Industrial Inorganic Chemistry

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Lecture – 49
Zeolites

Good morning everybody. So, we were still continuing with zeolite molecules.

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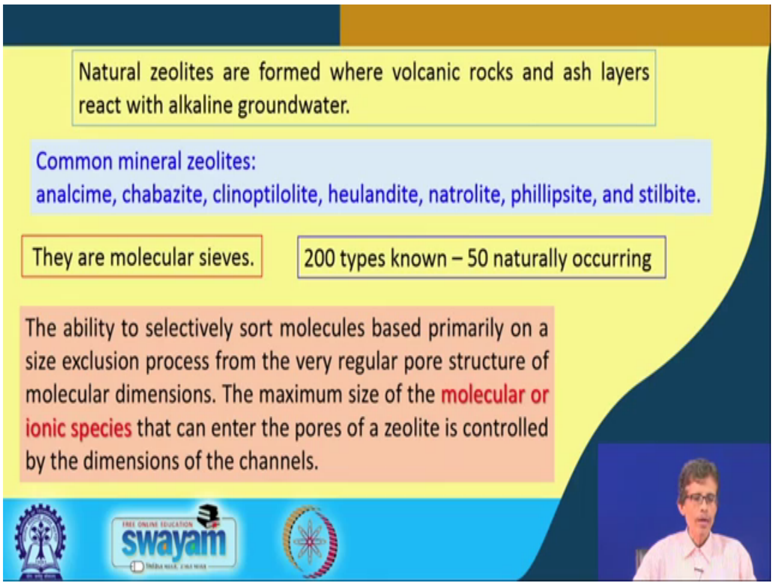

And how we see that this is a naturally occurring material and we get it from different types of rocks. So, natural zeolites are formed where volcanic rocks and ash layers basically react with alkaline groundwater. So, think of it typically in terms of a typical inorganic chemistry reaction, where we can think of that the material is that volcanic rock and you have the ash layers which are reacting if the groundwater is strongly alkaline. So, due to that reaction, we basically get the formation of the natural mineral which is your zeolites.

And this mineral type zeolites are of different one is an analcime, then chabazite, then clinoptilolite, then heulandite and natrolite and phillipsite and stilbite. So, these are typically of geological origin and these geological names are also sometimes it would be a little bit difficult, but we the inorganic chemists are always interested to know the basic composition. The chemical composition since, the formation of this natural zeolite is typically dependent on a typical chemical reaction in alkaline groundwater medium. So, we will be interested to know their actual formula or the composition chemically.

So, but we should have some tag basically whether we can call it as a zeolite a, b, c, d,e,f, g, h or so or a good name. So, these names are also sometimes very useful, because it has some historical references also, because historically when people identified these then characterized all these things. They still continue the name whenever they write in journals or the when they write in the books. They use this as the corresponding material. So, a geologist or a chemist or a physicist, they know very well which is your stilbite.

So, these are now a common tagging of these zeolite minerals. And we are basically interested to know what are the naturally occurring mineral sources of this zeolite, because we will be interested to make something in the laboratory; that means, the man made zeolites which will be of our demand and which will be of a different type.

So, how we get those information from the naturally occurring zeolites that we can use as very useful molecular sieves, because it has a very good framework structure, 3D framework structures like nowadays what we get different types of metal organic frameworks, because the metal nodes are there and we can have a typical spacer unit as the ligands like four-four does by pyridine. So, we get a huge structure which has a common similarity with that of your zeolites.

So, when we use these as the molecular sieves; that means, they have very useful pores and the pore dimensions are of the molecular size such that it can trap some molecules inside and we can go for some catalytic reactions based on the surface of the zeolite or the corresponding trapping of those materials. So, we see that a large number of this sort of zeolites are known in the literature. So, 200 types are basically known and out of those 200 types 50 are naturally occurring. So, we can have a very big source of naturally occurring zeolite molecules or zeolite materials.

So, people have characterized it nicely and people have identified that also and that gives rise to some good information, even for our synthetic methodologies or synthetic procedures that how we can go and make some of these zeolites in the laboratory. So, how we go for these particular species; that means, they can function as the different types of molecular sieves. The ability to selectively sort different molecules, why we call it as a molecular sieve; that means, it is some kind of filtering mechanism in terms of the molecular sizes and if it is dependent on the different sizes, we can think of is the size exclusion type.

