Non-ferrous Extractive Metallurgy

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Module No. # 05

Lecture No. # 14

Extraction of Metals from Oxides, Extraction of Magnesium

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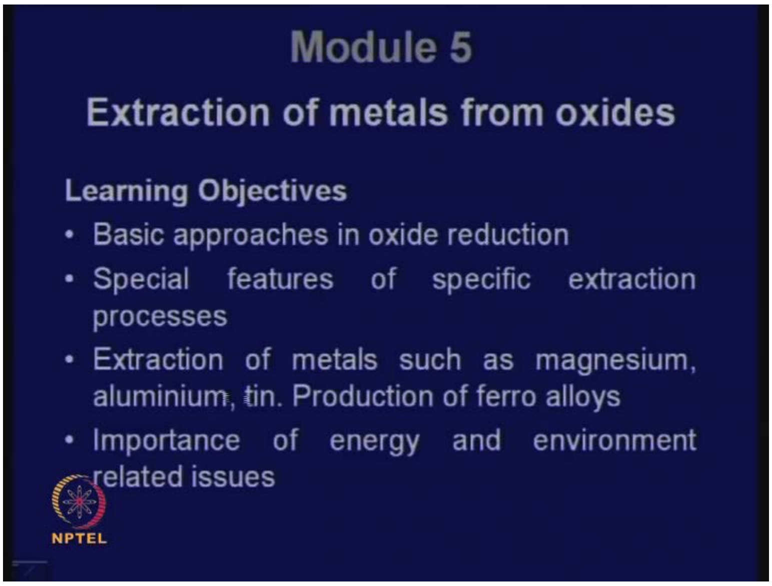

Module 5

Extraction of metals from oxides

Learning Objectives

- Basic approaches in oxide reduction
- Special features of specific extraction processes
- Extraction of metals such as magnesium, aluminium, tin. Production of ferro alloys
- Importance of energy and environment related issues

Friends, in my last lecture, I gave a conclusion of module 4. Until module 4, we did not take up any specific metal to consider its extraction process. We are going to start that, starting with this module, module 5. This module is about production of metals from oxide sources. Now, there are many many metals which occur in nature, in oxide form, one oxide or another. You are all familiar with iron ore, iron ore, or iron oxides, but this course is not about iron, but there are other metals, many of them, which are mostly found in some form of an oxide or could be a carbon, which can be converted into an oxide quite easily.

I will start with magnesium. Why magnesium? The reason, why I will start with magnesium is because it is a very straight forward pyrometallurgical process, easy to understand and the principles are also easy to follow. There could be other reasons to justify why I start with magnesium, but I need not go into that. Before I come to discuss production of magnesium from it source, let me first tell you what are the learning objectives about in this module.

The learning objectives are listed here – first, I will discuss some basic approaches in oxide reduction, which may or may not be of general nature, which may or may not apply everywhere, but for a large number of oxides, the basic approaches will be appeared; we will find that. Then, now discuss special features of specific extraction processes. As I indicated last time, there may be two metals occurring in nature, in oxide form, may be in similar form, but the way we extract them may not be exactly aligned. There are many reasons for that; we will discuss that.

Thirdly, we are going to discuss them individually. As I said, start with magnesium then, I will spend a good amount of time on aluminum or also discuss production of tin and production of ferro alloys as well as one or two others, I will make a passing reference. Earlier in my lectures, I had discussed why we will discuss ferro alloys also although this course is for non ferrous metals. Ferro alloys means alloys of non ferrous metals with iron.

So, it falls both in the category of ferrous metallurgy as well as non ferrous metallurgy, but there is justification of discussing ferro alloys in this course on non ferrous metals, because there are some metals, non ferrous metals which are largely produced as ferro alloys, and the reason for that is, that, these metals which are produced as ferro alloys are often important alloying additions in steel and they will be added as a ferro alloy. Because when you have the metal and iron together in an alloy form, that alloy dissolves much faster in steel also, that is, melting point is low plus it is easier to produce that ferro alloy rather than that alloying element, a non ferrous alloying element in elemental form.

