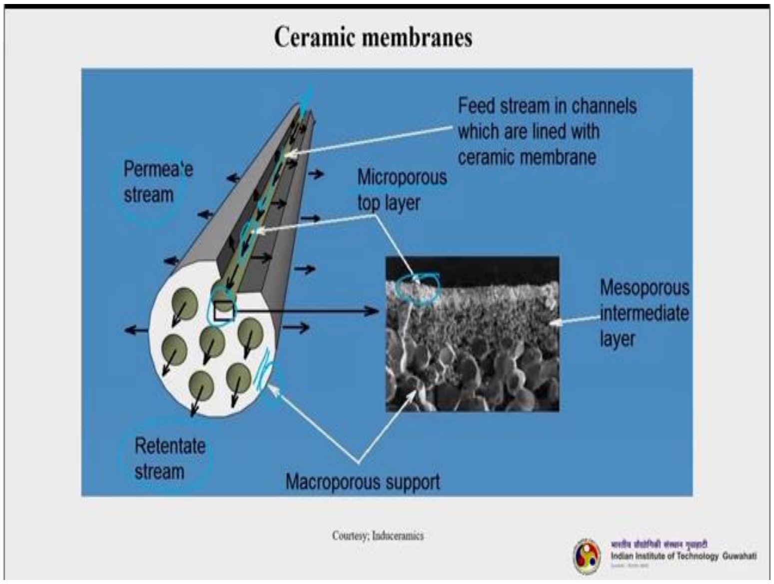

So let us carefully look at this particular slide which tells us about the hollow fiber ceramic membrane and it is caning electron micrograph image actually micrograph so you can see how the membrane actually looks like, so you can see this is this is the area okay this area particular area where it is seen this is the major porosity intermediate layer right? So then we can have the macro porous support which is this this area this white white portion you are seeing.

So this area is the macro porous support right, then we have this layer which is micro porous top layer okay which is this particular sections these areas okay so and this is what is the micro porous layer, actually that is doing the separation. So feed is actually flowing inside this this one particular hollow fiber tube so you can send feed from this side okay and there flowing you can see they are flowing here inside the tubes okay.

And permeate is getting out here okay and you can get the retente here directly coming from inside so the feed is flowing in the lumen or the pores okay and the hollow fibers this one the hollow ceramic membranes inside the hollow ceramic membranes and the permeate is get coming out through the macro porous support layer here okay.

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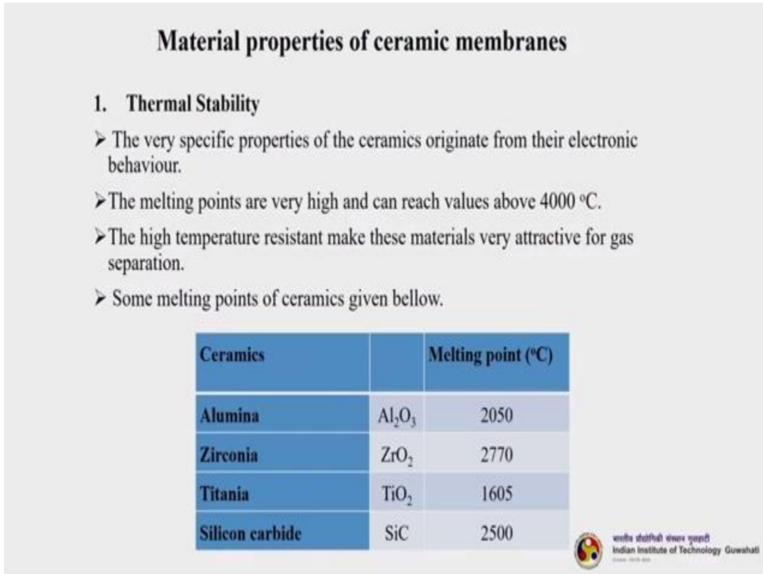

So let us quickly go through the material properties of the ceramic membranes so thermal stability there are very specific properties of the ceramics originated from their electronic behavior. The melting points are very high and a risk an almost 4000 degree centigrade the high temperature resistant make these materials very attractive for gas separation as I told you in the beginning also due to this their thermal resistance.

So they are extremely good for gas separation application as well as for pervaporation also some you can see some of the melting points of the ceramic membranes alumina is 2 0 5 0 0 cornea is 2 7 7 0 these are all in degree centigrades titania titanium is 1 6 0 5 and silicon carbide is higher 2500.

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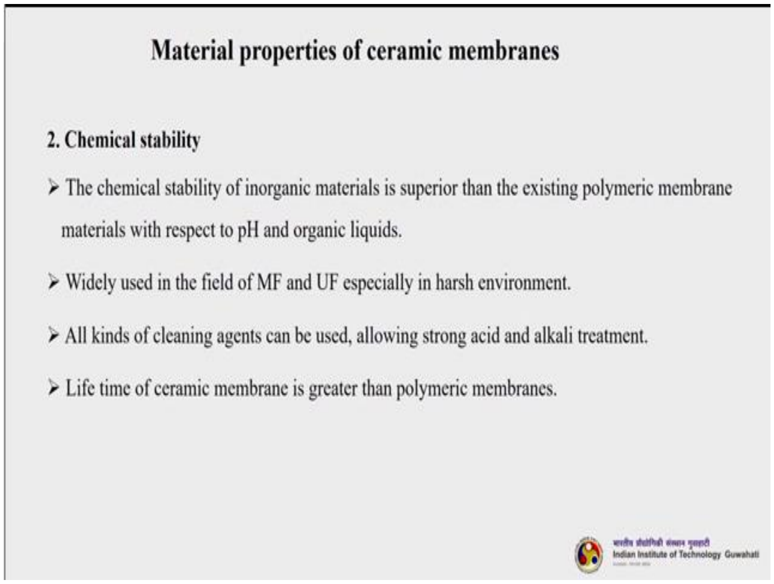

Then chemical stability the chemical stability of inorganic meterial is superior than the existing polymeric membranes with respect to creation organic liquids widely used in the field of microfiltration and ultrafiltration especially in harsh environment so all kinds of cleaning agents can be used allowing strong acid and alkali treat metals so however actually for cleaning purposes dilute acids and dilute alkalis are being used. So lifetime of ceramic membrane is anyway greater than the polymeric membranes.