So, selectively they can sort or they can identify the molecule based primary on a size exclusion process that means which are bigger can be retained and which are smaller can pass through that particular zeolite material. So from very regular pore structure of molecular dimensions, so you can have a very good pore structure such as we can have the trapping of methane or trapping of ethane also inside the pores of the zeolites. And in all these cases, the maximum size of the molecular or ionic species that can enter the pores of zeolite is controlled by the dimension of the channels.

So, whenever a particular type of zeolite, whether you have a zeolite x or zeolite y or zeolite a, we should know the size of the different pores such that we can use it as the typical material for absorption of those molecules inside those channels. So, if channels are there, so molecules will go inside and stay within the channel; and if we go for some other materials. Suppose your material that means, what is being trapped is a can react with b, so then we react it with the b such that some conversion between these reaction of a and b can give you c, and such that we can get c out of this reaction on the surface of these zeolites.

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So, what we find now that how we make those synthetic zeolites. So, at one hand, we have those naturally occurring zeolites and the other end we have synthetic zeolites. And since, we have seen out of 200 only 50 are naturally occurring so, 150 synthetically or the man made or the laboratory prepared zeolites we can have. So the first thing, what we can have the most useful material, what we can use for making these zeolite is the kaolin. So, it can be considered as the natural raw material.

So, kaolin would be the natural raw material for the synthesis of zeolites using other materials like that of our sodium aluminate and silica. So, you have kaolin, you have sodium aluminate and you have silica. So, we will be having something, so alumina silicate type of materials will get out of this material and how we can proceed for that synthesis that we see.

So, first thing what people can do for this is that dehydration or removal of water from the zeolite, because the zeolite material always can have huge number of water molecules, water trapped inside and sometimes the adsorption of those water molecules are there within the channels. So, that particular zeolite which has huge number of water molecules inside the channels can be used for some reaction which can be considered as a very simple hydration reaction. That means, in any reaction if we add water, it can be your hydrolysis also, but simple hydration reaction. Suppose some anhydrous material like calcium oxide we can put it over there, so which can be hydrated for giving you calcium hydroxide that we can do on the this particular zeolite material.

So, zeolite material can trap this and can react with the water molecules available to it. And if we now can have the corresponding material as its dehydrated form or the dried form of zeolites so, how to remove those water molecules. Because we all know that a molecule when can put some temperature or it can give it to the corresponding furnace, it can go for dehydration. Suppose simple calcium oxalate and is also some trapped water molecules we have synthesized, we have precipitated it.

So, freshly prepared calcium oxalate if we go for is dehydration process, it can have several steps of dehydration. That we also can monitor from different types of gravimetric analysis which can be controlled by temperature change which is known as thermo gravimetric or TGA analysis. Similarly, when we find that a high temperature basically not in the range of 100 or 150, but in the range of 450 to 650 is required to remove the whole amount of water which has been trapped inside the zeolite; so, we use something some specially designed furnace is not the simple air oven type box type of furnaces, but these are your rotary tube furnace. So, rotary tube furnace will be effective in making all these zeolites in is dehydrated form.

So, once we make these as the dehydrated form of zeolite that can easily go for trapping more number of water molecules or that can be used for high level of absorption of other molecules such as your vapor of alcohol or paper of other organic molecules or organic solvent molecules. Then once we have these two types, that one type is your naturally occurring and other type is synthetically prepared.

We can think of they are different types of applications which will be very useful to know. Because once you know the application of these zeolites, we can also assess its demand in the industry and then we can think of making new types of all these zeolites; because already some of these zeolite molecules are in good use and some of these preparations are patented still, because they are still used by those industry people for making some useful compound.

So, the first of its application is the typical e ion exchange zeolites. So, we all know that a particular type of zeolite or a particular type of resin that we call as ion exchange resins are there. So, we can handle the hard water where we know that it can have the dissolved salts of calcium and magnesium. And if we try to remove those calcium and magnesium ions by sodium and potassium to make the water sample softer which can be used for the typical ion exchange thing; that means, typical zeolite like that of your ion exchanger is saturated with in its sodium or potassium form.