So, it is very very justifiable that I discuss ferro alloys which contain iron as well as large percentages of non ferrous metals. Lastly, I would also discuss as I go along the importance of energy and environment related issues because many of them would be high temperature processes, and energy and environmental related issues automatically become very important.

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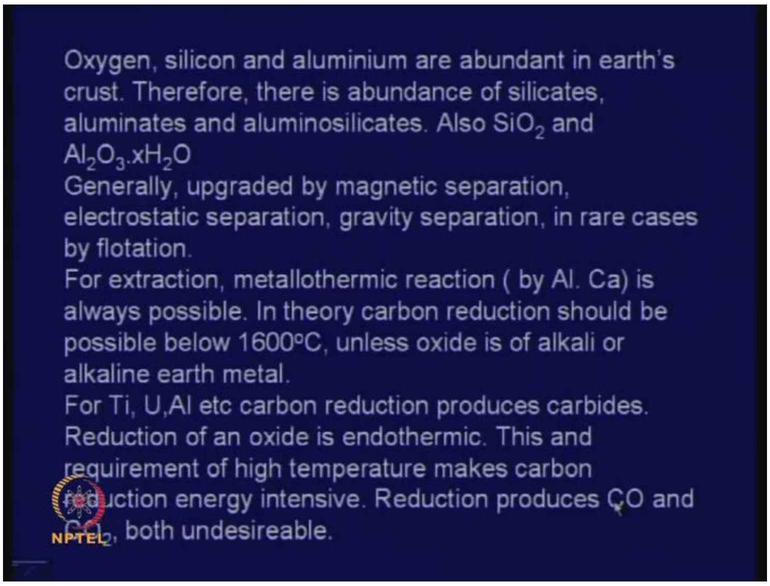

Oxygen, silicon and aluminium are abundant in earth's crust. Therefore, there is abundance of silicates, aluminates and aluminosilicates. Also SiO_2 and $Al_2O_3.xH_2O$

Generally, upgraded by magnetic separation, electrostatic separation, gravity separation, in rare cases by flotation.

For extraction, metallothermic reaction (by Al. Ca) is always possible. In theory carbon reduction should be possible below 1600°C, unless oxide is of alkali or alkaline earth metal.

For Ti, U,Al etc carbon reduction produces carbides.

Reduction of an oxide is endothermic. This and requirement of high temperature makes carbon reduction energy intensive. Reduction produces CO and CO_2, both undesireable.

It should be quite obvious to you that there should be no dirt of oxides in the crust of a planet, because if you remember a table that I had shown in the very beginning regarding relating abundance of elements, we had seen that oxygen, silicon and aluminum are at the very top. They account for most of the elements in earth crust, and then, we will have iron. So, if oxygen, silicon and aluminum are abundant, then it is quite natural that in earth's crust. There is an abundance of silicates, aluminates and alumina silicates. That is why you find sand everywhere.

One also finds abundant reserves of alumina l towards s. There also alumina silicate like a clay; it is an alumina silicates. Now, obviously all that you find in earth's crust they do have oxides, silicates or aluminosilicates, but if you are looking for a specific oxide, then you have to go through some concentration steps. We have to concentrate that particular oxide which we are aiming at from which we will extract - a metal or more than a metal.

Now, there are many methods of upgradation, magnetic separation, electrostatic separation, gravity separation, and in rare cases, floatation is also applicable. Now, this flotation that I have listed may be a different kind of floatation. By different kind, I mean generally in sulphide metallurgy when you float, the sulphide minerals float to the top and the gang material goes down. When we have mass of oxides which are very rich and the gang content is low, we may try a floatation process. Well, it is the gang which floats up, and the oxides you want, they do not float; it could be that kind of floatation. We will come to that as when it becomes relevant.

Now, you also know by now that oxides of aluminum and calcium are very very stable. Therefore, many oxides that we separate out can be in theory reduced by aluminum or calcium at a suitable high temperature. If you remember the Ellingham diagrams, the free energy temperature plots, free energies of formation and temperature plots for aluminum and calcium where far below than the free energy formation plots for many other oxides.

