

**Industrial Inorganic Chemistry**  
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**Lecture – 40**  
**Calcium and its Compounds**

Hello, welcome back where we are considering magnesium and its utilization.

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Direct chlorination of magnesium oxide in the presence of coal at 1000 to 1200 °C

$$2 \text{MgO} + 2 \text{Cl}_2 + \text{C} \longrightarrow 2 \text{MgCl}_2 + \text{CO}_2 \text{ (or CO)}$$

**Applications:** Over 60% used in the electrolytic production of magnesium, the rest being mainly used in the building industry

It is also used in the granulation of fertilizers, in the oil and sugar industries and as a binder for dust (in mining and in road building).

Book: Industrial Inorganic Chemistry  
By K. H. Buchel (Wiley-VCH, 2003)

The slide features a yellow background with a blue and orange header. At the bottom, there is a blue banner with the Swayam logo and a small video inset of Prof. Debashis Ray.

So, we have seen that in the first part of this application that where we use this magnesium chloride. So, as a typical salt is like your other metallic salts chloride salts like iron chloride, ferric chloride, ferrous chloride, nickel chloride, copper chloride it is also some kind of this salts so it has also huge demand if you have the good quality of magnesium chloride for the laboratory purpose or the laboratory supply. So, at the same time since we use these for some other purposes; that means, we know that it can have the high temperature withstand. So, it can use the in a building material in the cement or any other things.

Then one most important thing is we just now consider that it is also used in the granulation of fertilizers. So, you see that what we are making, we are adding this suppose your fertilizer is only made up of nitrogen, phosphorus and potassium. Your fertilizer is urea, your fertilizer is some other form, but you so that the crystallization

process; that means the granules we basically spray or we throw or we pour on the agricultural field where we make the good granules basically.

So, if the material so that is why we have seen that magnesium carbonate we are using for the anti caking agent of your table salt. So, it has some that type of property that when you use magnesium chloride, you can go for good quality of granulation; that means, it can help the granulation process while you go for making those granules out of those fertilizers.

So, one more advantage is that people have not thought of, but it is the good idea basically that is the innovation part of this thing, that if you use magnesium chloride for this granulation process what you are having, you are having a percentage of magnesium in it. It is not harmful for your fertilizer, it is not deadly for your soil health, it is not deadly for your plant health as well.

So, what you find that this particular want; that means, in the ppm level or ppb level a very small concentration of magnesium you are carrying to the soil and we all know that these magnesium is also a very good micro nutrient for your plant because this magnesium will be there in your chlorophyll otherwise the soil gets magnesium from some other sources. So, unknowingly what we are doing. So, this is the area where people can think of, people can imagine basically that this is improving the quality of that particular NPK fertilizer.

Because we know that suppose a one particular type of NPK fertilizer you have where we call is a 10 26 26; that means, 10 is to 26 is 26 percentage of nitrogen, phosphorus and potassium. Along with that you get certain thing which is in the order of 10 to the power minus 5 or 10 to the power minus 6 of magnesium, but that magnesium because the concentration level the balance of those concentration is very important for the soil, for the roots of the plant because it can take up that particular thing for its utilization to put that magnesium within the porphyrin ring of the chlorophyll.

That is why your chlorophyll is photochemically active it can store the corresponding reaction for these photon energies of the sun and you can go for good quality of photosynthesis because we never control the photosynthesis is a typical natural process, but if we consider then more and more amount of that magnesium will be incorporated. But by now what we are looking at by looking at the green vegetation, the colour of the

green material the leaf color basically what do you find that the leaf colour is very good; that means, the incorporation of magnesium as the chlorophyll is there, but we are not supplying magnesium as the fertilizer.

So, it is basically improving by quality of nitrogen, quality of phosphorus and quality of potassium and those balance basically keep the health of the soil, but now if we find that unknowingly the magnesium is going, but the magnesium what is added is the magnesium chloride is basically some material like some gum what we are adding to some material.