So, water will be added from that particular column basically like that of your chromatographic column. So, column chromatography we all know. So, a typical arrangement of this column which is packed with these zeolites and on the top if we pour that water sample containing your magnesium or calcium which is responsible for making the water as a hard material; or the sorry, the hard water molecule or the hard water. Then through that basically through that percolation of that water, through that ion exchange bed which is filled with zeolite. So, zeolite bed, when it passed through this particular zeolite bed, what happens? The ions are exchanged.

Now, we are looking for only the cation exchange, so it will be a cation exchange zeolite. So, magnesium and calcium will be exchanged with that of your sodium and potassium. So, all the exchange amount of your magnesium and calcium will be retained within the zeolite framework and the water which is being removed from that particular material is only saturated with or exchanged form of that with by your potassium and sodium.

Then we can use it for some kind of separation processes. So, mixtures of aromatic hydrocarbon isomers if we have, in such as the petrochemical industry when we are going for the refining process in the petrochemical industry, we get large amount of mixture of hydrocarbons. And it is a very difficult task or a tedious process to separate all these things. Suppose, we want to recover say the example given here is the recovery of para xylene. How we remove para xylene over there?

So, if we know that the para-xylene is a para isomer, so it and have a typical linear shape apart from your ortho and meta isomer. So, if we consider that the other two varieties; that means, the ortho form or the meta form can be retained within the zeolite framework, only the para-xylene form can pass through that particular channel because of their particular type of shape and the size of those particular channel. So, only like that of our filtration, we know that the small molecules or the small particles will be passing through the filter bed like that of it is also a filtering type of filtering process, where the para-xylene will be coming out of that particular zeolite bed and retaining that ortho and the meta isomer.

And the third variety what we can have is the very useful application of these zeolite molecules or the zeolite materials or the framework structures is as catalysts. So, we can have this catalyst because it is a solid surface it is giving and most of these are basically based on your silicon attached with OH, aluminium attached to OH at the end; that means, at the surface.

So, when the surface characteristics of all these zeolites are known and which is mainly made up of Si OH and Al OH type of bond, what we can think of that particular surface is typically acidic. So, a acidic reaction on a heterogeneous surface because the zeolite materials are insoluble in water, sometimes in soluble, some of those organic solvents or even in alkali or in acid medium.

So, if we go for some acidic reaction which is catalytically effective also, such as catalytic acid hydrolysis reaction. We can go for this or sometimes we can go for some transformation which can be triggered with the surface acidity of the zeolite, we can go for this. So, these reactions include basically what are the different types of reactions we can monitor or we can see or we can study with your use of your zeolite material is your first off one is your catalytic cracking.

So, we crack de-hydrocarbon molecules is broken down into small pieces such that we can get that useful material as your corresponding petrol, the corresponding diesel or the some smaller molecules or the gaseous products like that of your CNG type of molecules. So, small organic molecules like butane, propane, etcetera can be derived from the very large molecules what we can get from the raw petroleum.

So, the catalytic cracking can be achieved with the use of zeolites, then different types of isomerization, such that this particular type we have seen just now you can take always that example when what we are talking about is the para-xylene. So, the para xylene has been separated. So, we will retain with that of your ortho and say matter meta variety or say only ortho variety is there. So, ortho xylene is retained within the zeolite form.

So, if some other zeolite can be effective for its catalytic behavior, such that your ortho isomer can be converted to the para isomer. So, the same type of zeolite or the solid state reaction on the zeolite surface will be useful to convert the ortho isomer to the para isomer, then we can again separate it out the amount of formation of that particular para isomer from the ortho variety by using the previous process that means, your separation process.

Then we can have the typical alkylation that we know from the typical knowledge of your organic chemistry that we can go for the alkylation of benzene or even the toluene alkylation; that means, more number of alkyl groups can be attached to the aromatic ring, the aliphatic ring or sometime it is on the acid or it is on the amine. So, how we can use those alkylation, that can be sometimes triggered by this zeolite surface. Then sometimes the de-ox-waxing, the wax material or the wax molecules are very large type of this particular fat type of molecule, so this can be removed basically with the use of these zeolites.