So, in theory, we should be able to reduce many other oxides by using aluminum or calcium. This is in theory but it does not apply on all cases. For example, in theory, you may be able to reduce oxides of sodium or calcium, sodium or potassium, but then, the temperature required may be so high that the elements will volatile; you will not be able to collect. So, there are practical problems. So, the theory may say something but it may not be possible. There is another problem which I had also mentioned.

Oxides of titanium, uranium, aluminum, etcetera in theory should be reduced by carbon because we have seen that carbon monoxide becomes increasingly stable with increasing temperature and all oxides becomes increasingly unstable at high temperature. So, the, to plot cross, the free energy of formation versus temperature for carbon with formation carbon monoxide goes downwards. And for free energies of formation of oxides go upwards. There is always a cross over point. For stable oxide, it is very high; for lower oxide, it for unstable oxide; it is a lower temperature. So, in theory, even oxides have titanium, uranium, aluminum can be reduced by carbon.

But unfortunately there is another reaction which is also thermodynamically feasible that is formation of carbides. See, if you produce reduce try to reduce oxides of titanium, uranium, aluminum, etcetera by carbon, we will not be able to produce the metal; we end up producing a carbide. So, the theory that hints at something does not work. All oxides reductions are endothermic. They need high temperatures. So, the oxide reduction in general would need a lot of heat. Firstly, high temperatures require heat, and secondly, the endothermic. So, that will also need here. Moreover, if you are using carbon as a reducing agent, you produce CO and CO 2 both are undesireable; both I give you pollution problems starting with local problems, regional problems, global problems, global climate change everything.

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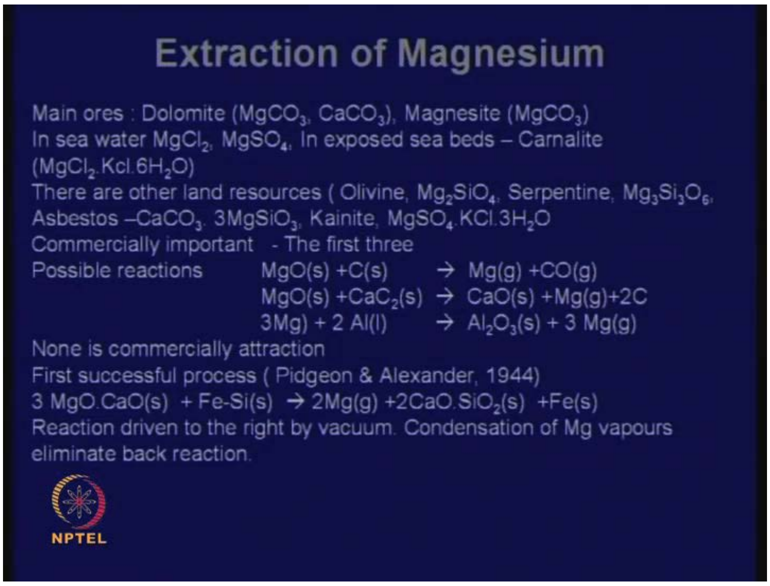

Extraction of Magnesium

Main ores : Dolomite ($MgCO_3$, $CaCO_3$), Magnesite ($MgCO_3$)
In sea water $MgCl_2$, $MgSO_4$, In exposed sea beds – Carnalite ($MgCl_2.Kcl.6H_2O$)
There are other land resources (Olivine, Mg_2SiO_4, Serpentine, $Mg_3Si_3O_6$, Asbestos –$CaCO_3$, $3MgSiO_3$, Kainite, $MgSO_4.KCl.3H_2O$
Commercially important - The first three
Possible reactions $MgO(s) + C(s) \rightarrow Mg(g) + CO(g)$
$MgO(s) + CaC_2(s) \rightarrow CaO(s) + Mg(g) + 2C$
$3Mg) + 2\ Al(l) \rightarrow Al_2O_3(s) + 3\ Mg(g)$
None is commercially attraction
First successful process (Pidgeon & Alexander, 1944)
$3\ MgO.CaO(s) + Fe\text{-}Si(s) \rightarrow 2Mg(g) + 2CaO.SiO_2(s) + Fe(s)$
Reaction driven to the right by vacuum. Condensation of Mg vapours eliminate back reaction.