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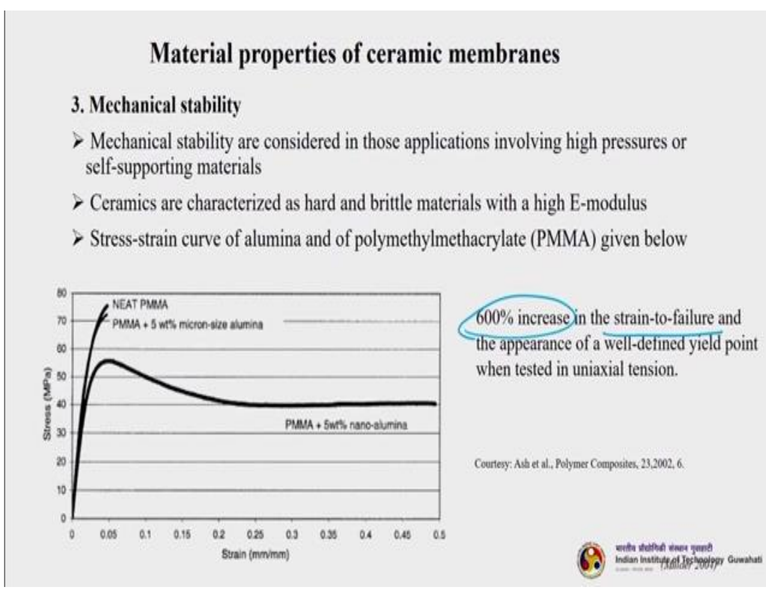

So then mechanical stability mechanical stability are considered in those application silver being high pressure or self-supporting materials. So ceramics are characterized as hard and brittle materials with a high elastic modulus so the you can see this stress strain curve of alumina and up PMMA which is poly methyl methacrylate which is given below in this particular stress and strain curve.

What he says that when you add the PM mm to 5 weight percent nano alumina then it is stress-strain relationship since that is actually has been increased to 600 pore so you can the 600 percent increase okay in the strain to failure and the appearance of a well-defined yield point when tested in a uniaxial tensile.

So this particular slide tells us that the properties the strength to failure properties actually increased. when you add nano alumina materials to the poly methyl methacrylate materials.

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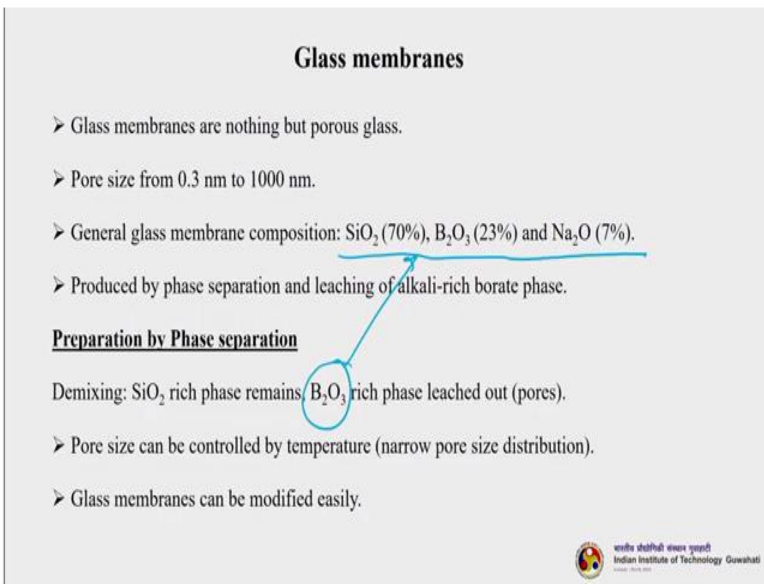

So then the next one is the glass membranes so glass membranes are nothing but porous, glass in the pore size actually ranged from 0.3 nano meter to 1000 nano meter so general glass membrane composition is this silicon dioxide seventy percent boron trioxide 23 percent and sodium oxide 7 percent this is a general composition however the compression also varies for different glass materials.

They are actually optimized to suit a particular application then produced by phase separation and leaching of alkali rich borate phase. So it is prepared by phase separation process in which silicon dioxide rich phase remains and the boron trioxide rich phase is leached out. So this particular phase has been leached out from this particular composition okay so pore size can be controlled by temperature.

So and we get a very narrow pore size distribution and glass membranes can be modified easily. it is easy to prepare actually.

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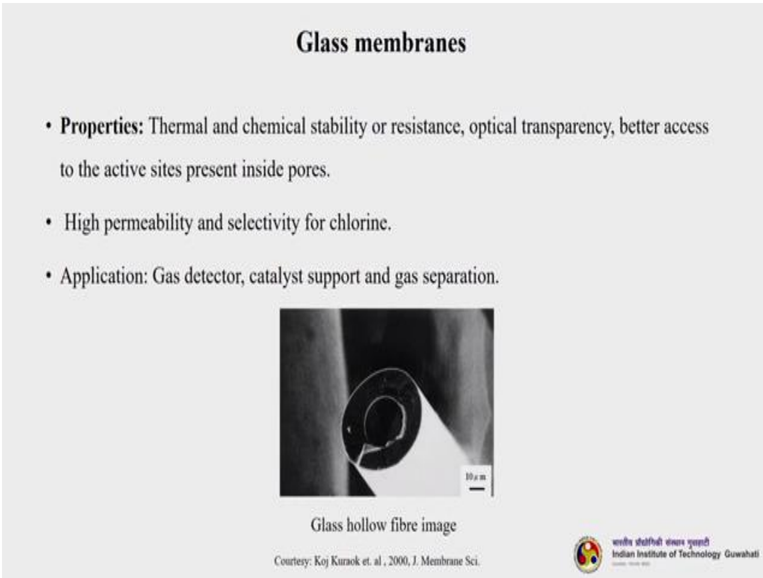

So the properties at thermal and chemical stability or resistance higher than optical transparency is there, that is another important thing when you go for some applications in which you need to understand and visually see what is happening inside it. Then better access to the active sites present inside the pores high permeability and selectivity for chlorine so they can withstand higher chlorine concentration.

If it is present in the stream then application is in a gas detector catalyst support and gets a pressure you can see one typical holder fiber glass membrane this is up around ten micron image this is.

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So next is the metallic membranes so these are dense that that dense metallic membranes are typified by palladium and silver membranes, so metallic membranes are not limited to palladium and silver but there are many okay, but these are widely used so paradis membranes are exclusively been prepared for hydrogen permeation and silicon membrane for oxygen permeation.

And their selective membrane actually palladium coated membranes for a selective membrane for hydrogen permission and silver coated selective membranes for oxygen permeation and they are prepared by cold rolling electroless plating, electroplating, chemical vapour decomposition which is called CBD or magnetron spluttering method. So the properties are they are highly selective but and better mechanical and thermal stability as well as they have a very long life.