So, is basically going for its changing the physical characteristics not the chemical characteristics is the added for granulation process, but unknowingly why we are supplying something which can add up chemically or which can value add chemically to that particular fertilizer because we are having magnesium chloride only if you put water, it is simply dissociate into magnesium 2 plus and chloride ions.

Similarly, it can go in the oil and sugar industries and as the binder for dust, because the dust particles can very well bind with that particular magnesium chloride in mining and in road building. So, if we add certain amount of magnesium chloride it can basically bind that particular dust material within the sample of this particular magnesium chloride.

So, everything whatever we are talking mostly considering again that particular single book is a very useful one also you have to follow you can follow this particular book which is your Industrial Inorganic Chemistry by Buchel Adal several other authors are there, they basically compile this thing very well from the background of the Chinese chemical industry to German chemical industry to the US chemical industry.

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**Magnesium Sulfate**

Anhydrous  $\text{MgSO}_4$   
Kieserite,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$   
Epsom salt,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$   
Potassium magnesium sulfate

Large quantities of kieserite, Epsom salt and anhydrous magnesium sulfate are produced in the processing of potassium salts from brines.

**Applications** Manufacture of potassium sulfate (from potassium chloride), sodium sulfate and potash magnesia (potassium magnesium sulfate).

Used as a fertilizer, in the textile industry, in the manufacture of building and refractory materials, in the pulp industry and in the production of animal feedstuffs and motor oil additives.

The slide also features a video inset of a man speaking, and logos for Swamyam and other educational institutions at the bottom.

Then we will move to see what is the situation for the other important magnesium salt which is your sulfate salt. So, how we get magnesium sulfate what we commonly known as mag sulf we know as a biochemical material as the biochemics sample, as inorganic sample we know that mag sulf is very useful for different purposes.

So, you have one composition is your anhydrous form no water molecule then kieserite is one water of hydration, then the Epsom salt what we know basically as the magnesium sulfate seven hydrate like your blue vitriol, white vitriol then use the Epsom salt also have because sometimes it is the common formula is you have the hepta hydrate form, then potassium magnesium sulfate is a double salt basically. So, is the magnesium sulfate and potassium sulfate double salt which is potassium magnesium sulfate.

So, the second one the monohydrate form which is known as kieserite, kieserite Epsom salt and other anhydrous magnesium sulfate are produced in the processing of potassium salts from the brine so we have the brine. So, where you have the potassium chloride, where you have the sodium chloride and where you have the magnesium chloride. If you are lucky enough to get the corresponding sulfate the anion part we are changing from chloride to we are going to sulfate.

So, that particular sulfate if we have and during the processing basically, how we crystallize if it is difficult to get a good crystal of magnesium sulfate we go for the double salt; that means, potassium magnesium sulfate. Because the double salt are more

robust one and its stability is more and its longevity is also more so instead of storing the pure magnesium sulfate or the hydrated form of magnesium sulfate we can store the corresponding double salt which is being made through the use of potassium sulfate.

Applications of this is that you get to have the corresponding potassium sulfate from potassium chloride if you add that means, it is a basically a good source of sulfate. So, any sulfate material even if you for industrially important other organic sulfates or anything will try always we can think of that whether this sulfate can be useful to go for any or making organic sulfate also like your detergents, like your Sodium Dodecyl Sulfates the SDS form and all.

These things this will be there where we can think of that the cheap material like sulfate if we can go or incorporate from the typical inorganic salts, right now we do not have that particular knowledge we do not have that particular amount of research or particular amount of development we do not know this will be there where we can put that particular sulfate from magnesium sulfate to any other backbone or including your organic backbone.

Then making of sodium sulfate and potash magnesia that means, potassium magnesium sulfate the last one which we are talking about. It can be used therefore, as just now we have discussed a little bit about the corresponding material improving the physical characteristics with the addition of magnesium chloride, but it can directly be used as a fertilizer because we supply magnesium as your source of magnesium for making the chlorophyll.