So, there are practical problems with high temperature reduction processes. We will see what we can do, what we cannot do. Let us start with magnesium. Now, I might start with the uses of magnesium. You do not see magnesium being used in our everyday life, not like aluminum. We have aluminum vessels, containers, aluminum doors and windows, but in many alloys, there is magnesium. You also see magnesium in many places unseen like without magnesium, it cannot have fire crackers.

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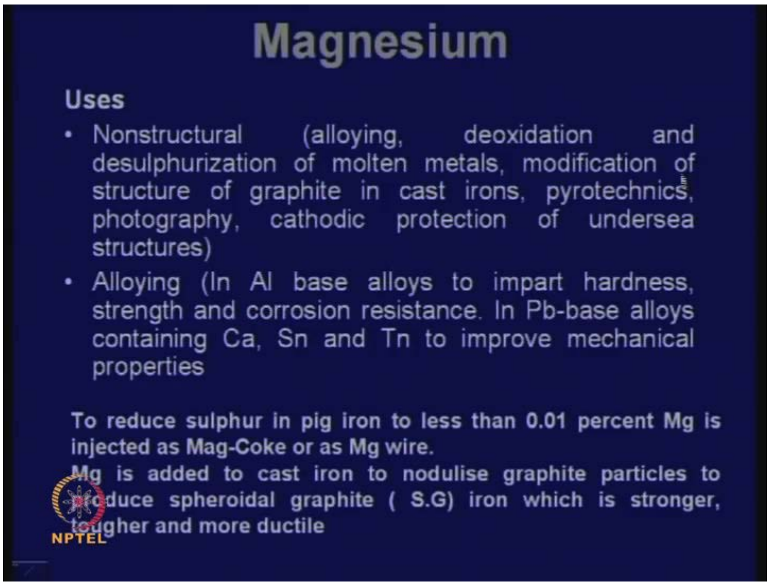

Magnesium

Uses

- Nonstructural (alloying, deoxidation and desulphurization of molten metals, modification of structure of graphite in cast irons, pyrotechnics, photography, cathodic protection of undersea structures)
- Alloying (In Al base alloys to impart hardness, strength and corrosion resistance. In Pb-base alloys containing Ca, Sn and Tn to improve mechanical properties

To reduce sulphur in pig iron to less than 0.01 percent Mg is injected as Mag-Coke or as Mg wire.

Mg is added to cast iron to nodulise graphite particles to produce spheroidal graphite (S.G) iron which is stronger, tougher and more ductile

Now, I am listing here some uses of magnesium. The non structural uses will include alloying in magnesium in many other places. Since magnesium oxide produces a stable, magnesium produces a stable oxide. It is using de oxidation. You want to remove oxygen from some place, add magnesium. You want to remove sulphur from some metals, add magnesium because magnesium sulphide is also very stable.

So, in molten metals, we will add magnesium for de oxidation and de sulphurization. In steel, magnesium is added for modification of structures of graphite in cast irons. You read about modular cast iron that in cast irons, if you add magnesium, then the cast iron flex become nodular rounded. So, the entire property of cast iron changes. I also mentioned the cast iron is using pyrotechnics that is in fire crackers. It used to be very commonly used in photography, because when it burns, it emits a lot of light. So, 40, 50 years ago we use to have those flush bowls which would, which would, burn once lot of light; there are magnesium filament.

Another very interesting use of magnesium is in cathodic protection of undersea structures. You must understand that. Suppose there is a port and there are lot of structures where the pillars are going into the water. Also those that are above the water, they are also exposed to saline environment, both go under, both undergo corrosion. Now, magnesium is used in cathodic protection means chunks, tablets, rods of magnesium are connected to the structure and allow to remain immersed in that environment, in water or in the environment.