So applications are membrane reactors and gets the person this particular image says so the a stainless steel membrane.

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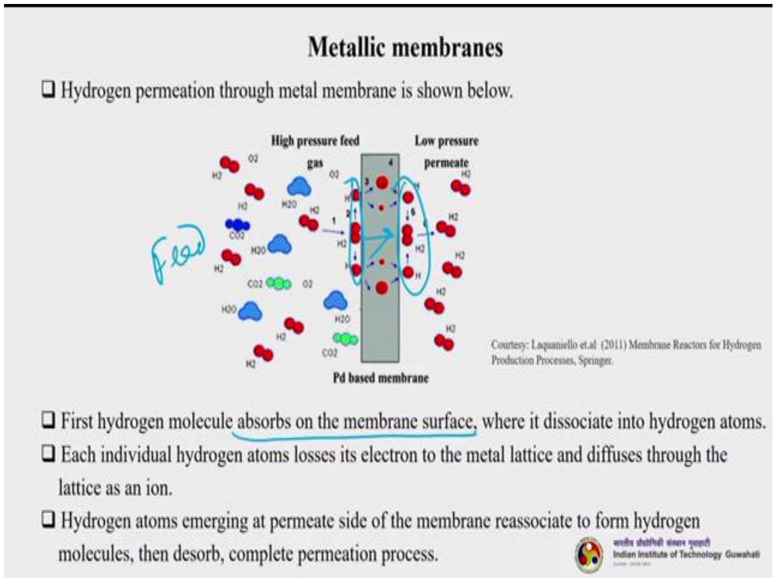

So let us see how hydrogen permeation actually happening using this particular palladium based membrane, you can see from a composition of gases which is there in the feed set this is the feed side okay and what is our intended application, intended application is to selectively SEP permeate hydrogen, so that we get a pure hydrogen and the permeate side so the a particular membrane which is being prepared which is palladium based membrane.

What it will do actually so first the hydrogen molecule is absorbs on the membrane surface here then getting absorb on the surface of the membrane, so when they observe what is happening so the hydrogen is dissociating into hydrogen atoms right? So after the dissociation every individual hydrogen atom loses its electron to the metal lattice and diffuses through the lattice as an ion so now they will diffuse through okay.

So then once the diffuse across the membrane and reaches the permeate side so the hydrogen atoms emerging at permeance have their membrane again reassociate themselves to form hydrogen molecule okay so once they come here again there he associates to become hydrogen okay then deserve and complete formation process starts so the membrane is made in such a way that it will selectively only permit hydrogen in the form of hydrogen atoms okay.

And then once they come into the permeate set these hydrogen atoms will reassociate to form on the hydrogen molecule and similarly oxygen selective membranes and other gases selective membrane such as carbon dioxide selective membrane are also be prepared.

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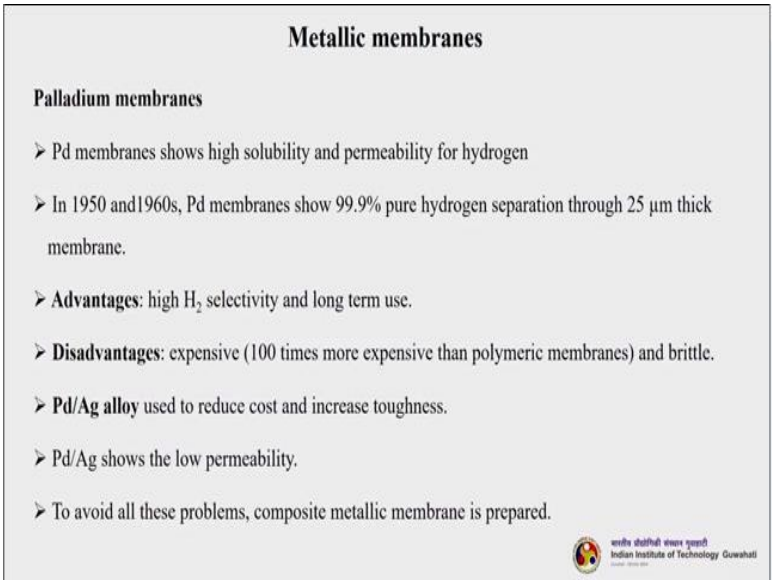

So palladium membranes so high solubility and permeability for hydrogen I am talking about this particular application which we just discussed then in 1950s and 60s palladium membranes so 99.9 percent pure hydrogen separation using a 25 micron thick membrane. So the advantage is high selected hydrogen selectivity and a long life of course and disadvantages it is extremely expensive almost 100 times more expensive than any polymeric membrane.

And it is brittleness then palladium and silver alloy used to reduce cost and increased toughness, so to increase the to reduce the palladium membrane cost silver has been added okay and alloy has been prepared so it has reduced the cost as well increase the toughness so this particular palladium silver alloy shows low permeability and to avoid all these problem composite metallic membranes and now a days prepared.

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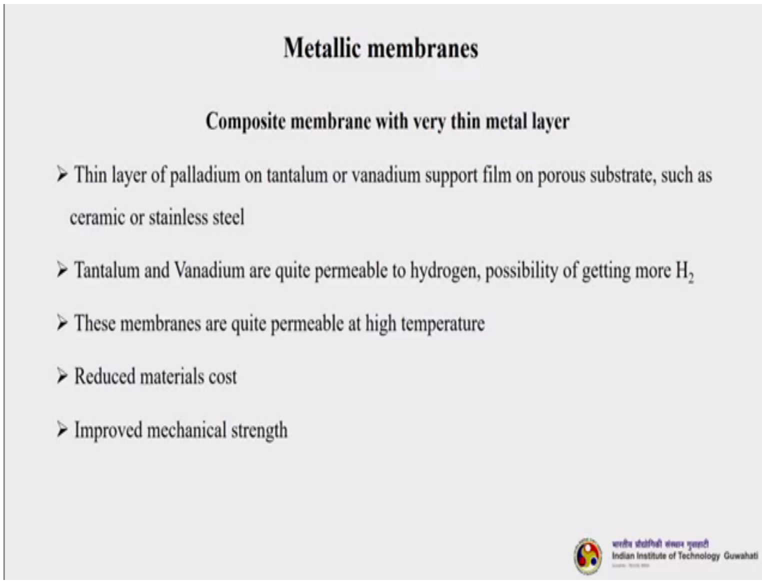

So a composite membrane with a very thin metal layer will give a better separation why thin layer because thin layer will provide less resistance to the transport of the solute. So thin layer of palladium either on tantalum or vanadium support film on porous type that is usually prepared such as ceramic or stainless steel tantalum and vanadium are quite permeable to hydrogen the possibility of getting more hydrogen.