It can be useful for textile industry, in the manufacture of different high temperature withstand material and building as well as in refractory, in pulp and paper industry and in the production of animal feedstuffs and motor oil additives. So, motor oil additives if we want to improve the quality of those motor oil in some purpose; that means, the viscosity, the temperature withstand and any other physical there are large number of physical characteristics are there such that you can you cannot use any oil that mineral oil as the motor oil for that particular purpose.

And then animal feed stuff is that means, it is magnesium added animal feed stuff because the animals like your human being, also the plant origin everybody required magnesium. So, increasing those animal feed stuff quality we use this.

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**Calcium and its Compounds**

5<sup>th</sup> most abundant element in the earth's crust at ca. 4%

Calcium carbonate (limestone, chalk, marble, shell limestone, calcite etc.)

Calcium magnesium carbonate (dolomite,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ )

Calcium sulfate (gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and anhydrite,  $\text{CaSO}_4$ )

Calcium phosphate [apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ], calcium fluoride (fluorspar,  $\text{CaF}_2$ ) and calcium aluminum silicates (anorthite,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).

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Then from magnesium we just quickly move to calcium. So, calcium and its compounds so not only the pure calcium because the calcium in its metallic form we always have like that of your sodium; sodium blocks we know, calcium blocks we know, potassium blocks we know. So, is the 5th most abundant so we are going down basically now it is 5th most abundant on the earth crust an about 4 percent we basically get, but most of the time we get is in a very chip source which is your calcium carbonate, the limestone.

So, the lime is the most earliest informations what people have it historically, similarly the lime what we talk about for its chemistry the limestone which is your calcium carbonate, how we handle that thing, how calcium carbonate is reacting with acid and all these thing from our early school days. So, calcium carbonate you can have it from limestone to calcite including chalk, marbles, shell limestone and everything. So, shell limestone what we are getting basically if we think that there are lives.

So, biologically these calcium carbonate things are also very important and in the biological world, the protein world or the protein environment the crystallization of those calcium as calcium carbonate are also very important. In human being also in the our eardrum we require something which is formed along with your bone formation because calcium is there a small bone which is controlling our balance basically and all these things the special quality of bone how you think of. How you differentiate it from that of

your appetite, the bone appetite which is also a calcium phosphate, fluoro phosphate or hydroxy phosphate type of thing which is different.

So, calcium starting from your material from the world of your refractory material or the road material or anything like that of your limestone, from the limestone world to the biological world to our bone our teeth everywhere we can think of only the calcium. So, not only calcium as material, not only calcium as your inorganic chemistry point of view as well as calcium which is also important in your biological world.

So, calcium in biology is also a huge subject and we should have very good idea about that calcium because calcium is another supplement for making new types of your medicine, your new types of pharmaceuticals and also the calcium added all the food material. So, the health drink to any other food material which are nowadays pretty costly. So, the protein X or the B protein type of thing what we consume in a lesser amount, but which is also giving you huge amount of huge supply of the protein.

So, your calcium deficit basically can be supplemented not from milk, not from eggs and all other thing can be supplemented from this food material. So, those food material or the making of those food material also will be another area where people can think of, people can depend on the calcium supply or the calcium carbonate supply from the industry. So, we get dolomite along with limestone.

So, another very cheap and very useful sources your dolomite and it is very important molecule basically when we study chemistry also in our chemical world also, we studied dolomite very easily and very useful way because we can analyze calcium content, we can analyze magnesium content and also their thermal stability than material stability and how it is losing the water of hydration, how its losing its carbon dioxide form or carbon monoxide form from the carbonate.

How the decomposition pattern of the individual carbonates are taking place because the decomposition pattern; that means, the thermal stability of magnesium as magnesium carbonate or the thermal stability of magnesium as magnesium carbonate are different. So, if we can go for thermo gravimetric analysis the thermo gravimetric analysis can tell us the typical decomposition pattern at which temperature one particular form is stable otherwise it will be decomposed into magnesium oxide or sometimes the typically

magnesium carbonate and the carbon dioxide removal and also the removal of carbon monoxide. Then we have gypsum.