The idea is that magnesium is more electro positive, more reactive than iron. So, if there corrosion going to take place, it will be the magnesium which will get corroded. So, magnesium gets corroded protecting the steel structure which is less reactive than magnesium. Actually some of our colleagues and I had gone to Paradeep port once suggesting to the port authorities that they adopt this, because we saw in the structures that they were standing on pillars many of them had been eaten away means a structure going like this. Just near the water, there is a big dent means that is where corrosion is taken, actually maximum corrosion take place when there is a three phase boundary. There is air; there is metal and there is water level. That is where maximum it takes place.

We said that if you just hang some magnesium from the structure, you have protect the structure. Now, some of them thought they have actually asked me - will it grow back again? No, that is not possible. Magnesium is not going to make the structure go back to the original dimension, but it would not allow further corrosion of that. So, that is called cathodic protection that you use a magnesium cathode to protect the rest of the structure.

Now, there are other uses in alloying, in aluminum base alloys, it imparts hardness, strength and corrosion resistance. In lead base alloys containing calcium, tin, etcetera, that improves mechanical properties. I have mentioned that its used in desulphurization and de oxidation is an example in pig iron less than 0.01 percent magnesium is injected at mag-coke or magnesium wire.

The way you add is very interesting. It comes in the wire from it continuously rotated and where goes into the melt and goes on dissolving or there can be a something called mag-coke. That coke mixed with magnesium that can be put in there also. The reason why you have to be careful, otherwise magnesium will float. It is a very light metal. You cannot take magnesium and add in steel; nothing will happen. It will float up and it will burn off. So, you will have to push in on wire or push in their form of mag-coke which will go to the bottom.

As again I have mentioned earlier that it is added to cast iron to nodulise graphite particles to produce spheroidal graphite which is called S G iron, which is stronger, tougher and more ductile. Where does magnesium come from? Magnesium comes from two main sources - dolomite which is written as magnesium carbonate, calcium carbonate together or we can write it as MgCa CaCO 3 twice.

The mineral composition is MgCa CO 3 twice or magnesite which is only magnesium carbonate. This is far more common. There is magnesium in sea water also in the dissolved state as magnesium chloride or magnesium sulphate. There are some exposed sea beds where the water has dried off and there is extensive deposits of carnalite which is written as MgCl 2 KCl 6 H 2 O. It is called carnalite a mineral of this component. There other source like olivine which is a silicate, serpentine, which is also a silicate, asbestos.

The common asbestos you saw that is used for roofing is also a mineral calcium carbonate 3 MgSi O 2. Say it is a combination of calcium and magnesium. Another is called kainite - MgSO 4 KCl 3 H 2 O. Need not remember all this. We should know that the first three are important dolomite, magnesite and the, whatever is available in the sea either in exposed beds or in sea water, for that there will be different process. Let us try to understand how we get magnesium from dolomite or magnesite. The logic should be simple that if you have a carbonate, you can heat it produce MgO reduce by carbon Mg plus CO, or if you have dolomite which is magnesium carbonate dot calcium carbonate or MgCa CO 3 twice, that can also be reduced by carbon or you can take magnesium oxide. It can be reduced by calcium carbide to produce calcium oxide, magnesium and carbon or magnesium oxide can be, there should be an ore here. I am sorry, write it three MgO 3 MgO. It can be reduced by aluminum produce alumina and magnesium vapour.

Unfortunately, none of them look commercially attractive for various reason. I rather not go into that either to temperature requirement is very high and recovery is not good; product does not come, the way you want it etcetera, etcetera. The most commercially in attractive process is reduction of MgO CaO that we get from dolomite by ferrous silicon, where the silicon actually is the reducing agent. You can write the reaction as this magnesium vapour a slag 2CaO SiO 2 plus iron solid.

We will do a thermodynamic analysis of this to show that you simply cannot heat decomposed dolomite MgO CaO with ferrous silicon and get magnesium vapour. You cannot because normally this reaction is not feasible. We have to drive it to the right, and to drive, we will have to manipulate the vapour pressure of magnesium. You have to bring in down, so that the reaction moves rightward.