Then as we have seen as ion exchanger material or the adsorption material, so we can also have some good idea in using this as adsorption agent. So, if we want to purify the gas, sometimes the gas is contaminated with some other unwanted gas molecules. So we can use this; that means, we can pass the gas molecules through that particular zeolite material. Such that if we want to purify hydrogen; the typical hydrogen which is nowadays of good demand for its corresponding efficiency as fuel. So, hydrogen as fuel in large tank or it can be liquid or it can be gas also because you can produce the gas from the liquid form and then it can be passed through the zeolite such that the other unwanted gases like that of your carbon monoxide or nitrogen can be removed through this particular process of using zeolites.

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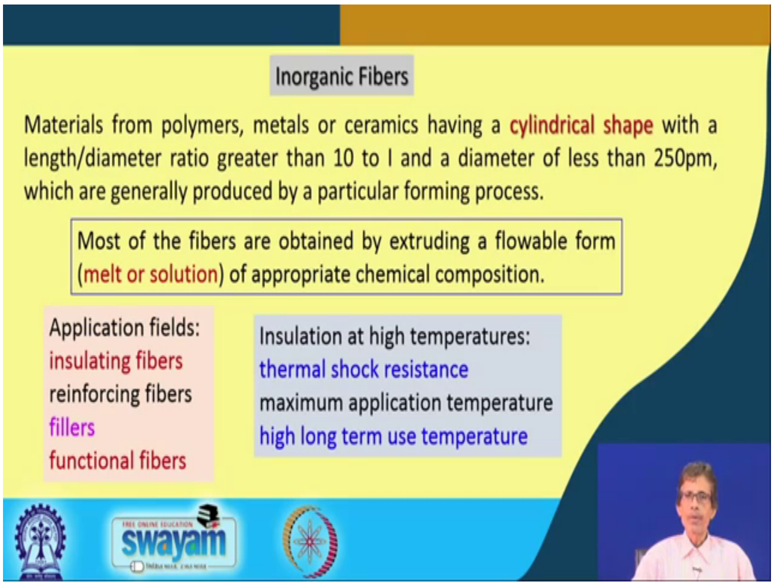

Now, we move quickly to the inorganic fibers. So, zeolites we have seen is a three-dimensional framework type of structures, a big structures. Now, what is known as inorganic fibers. So, we know that different types of other fibers like your cloth fiber that is we make from the organic molecules, then the polymeric fibers also. Then what we can classify as the typical inorganic fibers and what are the different types of industries can use those and what are the other industries which can produce those inorganic fibers.

So, we can have these from the polymers, we can have it from the metals because since we are talking all together. We are not separating this polymeric material as we are not discussing in the inorganic industrial chemistry class, but we will discuss because whether the system or the industry which are producing the metal fiber or the ceramic fiber can also handle the polymers such that we can have also the production from the same instrument or the same type of industrial application of from that particular industry.

So, metals and ceramics when it is formed in the fiber form, so thread form, we can use add in a form which is of cylindrical shape. Because threads are definitely the fibers will have a cylindrical shape, the shape is typically a circular cylindrical shape with the length and diameter ratio greater than 10 to 1. So, when the length to diameter ratio that means, your length is 10 times higher than that of your diameter and diameter is less than 250 picometer.

So, if you have a typical ratio; so, ratio and we can have a diameter in the range of 250 picometer which are generally produced by a particular forming process that means, the production process. That a particular type of process or the industrial process can be used for the production of these sorts of fibers.

And most of these fibers are obtained by extruding a flowable form. Then how we make it basically, because we can have in the liquid form and the liquid which can be passed through some channels and the channel will giving you some thread like arrangement that means, we can have a melt or some solution. So, from a molten state of that material or the solution state of that particular material can be used for of appropriate chemical composition, whether you are using that as the polymer or whether using; we are using it from the metal or the metal sheet or the metal block.

So, we use these for in the different application area and those applications are the most one is very useful as some insulation, because we all know that you can have the heat exchange thing; that means, if we want to enclose something which is very highly heated such that the temperature loss would be less, so we use it as some insulation. So, insulation fiber is can be used for this. Then do reinforcing fiber; that means, the strength of some other fiber can be improved with the introduction of these inorganic fiber. So, the inorganic fibers can have a good application in reinforcing the other type of fiber.

It can also be used as fillers; that means, some material where we can have some filler material such that we can have a big block we can make. Then sometimes we can have also the functional fibers; that means, we can modify those fibers. So, you can have the basis; that means, there is some support fiber which is of inorganic origin. So, inorganic basic fiber we can have. And on that, we can derivatize something with respect to those functional groups which will be available on the surface of those.