So this is why actually there is my a tantalum and vanadium are particularly chosen so these membranes are quite permeable at high temperature so they will reduce the overall material cost and improve the overall mechanical strength

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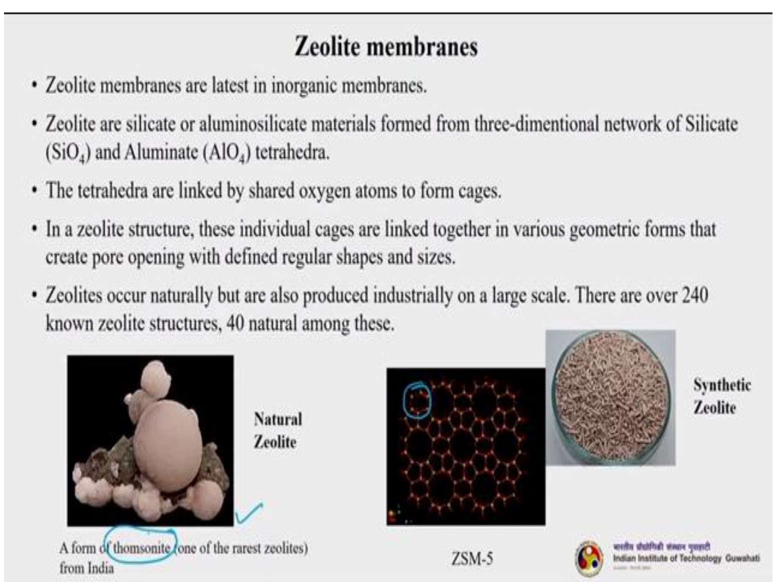

Now let us come to the important class of ceramic membranes which are called zeiolite membranes so zeiolite are very interesting materials so zeiolite membrane said latest in the inorganic membrane series so zeiolite water zeiolite so their silicate or alumina silicate materials form from a 3 dimensional network of silicate illuminate tetrahedra okay and this tetra hydras are linked by oxygen atoms to form the cases okay.

So you can see how it looks like in a particular this is this is a case okay, so her energy alight structure these individual cases are linked together in various geometries that forms the pores actually okay with defined regular steps and sizes so zeiolite occur naturally but are produced industrially on a large scale also synthetically so there are about 240 non zero light structures out of that almost close to 40 a natural among them.

So you can see this particular image it is a natural zeiolite it is thomsonite this is this is one of the rarest zeiolite which is found in India okay. Here you can see this is a ZSM-5 okay this is a commercial zeiolite synthetic and prepare synthetically

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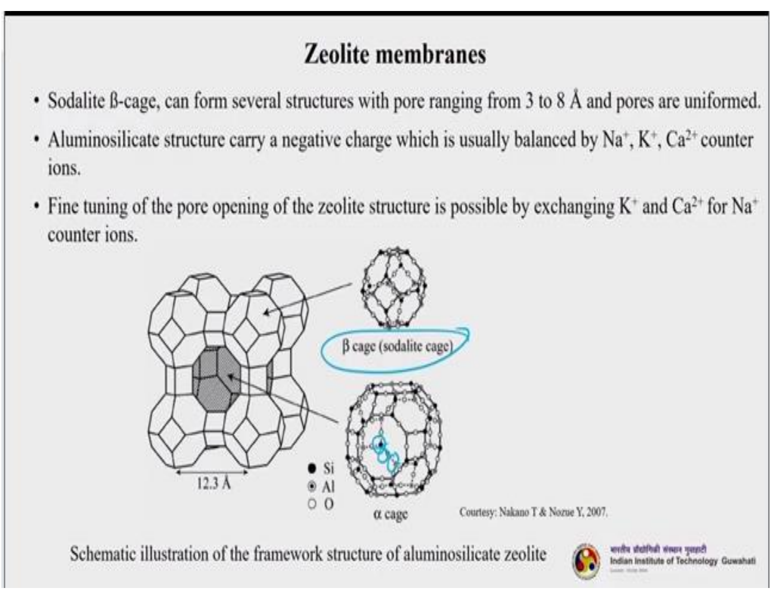

So sodalite beta cage can form several structures with pore ranging from 3 angstrom to 8 angstrom okay and pores are uniformed. So you can see this is a particular beta case sodalite cage okay so you can see this is yes silicon aluminum and oxygen okay they are present okay you can see this is actually silicon okay then this is aluminum and this is oxygen okay so they are present in such a way that the form cases which are called this beta cages.

So relate cases okay I mean alumina silicates structure they carry a negative charge which is usually balanced by the sodium potassium or calcium counter ions so fine tuning of the pore opening of zeolite structure is possibly done by exchanging potassium or calcium for sodium counter ions.

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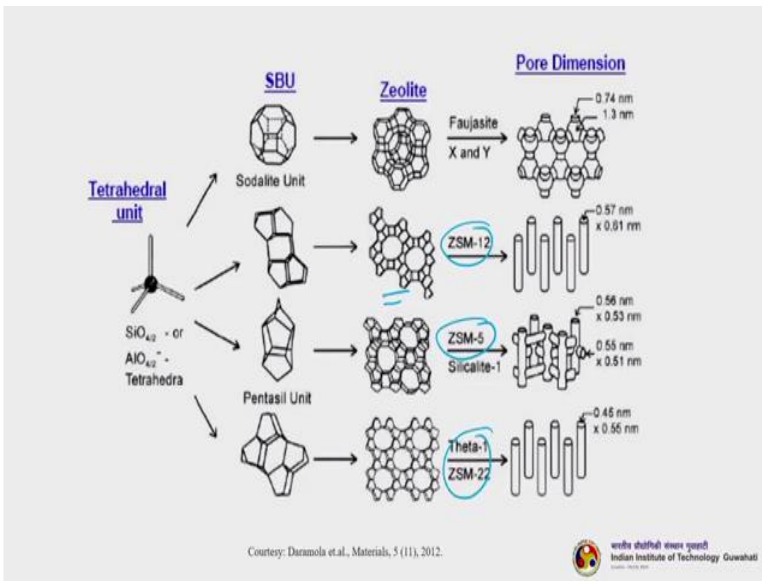

So this particular slide tells us about different types of zeolite membranes okay and how in about their pores dimension so the first one is faujsite okay you can see the dimensions of the force is actually 0.74 nanometer to 1.3 nanometer and the next one is this is ZSM 12 okay the structure is something looks like this okay and they have this cylindrical types of pores of 0.57 nanometer pore diameter.