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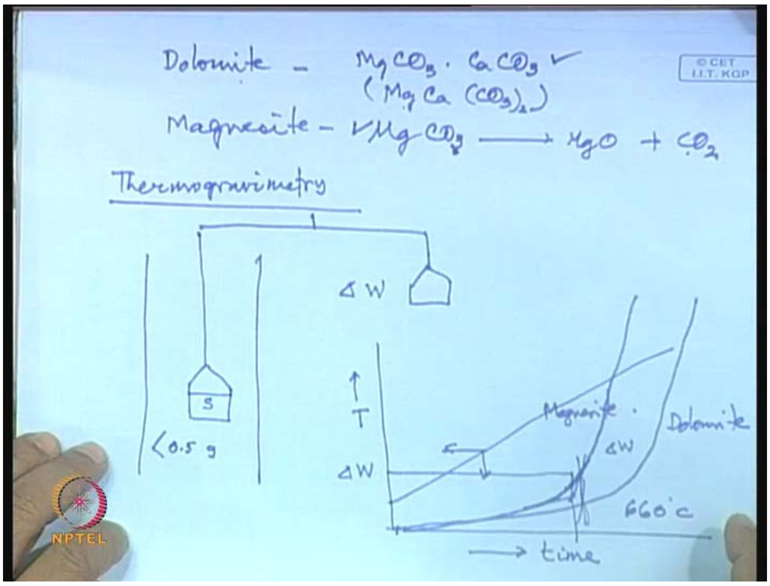

Dolomite - $MgCO_3 \cdot CaCO_3$ ✓

$(MgCa(CO_3)_2)$

Magnesite - ✓ $MgCO_3 \longrightarrow MgO + CO_2$

Thermogravimetry

So, reduction is driven to the right by vacuum condensation of magnesium vapours and that will eliminate back reaction also. Now, before I proceed with this, let me ask you simple question. We are talking about two main things - one is dolomite which is MgCO 3 CaCO 3 or you can write it as MgCa CO 3 twice or we are talking about magnesite MgCO 3. How do you know at what temperature it will decompose? There is a very simple way of finding that in the laboratory. That is why thermogravimetry.

By thermogravimetry we mean that inside a furnace, we keep a small amount of the sample magnesium carbonate or dolomite. The sample size can be very small may be say 0.5 gram horrible less. This is connected to a balance. Now, this furnace is heated and we put it the time temperature plot like this with temperature rises, with time and we keep measuring its weight. We will find that initially there will be the way, there will be no weight loss, but as the decomposition starts, this will start losing weight and the balance can measure it. There is a device for equilibrium equilibration.

So, we can put it like this. This is temperature versus time plot. Let us plot weight loss means W delta W between this and this. Initially it is balancing then start rising then. If you plot the weight loss, we will find that initially there is no weight loss, but after sometime it begins to lose the weight. This temperature where it is beginning to accelerate the weight loss will call it the decomposition temperature.

Now, please mind you what is the meaning of the word decomposition temperature. Talk about the boiling point of water. You know if you take water leave it here in a dry weather, it forms vapour. Does not mean it is boiling. If you increases the temperature, more vapour will come out. We say that under one atmosphere pressure, the boiling point is 100 degrees. It means at 100 degrees, it decomposition gives rise to partial pressure of vapour equal to 1 atmosphere.

So, 100 degrees boiling point of water means the pressure of steel will be one atmosphere at 100 degrees. There is pressure at steam below 100 degrees also. Water is decomposing even below 100 degrees, but by decomposition temperature, we mean 100 degrees when at it is one atmosphere, under one atmospheric pressure of water, which means now its pressure has exceeded the pressure all around.

If we take water to a higher temperature, higher altitude on top of Mount Everest, there the atmospheric pressure is low. So, the water will boil at a lower temperature, because you do not take one atmospheric pressure to have boiling; you can, you do heat less than that. That is what a higher temperature cooking becomes very difficult because water liquid water will not acquire the high temperatures that you get in the planes where the pressure atmospheric pressure is higher.