So, when we are use it as your insulating fiber material, what we can have? We can also think of that whether we can use it at for a very high temperature because we know that the different types of ovens we use, different types of furnaces we use, even for the laboratory use also day to day laboratory teaching research or industry. So, the thermal shock resistance, it should have a good amount of help for to resist the thermal shock if we put this material as a typical insulating material.

Then we can have a maximum application of the temperature; that means, if it is insulated, so we can go to a very high temperature. So, maximum application temperature for high temperature applications should be there and high long term use temperature; such that, the material should withstand the temperature up and down for a longer period. Such that, the material strength can also be charged if we use it for their corresponding insulation material that mean inorganic fibers will be much more superior compared to other types of fibers.

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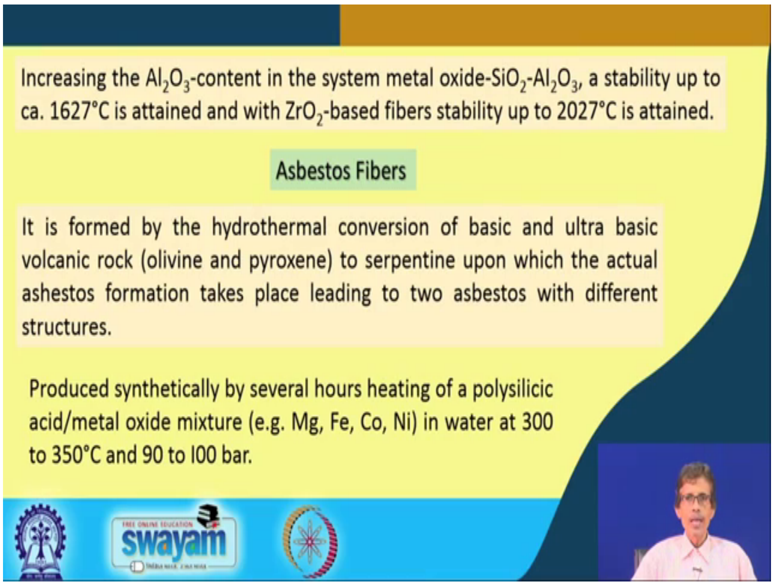

So, when we can have certain type of this fiber, where you can have alumina, we can have silica and other types of metal oxides. So, you see these inorganic fibers we can think of as a typical metallic fiber, but the metallic fibers will not have that capability that means, it cannot have that much insulation capability. So, we can think of another naturally occurring thing that we will also discuss those are asbestos.

So, asbestos fibers are also very good and useful in organic fibers which can be used for your temperature insulation. Now, along with that if we think of some material or some fiber preparation out of some metal oxide that means your iron oxide itself or zinc oxide, then silicon dioxide, the silica, the sand and alumina. So, if we increase the Al 2 content, that means, we all know that the alumina can withstand a very high temperature because we know for the thermogravimetric analysis, we use alumina crucibles. Small alumina crucibles we use for the laboratory use withstand a very high temperature say up to 700 or 800 degree centigrade. The crucible material is made of therefore of aluminium.

So, what happens now if we see that if we change or if we allow the corresponding alumina content in the system, where you can have three component, one is your metal oxide, other is your silica and third is your aluminum. So, we can reach up to a temperature range of plus 1600; that means, say around 1627 degree can be attained with the use of that particular composition of that inorganic fiber. And replacing this that means, if something can be obtained from zircon or zirconia or the zirconium dioxide; so if we have the zircon that means, zirconium based fiber, so that zirconium dioxide based fiber can have stability up to 2027 degree centigrade can be attained.

So, what we see that; now, the temperature resistance or the temperature with stand can also increase, with the increase in the corresponding composition or changing the composition. So, if we move from alumina, already we have seen the alumina as alumina crucible can withstand and temperature, then if it is mixed with silica and other metal oxides, so we can increase that temperature to the double amount say around 750 to 800 to 1600 plus.

Then if we put zircon or the zirconium dioxide, we can go up to 2000 degree centigrade which is a very high temperature for industrial use. So, any container any channel any pipe can be made of this sort of fibres which can withstand a temperature of 2000 plus. Now; just now, what I told you that we can think of something which is also again a naturally occurring material like that of your zeolite is your asbestos.