Then the next one is ZSM-5 another class of ZSM membrane okay in the presence of silicalite1 one actually so it is a pore structure again cylindrical pores originally very different way the pore size is usually 0.45 sixth nanometer and the next one is Theta 1it is a ZSM 22 zeolite okay it is pore size pores are also again cylindrical and from 0.45 nanometer is the pore size.

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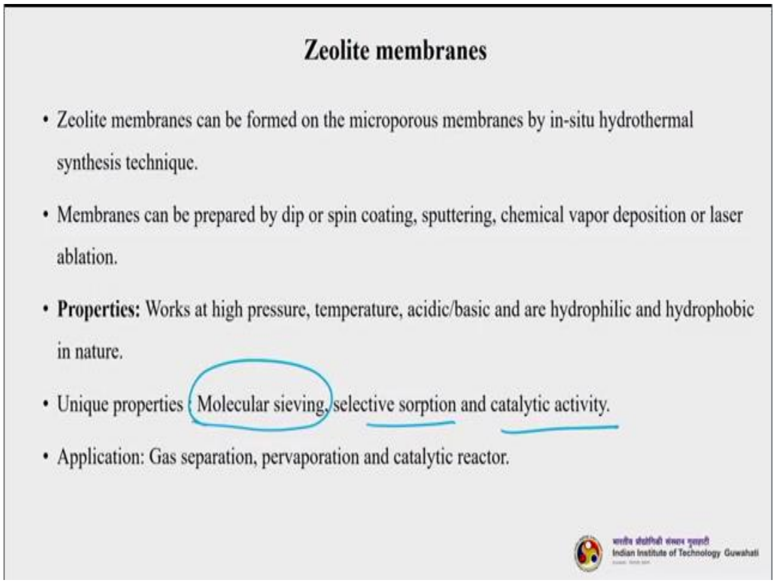

So zeolites membranes can be formed on micro porous membrane by using a in-situ hydrothermal synthesis technique, membranes can be prepared by dip or spin coating sputtering chemical vapour decomposition or laser ablation so the properties at that they work at a very high or a limited pressure temperature they can withstand harsh acidic and best second best conditions and their hydrophobic or hydrophilic both in nature.

So you can choose zeolites in such a way that either we can target at a hydrophilic membrane or a hydrophobic membrane. So the unique properties that that it is something called molecular sieving, so different molecules can be sieved using particular types of membrane so as to get a easy separation and they have selective surface on as well as they have catalytic activity so due to this.

Catalytic activity they are used in the catalytic membrane reactors okay. Application is gas separation pervaporation and catalytic reactor.

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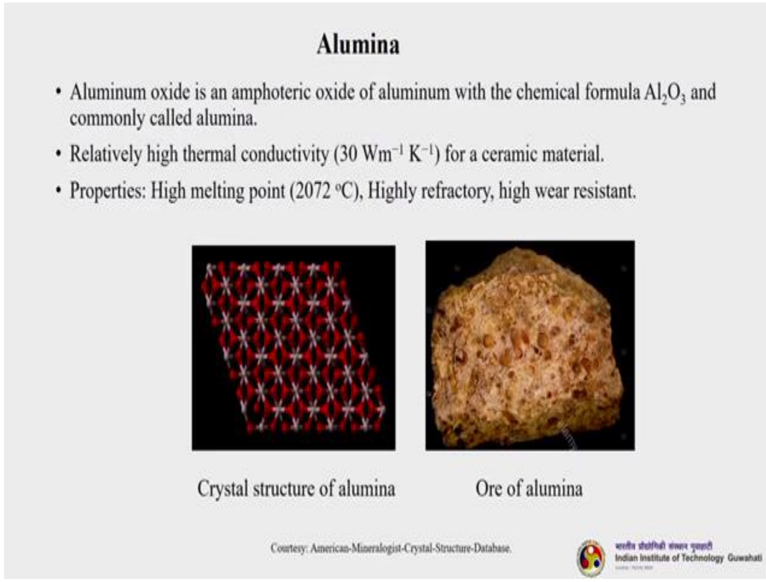

So the next class of material is alumina so alumina is aluminium oxide is an important aqaq side of aluminium with the chemical formula of al2o3 and commonly called as aluminum so relatively high thermal conductivity for a ceramic material and properties at that its high its melting point is very high 2072 degree centigrade and and they are highly refractory and their high wear resistance okay.

So you can see how the crystal structure of alumina looks like and this is a over of the alumina from which alumina actually is being prepared.

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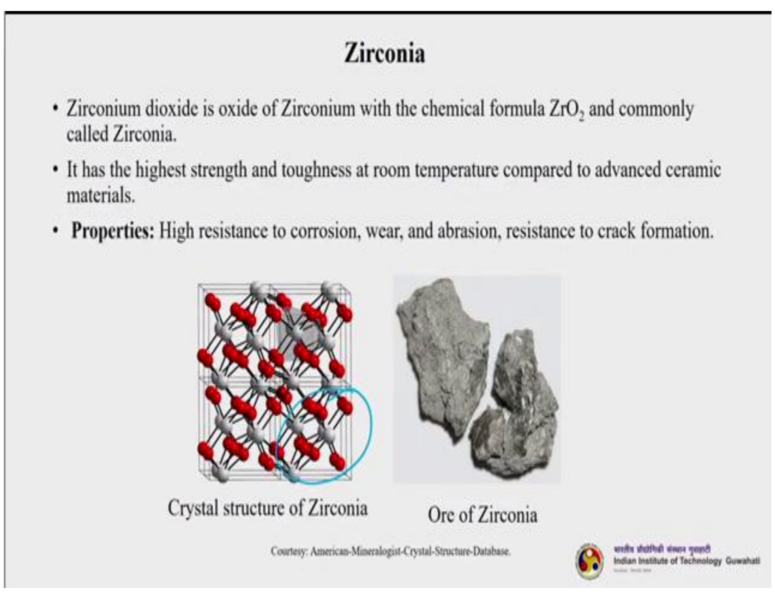

So the next class is zirconia or zirconium so it is basically zirconium oxide is the oxide of zirconium with the chemical formula zro2 and commonly called zirconia so it has the highest strength and toughness at room temperature compared to any advanced materials, this is why this is very interesting for higher pressure high pressure applications and the properties at high resistance to corrosion.