Similarly, when the pressure MgCO that decomposing into MgO plus CO 2, when CO 2 two pressure becomes one atmosphere, we call it is the decomposing with temperature. The same thing goes with dolomite also. In the case of dolomite also if you plot the weight change, we will find weight change initially will be small. Again at some temperature, it will rise. Which will decompose earlier? Will this decompose earlier or will this decompose earlier? Now, you can apply your common sense. In the case of MgCO 3, MgCO 3, you have pure MgCO 3, whereas in dolomite, you have MgCO 3 in solution. So, it is in more stabilized form.

Therefore, one has to go to a slightly higher temperature to decompose dolomite, for dolomite. This is for magnesite, is that clear? Magnesite will decompose more easily because pure, but in dolomite, magnesite is in a kind of solution. There is calcium carbonate also. So, it will decompose later. Now, generally the decomposition temperature of MgCO 3 is around 660 degrees centigrade. There is another way in the laboratory find out decomposition temperatures and that is why differential thermal analysis.

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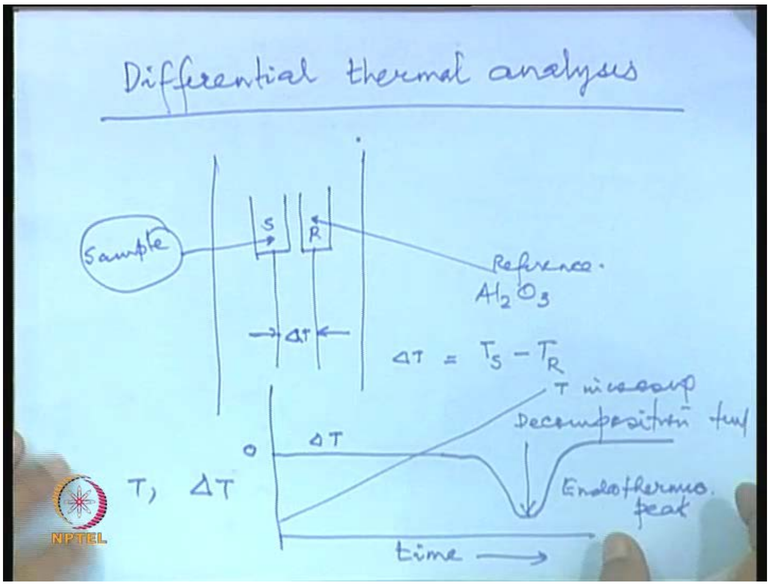

In this two small crucibles are kept close together. In a furnace each with a thermo couple in one, we keep the sample, that is, dolomite or magnesite. In another, we keep a reference material like alumina where nothing happens when you heat. It does not decompose, does not lose weight, it does not gain weight. What we and there are no enthalpy changes also and there is an arrangement to measure the temperature difference between this two delta T is equal to T S minus T R. Again what we will do is with time, we will slowly increase the temperature of the furnace; we constantly measure delta T.

We will find initially delta T is 0. T is going up like this increasing. This is delta T; it will be initially 0 because nothing is happening here; nothing is happening in the sample. They both being heated at the same rate. They both increasing in temperature, but they are equal means there is no difference in between the two.

But a time comes where a decomposition reaction starts here in the sample, and when a decomposition reaction starts, it rise in temperature gets arrested. So, the reference goes up. So, the delta T between these two reference temperature continues to grow up, but the samples temperatures cannot grow up because of decomposition reaction is taking place and it is an endothermic reaction. So, they will build up a delta T. After it is all over, it will again catch up and they will both grow up. So, the plot will be something like this; it is an endothermic reaction.

Again try to understand. Side by side we are rating two crucibles - one has the carbonate sample; the other has the reference. There is no change difference in temperature between the two. They are both rising, then suddenly decomposing starts here. Temperature cannot go up anymore; it is an endothermic reaction. This continues to go up with the furnace temperature. This one lands behind until everything is over and then it will go and catch up with n. So, the delta T will plot an endothermic peak. This is known as decomposition temperature which will be around 660 degrees.