So, you see starting from your limestone to dolomite to calcium sulfate which is there your gypsum we know we have we can have the corresponding anhydride is known as the corresponding anhydrous form which is anhydride and we know that one other form in between we have the plaster of Paris.

Then we have the calcium phosphate which is your apatite, the fluorapatite, then calcium fluoride which is also the fluorite already we have talked about while we are talking about the corresponding isolation of fluorine. And the fluorine based materials, the acid spar and all these things we have already discussed in our previous classes, but now you will think of the relationship between these things because your fluorite we have handled somewhere due to the production of fluorine and fluorine bearing including the organic organofluorine compounds, now we are handling the same fluorite for getting calcium.

So, you see the same material fluorite can be useful for an industry development; industrial development which is dependent on the production of calcium similarly the same material is also useful for the production of fluorine and the fluorine based compounds.

Then if you are lucky enough to get some more complicated material which is available very cheaply is your calcium aluminum silicate. So, silicate materials are also very useful only problem that you can have it as the refractory material as a building material and all other things because it is not so always very easy to take out the individual elements out of this material. That means the individual element like calcium, the individual element like aluminium or individual element like silica removal up all these things from this material will be not so easy.

So, this particular anorthite *a n o r t h i t e* anorthite typically you remember the spelling also sometime so is basically a silicate by which is double silicate because the formula contains twice  $\text{SiO}_2$ , at we all know that most of these silicates is a monosilicates this  $\text{SiO}_4^{2-}$  which is a form of the corresponding anionic form of cyclic acid. So,  $\text{SiO}_4^{4-}$  is basically what we get so  $\text{SiO}_4^{4-}$  when it is coupled together we get a disilicate which is nothing, but one of the bridging unit is formed through  $\text{SiO-Si}$  bond.



So, it will be Si<sub>2</sub>O<sub>7</sub>. So, that Si<sub>2</sub>O<sub>7</sub> unit having a charge of 6 minus because you should know the corresponding charge balance what oxygen is giving; oxygen is giving two negative charge there means 4 minus and silicon is 4 plus.

So, 2 silicon is giving you 8 plus charge then, you have the 7 oxygen; that means, 7 into 2 is 14; that means, overall charge on that particular species is 6 minus. Then you have the corresponding cationic charge balance not only from the core of the silicon, but also you have the freely available calcium as well as aluminum. But if your aluminum is also present there as the aluminate form so it will have a networking of a very complex structure, but the basic building block for these is your disilicate that means, Si<sub>2</sub>O<sub>7</sub> unit.

Again we will just follow from that particular book because I only just giving you that example because this particular course is only designed on that particular book and other informations. So, if you are eager to study something little bit extra you can follow that particular book, otherwise you can follow all other things what we are falling in a stepwise manner.

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**Metallic Calcium**

By the thermal reduction of calcium oxide with aluminum in vacuum at 1200°C

$$6 \text{ CaO} + 2 \text{ Al} \longrightarrow 3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 + 3 \text{ Ca}_{\text{gaseous}}$$

The resulting calcium vapor is condensed and collected.

Calcium is utilized in the manufacture of special metals such as zirconium, thorium, uranium and the rare earths, as a refining agent in metallurgy (steel, copper, magnesium, tantalum, lead) and in the manufacture of calcium hydride (hydrogen source).

So, from those sources we go for getting metallic calcium simply you can go for thermal reduction of calcium oxide so you have the limestone, you have the calcium carbonate or you have the gypsum you burn it, remove the carbon dioxide from it, get the calcium oxide. So, the underlying principle or the underlying inorganic chemistry what I try to

emphasize every day in every class is that try to follow the basic inorganic chemistry behind that. That means, you should be very strong in inorganic chemistry because the industry what they hire basically large number of different types of people they hire engineers, they hire metallurgical engineer, they hire electrical engineer, they hire mechanical engineer.

But most of the time since the methodology the process the procedure everything is known they do not hire, they do not take any inorganic chemist, but for all these industries you can have some idea that if you know very well then organic chemistry and you have that aptitude for imagination, for the development of new processes you can rely on these things looking at that particular area that where you are producing this particular material. So, you must be a master in inorganic chemistry first then you try to tackle those problems in terms of their your understanding or your knowledge in terms of inorganic chemistry.