Wear and abrasion resistance to crack below you can see how the zirconium molecules are actually networked together. So with this type of bonding actually this is the reason why they give a very higher mechanical strength.

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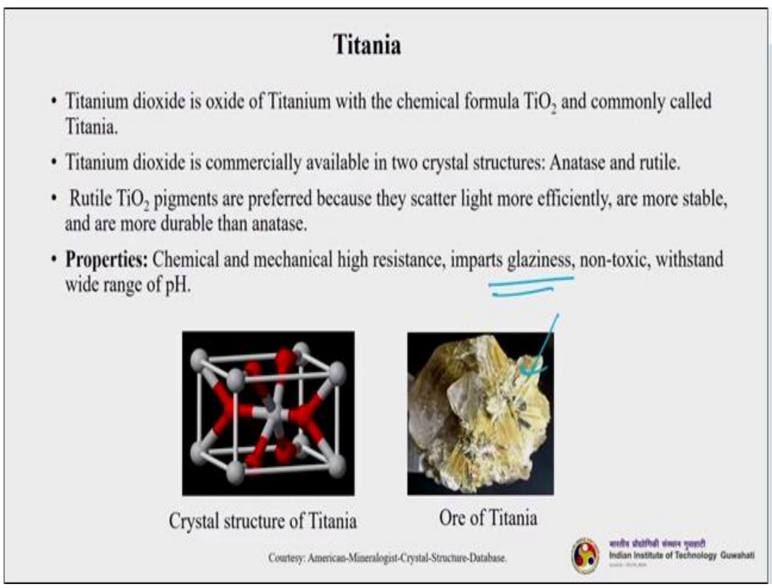

The next class is Titania, titanium dioxide or is the oxide of titanium with the chemical formula tio2 and commonly called titanium so titanium dioxide is commercially available in two crystal structures one it Anytus and another is is you tile so you tile titanium oxide pigments are preferred because they scatter light more efficiently and are more stable and are more durable than anatase.

So the properties are chemical and mechanical higher resistance it imparts something called a glaziness you can see from this particular image over of the titania also itself also look so glazed and it put non-toxic environmentally this is used and it can withstand wide range of pH so this is the crystal structure of how titania actually looks like

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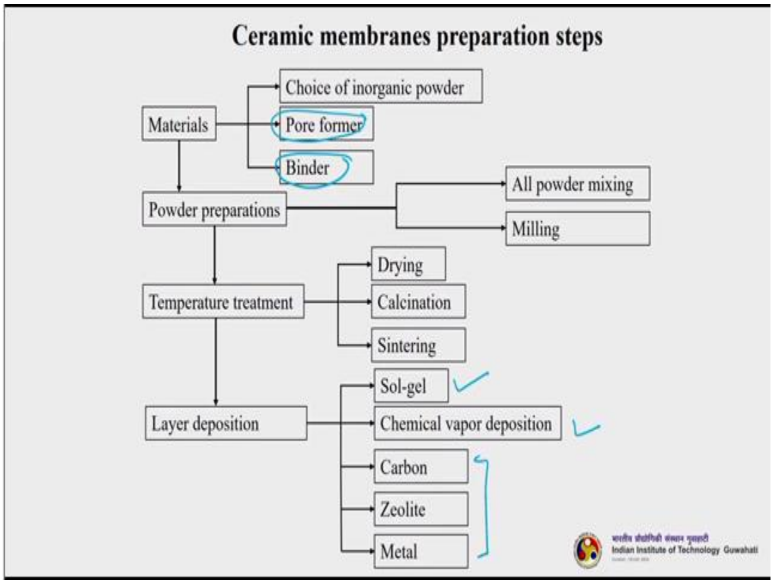

So let us just quickly go through and understand how ceramic membranes are prepared we will discuss this in future classes okay, so once you choose the materials so you basically choose the choice of inorganic powder from which you want to prepare the membrane and you have to add two things apart from other small similar things the two major things one is called pore former and another is called binder support.

For more certain agents which helps in forming the pores okay actually the degrade and form words and binders are the materials which will bind together this inorganic powders performers and other materials together, you need some binding agent to bind okay apart from water of course will be used to prepare the composition so you can then then you go for the powder preparation.

So you can mix the powders and then you go for milling then the temperature treatment like drying, calculation, sintering will be there and then final layer deposition which can be done by either by sol-gel method will by CVD method or you can use carbon zeolite on metals any this type of materials

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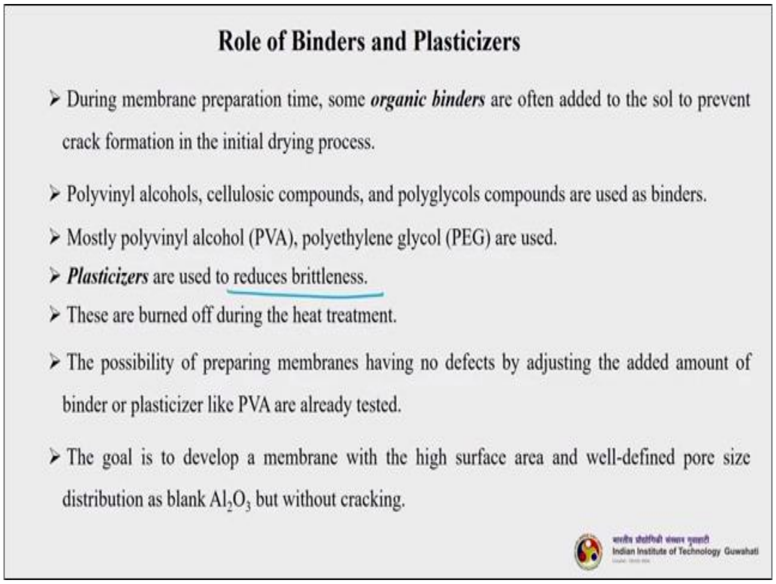

So let us just quickly go through what is the role of binders and plasticizers so during membrane preparation some inorganic binders are often added to the salt to prevent crack formation in the initial drying process, so this is very important because once the crack forms you cannot further go for the membrane preparation you have to stop it. So polyvinyl alcohol cellulosic compounds and poly glycols compounds are usually used as binders.

So mostly PVA and PG are being used so plasticizers are the materials which used to reduce the brittleness so as you know ceramic membranes are highly brittle, just to decrease the brittleness some plasticizers are being used. So they are actually burned up during the heat treatment process the possibility of preparing membranes having no defects by adjusting the added amount of binder or plasticizer like PPR already being tested.