So, we can have very useful or interesting fiber, inorganic fiber is your asbestos fibers. And these are formed for a particular type of reaction we call as a natural reaction, where is known as hydrothermal reaction or hydrothermal conversion where water is available and at very high temperature below the earth surface also. A basic and ultra basic volcanic rock because we know that the melt from the core of the earth is coming out in some of the orifices as the corresponding volcanic eruption.

So, what is coming out as their particular volcanic rock is your olivine and pyroxene and which can be converted to serpentine upon which the actual as asbestos formation not asbestos formation takes place leading to two asbestos with different structures. So, during that particular process, so the volcano which is coming out forming your volcanic rock so, when it is cooling down basically; so, when it is cooled down so the conversion is already taken place and the one form basically can be separated into two other forms having two different structures. So, when they are structurally different we are happy to get two different types of asbestos systems or asbestos molecules.

So, knowing that particular information that it can be formed from volcano or from the volcanic rock which are mainly olivine and pyroxene. We can produce these synthetically by several hours heating, so very high temperature which can be making your hydrothermal reaction, such that we can think of a corresponding conversion which can be considered as a hydrothermal conversion. So, which is basically based on poly silicic acid we know the silicic acid silicon attached with four hydroxy groups, we know that the mono nuclear one which can be a poly nuclear one.

So, a mixture of poly silicic acid which is giving you the silica content as well as the metal oxide content from the different metal oxides like magnesium, iron, cobalt and nickel. So, these magnesium two nickel oxides can be given in water not at very high temperature, but only 300 to 350 degree centigrade, but you put some pressure. So, hydro; that means, in water medium then thermal that means, the temperature at some high pressure also, because under the earth crust close to that of our earth mantle, we can have a very high pressure situation also.

So, this particular reaction can take place at a very high temperature and high pressure. So, not very high only 90 to 100 bar and a temperature of 300 to 350 degree can be useful for giving you the opportunity to produce synthetic asbestos fibers.

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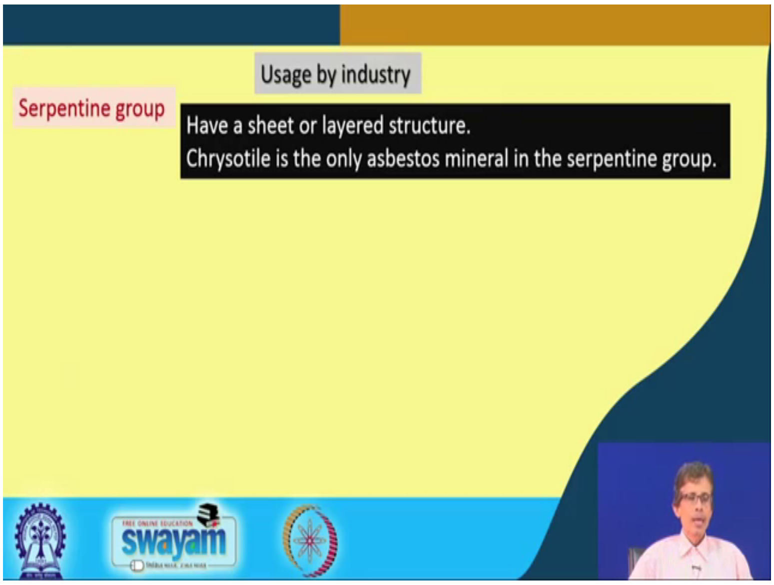

Then we will see will continue to our next class that how we use this as in the industry. So, industry people can have the use of this material for the different purposes. So, we will slowly will see from one group to another because we just now have told you that we can have the serpentine group which have a particular type of structure, the serpentine group have a seat or layer structure. So, that seat or layer structure can be utilized for one particular use or one particular purpose.

Then chrysotile is the only asbestos mineral in the serpentine group. So, this is the form basically chrysotile. So, chrysotile is one particular form which is coming out from that particular serpentine group. So, we can have a huge table, but we will not bother about all these complicated names and all these things. So, one will take one or two examples out of that, such that we can have the basic structure. And we will again will be interested to know the corresponding chemical composition that will see in our next class.

Thank you very much.