So, a simple thing that you remove that particular one and you know now temperature where you can burn that particular dolomite or calcium carbonate you know the temperature if you run only the TG experiment the Thermo Gravimetric experiment. So, above that temperature only thing only difference is that when you use huge amount the bulk amount the temperature would be high your reactor would be different, but otherwise you should know theoretically the exact temperature where your calcium carbonate or where your magnesium carbonate can be removed in terms of your magnesium oxide or calcium oxide.

So, you use the reducing agent not magnesium or any other thing now you go for aluminum, for calcium reduction we will be using now aluminum at a very high temperature again and again in vacuum because we always exclude oxygen. So, at 1200 degree centigrade what is happening over there that you reduce calcium oxide with alumina we get something where you get calcium in a complex form with that of your alumina.

So, you are allowing basically why you are using aluminum as your typical reagent for your reduction because we are getting or converting that particular aluminum to aluminum oxide; that means, it is a complex form of alumina tagged with calcium oxide, but at the same time some amount of calcium will be freed away as calcium as the

metallic calcium or at 1200 degree centigrade; that means, a very high temperature it is in the vapor form or in the gaseous form.

So, whatever vapor is there so is a difficult one that way that you have to have the corresponding pathway or the channel where you guide the calcium vapor to pass and you cool it and you get the corresponding contest form of calcium and the calcium as its corresponding metal. And the utilization is that again as we have seen in case of magnesium that it is again can be utilized for the making of different other from zirconium to different rare earth material for its reduction process as also as a refining agent in metallurgy.

So, metallurgical engineers or metallurgists are very much dependent on the availability of the calcium. So, industry is very much dependent on calcium what are those industry? The industry which are producing steel, which are producing copper, which are producing magnesium and which are producing tantalum and lead and also in the manufacture of some useful material, useful reagent which is very useful not only in industry, but also in the laboratory that common teaching laboratories or the different research laboratories which is your calcium hydride. Because the calcium hydride  $\text{Ca H}_2$  not any other sodium hydride not lithium hydride they have other difficulties is the safer material for giving you hydrogen for any other useful reducing agent for the reduction.

Suppose we want to have a very high purity of any organic solvent so not only the sodium wire or the sodium metal can solve this particular purpose because that is also a very good reducing agent, but sometimes we have to use this specialty reducing agent which is your calcium hydride. So, calcium hydride is your specialty chemicals, if you have the bulk chemical, if you have the commodity chemical.

So, you can have all 3 together. One way you can think of the calcium as the bulk material calcium as the mineral, calcium is the ore what we are getting from the earth's surface then we try to convert it to a bulk material or a commodity material based on your dolomite or your limestone or chalk.

Then you try to get the calcium metal. So, slowly we are improving which is known as the value addition it will be costlier, costlier and costlier. So, what we get, you get the calcium metal and that calcium metal can be used for the production of calcium hydride

for the step of your price rise, because you have to use hydrogen from hydrogen gas or any other more important hydrogen source like that what we have seen earlier while we are talking about the sodium as well as boron for making your sodium borohydride or lithium aluminum hydride.

So, these two things already we have discussed which is your sodium borohydride, which is your lithium aluminium hydride now the third category of this particular type of hydride which is very sophisticated one is a costly one and not a very good quality we are making in our country almost of the time we have to imported which is your calcium hydride.

So, is a very good source and very useful source, but only thing is that your formula or your status of this is completely different, but it is typically a hydride or hydrogen source.

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Calcium Oxide and Calcium Hydroxide

$$\text{CaCO}_3 \xrightarrow{>900\text{ }^\circ\text{C}} \text{CaO} + \text{CO}_2$$

Various shaft furnaces (A furnace in the form of a vertical cylinder in which hot gas is forced upwards through the contained solids) or rotary tube furnaces are utilized as calcining units.