The goal is to develop a membrane with a high surface area and well-defined pore size distribution as a blank alumina but without any cracking

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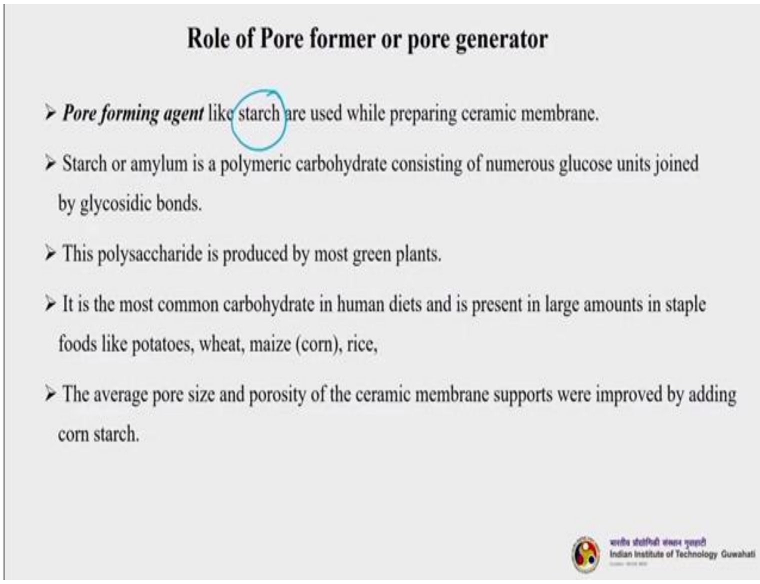

So the next is that all up for a port former of pores generator support performing as a firming agents like starch are used while preparing ceramic membranes we have many more materials starch is also being used you know starch or amylum is a polymeric carbohydrate consisting of numerous glucose units joined by glycosidic bonds so this polysaccharide is produced by most of the plants.

And it is most common carbohydrate in human diets and is present in large amounts in staple foods like potatoes, wheat, maize and that is corn and rice etcetera and the average pore size and porosity of the ceramic membrane supports when improved by adding constants so in this we come to the conclusion of this lectures wherein we have understand what is the ceramic membranes how they are prepared and what is their properties advantages and disadvantages.

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Commercially available Inorganic membranes

Manufacturer	Trade Name	Membrane Material	Support Material	Membrane Pore Diameter	Geometry of Membrane Element	Tube or Channel Inside Diameter (mm)
Alcoa/SCT	Membralox®	ZrO_2 Al_2O_3	Al_2O_3 Al_2O_3	20–100 nm 0.2–5 μm	Monolith/ Tube	4 and 6
Norton	Ceraflo®	Al_2O_3	Al_2O_3	0.2–1.0 μm 6 μm (symmetric)	Monolith Tube	3
NGK		Al_2O_3	Al_2O_3	0.2–5 μm	Tube	7 and 22
Du Pont	PRD-86	Al_2O_3, Mullite, Cordierite	None	0.06–1 μm	Tube	0.5–2.0
Alcan/Anotec	Anopore®	Al_2O_3 Al_2O_3	Al_2O_3 Al_2O_3	20 nm 0.1 μm 0.2 μm	Plate	
Gaston County Filtration Systems	Ucarsep®	ZrO_2	C	4 nm	Tube	6
Rhone-Poulenc/SFEC	Carbosep®	ZrO_2 ZrO_2	C C	~ 4 nm 0.08–0.14 μm	Tube	6
Du Pont/ CARRE		$Zr(OH)_4$	SS	0.2–0.5 μm	Tube	~ 2
TDK	Dynaceram®	ZrO_2	Al_2O_3	~ 10 nm	Tube	≤5
Asahi Glass		Glass	None	8 nm–10 μm	Tube/Plate	3 and 10

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So before we wind up we will just quickly go through this particular slide where this tells us about the different types of commercially available inorganic membranes. So these are the first column tells us about the manufacturer the name of the manufacturers you can see that different companies like Du Point, NGK then TDK okay and the trade name then the next column is that trade name of the membrane.

So the let us see the first one which is called membrane locks okay, so the membrane material he is here as econia moxa dioxide alumina and the support material is again alumina the membrane pore diameter ranges in the two hundred two hundred nanometer 0.22 pipe micrometer and that particular range okay the geometry of the substance geometry of the membrane element is actually monolith or tubular type.

And the tube or channel inside diameter is 4 to 6 mm now these particular tube diameters on this can be varied also and this tells us about that we have huge number of companies they are actually the list is more, so I have just tried to saw some of these commercial membranes there are many companies across the globe, which are preparing the ceramic membranes and they are excellent in performance okay

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Table. Classifications and characteristics of membrane processes.

Driving force	Membrane process	Permeate	Retentate	Type of membrane
Pressure difference	Microfiltration (MF) (0.5-2 bar)	Dissolved solutes, water	Suspended solids	Symmetric microporous
	Ultrafiltration (UF)	Small molecules, water	Polymers, proteins, micelles, colloid particles	Asymmetric microporous
	Nanofiltration (NF)	Monovalent ions, water	Small molecules, divalent salts	Thin-film membrane
	Reverse osmosis (RO)	Small polar solvents, salts, water	All solutes	Asymmetric skin type
	Pervaporation (PV)	Volatile small molecules, water	Low volatility species; species less soluble in the membrane	Asymmetric homogenous polymer
Concentration difference	Diffusion dialysis (DD)	Small molecules, water	Large molecules	Nonporous or microporous
	Membrane extraction (ME)	Gases, solutes, vapors soluble in the extractant	Components of feed insoluble in extractant	-----
Electrical potential difference	Electrodialysis (ED)	Ionized solutes, water	Non-ionic solutes	Ion-exchange membrane
Temperature difference	Membrane distillation (MD)		Molecules < 1 nm	Microporous

Before we wind up this particular lecture let us quickly glance through what we have discussed since last three four lectures okay. So we have discussed about the membrane by six we have are try to understand how separation takes place using different type of membrane okay and different types of membrane classification and various processes so this next two slides this slide in the next slide we will just quickly glance through what we have understood.

So this is again I am just trying to group everything in a single slide so in which this tells us about the classification characteristics of membrane processes, the first column rest on the driving process so we can have either pressure difference that I've been puts or concentration difference electrical potential difference of temperature, so under pressure dependence we have microfiltration ultrafiltration nanofiltration reverse osmosis and pervaporation.

So as you go from micro filtration to RO and PB okay the pore size actually decreases howe ver the pressure that is required for separation is increases okay so the type of membrane is we that we can prepare a symmetric micro porous either we can have a symmetric micro porous membrane also we can have thin film membrane also which is again an isotropic membrane and we can have a symmetric skin type of membrane okay.

Or homogeneous polymer type of membranes so all these possibilities are there using polymeric membranes then the applications is actually in water and wastewater treatment desalination is one of the most important application okay, and it we can go for fractionation of macromolecules also then in the concentration different process either we have diffusion dialysis or membrane extraction okay.

So we can use both non porous or micro porous membrane as the case may be so under electrical differents potential difference we have electro dialysis okay so the permeate is actually ionized solution water and the retentate is non ionic solutes okay ion exchange at the membranes at the membranes which are used for this electrode surface so we have cation exchange membrane we have an ion exchange membrane.

And we have bipolar membrane also having both fixed cation and anions imparted on that particular membrane then under temperature difference we have membrane distillation here we separate solutes which are less than one nanometer it comes to the retentate side okay and my usual micro porous membranes are being utilized for these purposes.

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Table. Selected industrial applications of membrane processes.

Membrane process	Industrial application
Microfiltration	Wastewater treatment, membrane bioreactor, sugar, fruit, wine tea industry, fermentation broth concentration.
Ultrafiltration	Drinking water, membrane bioreactor, diary, meat, fruit and brewery industry, protein/enzyme purification, heavy metal removal by micellar enhanced ultrafiltration
Nanofiltration	Drinking water, wastewater treatment, sugar and tea industry, dye removal
Reverse osmosis	Deionized/drinking water preparation, wastewater treatment, diary, fruit/vegetable, wine and sugar industry, heavy metal removal
Gas separation	H_2 recovery, CO_2 separation
Pervaporation	Ethanol dehydration, organic material recovery
Electrodialysis	Demineralized water, wastewater treatment, diary and Sugar industry

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And let us quickly go through the different applications once again though we have discussed in last few classes. So mean micro filtration the wastewater treatment membrane, bioreactors, sugar fruit wine, tea industry okay fmentation and broth concentration all these things have typical applications of micro filtration so similar applications are also can be done by ultra filtration okay.

And we can use also for alter filtration for the separation of proteins and enzymes and antibodies so, then nano filtration which is being utilized for drinking water wastewater treatment purposes as well as suger and tea industry and dye removal for textile effluent then reverse osmosis the classical example is of course the desalination and drinking water preparation then wastewater treatment.

Of course then it see it can be used in dairy and fruit vegetable industries wine and sugar industry as well as heavy metal removal from various effluents. Then gas separation we can have hydrogen recovery we can have carbon dioxide separation we can go for nitrogen enrichment and there are several. under pervaporation we can go for a higher ethanol dehydration organic material.

If you remembrane that making alcohol free beer is another application of using pervaporation membrane then using electro dialysis we can again go for this desalination process the demineralized water wastewater treatment and diary sugar industries. so we have come to the conclusion of today's class.

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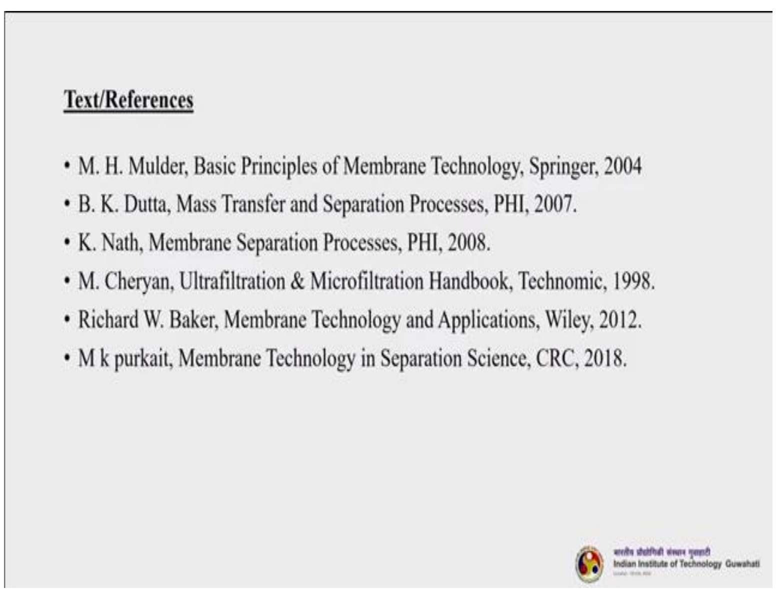

So as usual again I am showing you this the slide which containing the different names of the books okay for the text and referent purposes so you can refer them for some of the materials so most of the materials are taken from these books then in the next class

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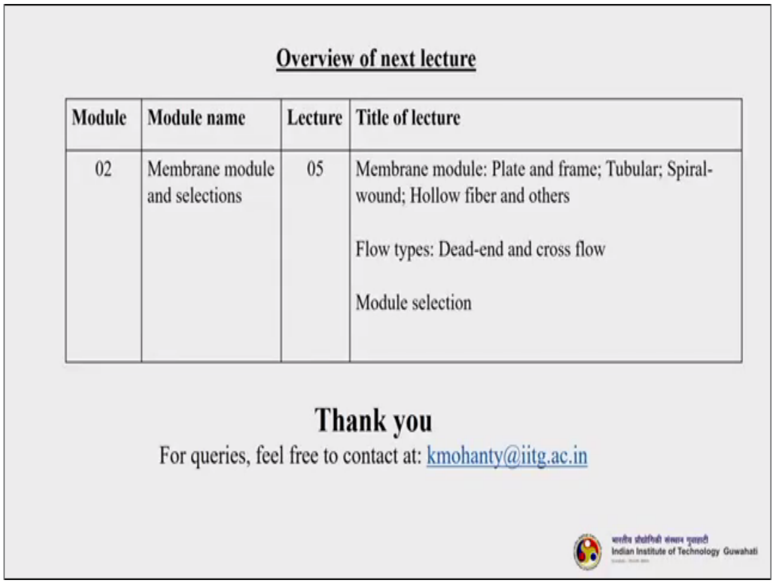

So that will be the module 2 and lecture 5 we will discuss what are the different types of membrane module, what is a membrane module? what are the different types of membrane modules exist? So in we will discuss in detail about plate and frame tubular spiral-wound and hollow fiber and other metal materials and what are the different types of flow types that is happening inside the membrane module as well as how we will select a particular membrane.

That is also very important we need to understand how to select a particular membrane module membrane as well as membrane module. So thank you very much and if you have any query please feel free to write to me at kmohanty@itg.ac.in thank you very much.