Calcium hydroxide is produced by the slow addition of water (slaking) to calcium oxide, the process being strongly exothermic.

The slide also features logos for 'swayam' and 'All India Council for Technical Education' at the bottom, and a small inset image of a man in a white shirt and glasses.

So, what will be getting there then next is like that of your magnesium oxide because we are talking all the time like that metal itself, then its corresponding oxide form and then we get in the terms of its corresponding formation in that of our your hydroxide. So, we go for calcium oxide as well as calcium hydroxide you go for again a 1000 degree temperature. So, always try to remember it something in terms of some temperature range is that whether we will be able to go for some reaction within 100 if it is not

stepwise up to 500 you can remember little bit; that means, what we can get up to 200, what you can get up to 300, then 400 and then 500.

Then in a 500 scale basically what you are not able to achieve up to 500 like that we are making now just now we have seen making magnesia 3 categories or 3 types of magnesia we have seen our previous class, that 3 different temperature ranges we are thinking of one is below 600, another is close to 2000 and another is close to 3000. So, what you find over here is that, around 1000 you just simply burn it. So, burning of this particular process is giving you that calcium carbonate calcium oxide and carbon dioxide.

So, if you think of little bit because these all these things are thermal reactions and why do not you think in this particular form that one of the most important compound of calcium we study from our school days, you study in our college university in everywhere. And then we reach a particular laboratory whether it is industrial laboratory, industrial r and d laboratory or a research a typically academic research laboratory somewhere will be using that particular calcium very important calcium compound that will talk in within few minutes also or maybe in the next class is that is your calcium carbide.

So, if we can have you can imagine basically imagination will give you some new areas, new avenues for industry for everything that if you have calcium, if you have carbon also because carbonate has carbon that carbon is your typical source of carbon whether we will be able to get calcium carbide  $\text{CaC}_2$  out of your calcium carbon which is not known yet. So, that way all these thermal reactions you can think of what is going away what gaseous product is going away what you are living behind.

So, still it has the typical affinity of oxygen carbonate one part as carbon dioxide is removed, but it still had one oxide calcium oxide it is there. So, that calcium oxide above 900 or above 1000 you heat it you will get that calcium oxide. So, that is the simplest process of making industrially important species as calcium oxide.

So, what we use basically there we require shaft furnaces which is nothing, but a furnace in the form of vertical cylinders in which hot gas is forced upwards through the content solid. So, you have the solid; solid means you have calcium carbonate as well as the

formed calcium oxide of different sizes of these grains. So, grain sizes are different, but you have the inter grain space and that inter grain space is important to pass those gases.

So, whatever carbon dioxide will be forming over there will pass through so all these furnaces you can use only the shaft furnace. So, like your rotary furnace or other different forms of is the design. So, design of these furnaces are very important because your mechanical engineer, electrical engineer and all these will help in designing all these things. But as a chemist as inorganic chemist you can have also some important contribution to make that you can think of that I will just take out that gas from the side arm of the furnace or I can take out that gas from the top or some other intermediate positions.

So, what you can think of that designing can help in removing that particular gas and the gas is basically coming over through these all these grains. So, how you can get those grains of the different size because if your starting material which is your calcium carbonate is of different shape and size or different grain size your formed calcium oxide is of different shape or sometimes you can do it in rotary tube furnaces which is we use for your calcining process.

So, you have the calcium as calcium oxide and if you add water in it is giving you the corresponding calcium hydroxide. So, that is also a typical direct process of making calcium hydroxide which is known as slaking. As we know from our again from our school days the slake line we know what is slake line. So, that is also basically the process which is known as slaking which is typically industrial term which is regular and controlled addition of water to calcium oxide.

And because everything is very much heated because the reaction is very temperature removing one; that means, is exothermicity of the temperature is very high. So, solution will come at immediately it can boil if you add very quickly the water. So, slow addition of water for this particular formation of this hydroxide will give you the corresponding slake line and those slake lines has huge application in all the different industrial sectors ok. So, that is about this particular part of calcium ok.

Thank you very much.