Now, so, these are two common methods of finding out what will be the decomposition temperature of magnesium carbonate. Now, once we have got, we, once, once, we have roasted rather decompose the dolomite, we have MgO CaO and then we can reduce it by ferrosilicon. Basically, the reducing agent is silicon. Iron is not the reducing agent is silicon. Why I am writing ferrous silicon, because in the market, it is much easier to procure ferrosilicon because ferrosilicon is produced as a ferro alloy. Producing pure silicon is lot more problematic nor is it required. That is why although silicon is the reducing agent. We are adding ferrosilicon as it is here.

But that also is an advantage. This ferrosilicon is iron part will play a role and I will come to that. Anyway, this reaction is like this. Magnesium will produce vapour, calcium will combine with silicon because silicon is the reducing agent. Iron is there. It really did not have a role as a reducing agent; it will be left free as a solid because the reaction is occurring around 1000 degrees.

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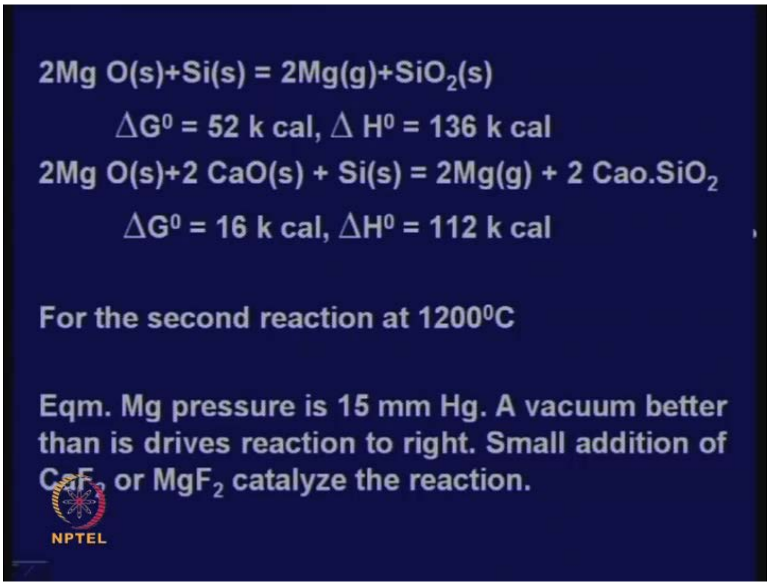

$2MgO(s)+Si(s) = 2Mg(g)+SiO_2(s)$

$\Delta G^0 = 52$ k cal, $\Delta H^0 = 136$ k cal

$2MgO(s)+2CaO(s) + Si(s) = 2Mg(g) + 2 Cao.SiO_2$

$\Delta G^0 = 16$ k cal, $\Delta H^0 = 112$ k cal

For the second reaction at 1200^{0}C

Eqm. Mg pressure is 15 mm Hg. A vacuum better than is drives reaction to right. Small addition of CaF_2 or MgF_2 catalyze the reaction.

Now, if you make an analysis, thermodynamic analysis of both the reaction, one is that the reduce MgO by silicon. I am ignoring iron for the moment because iron really has no role excepting that in ferrosilicon iron is the vehicle for silicon. So, we consider decomposed magnesite which is 2MgO. It will be reduced by silicon to produce Mg, vapour and silicon. For which the free energy change in the reaction is plus 52 kilo calories, which means if you have pure MgO, pure silicon, if Mg is coming out as one atmospheric pressure, I have now silicon is there as silica unit activity. Then the reaction is thermodynamically not feasible.

Now, if silicon is to be taken as a ferrosilicon where the activity of silicon is less than one, it is convenient to have it that way, but then the reaction becomes more unfeasible, because then the activity of silicon less than one means the reaction will be driven to the left, generated it into the left. Coming to decomposed dolomite which is I am separating out 2MgO and 2CaO as though we have to separate. This is also positive 16 less than that, but it is also positive. Now, consider the second reaction. You can write delta G naught is equal to minus RT l and K and the K will be equilibrium constant activity of CaO SiO 2 PMgO to the power square activity of silicon, activity of CaO, activity of MgO. Let me write that.

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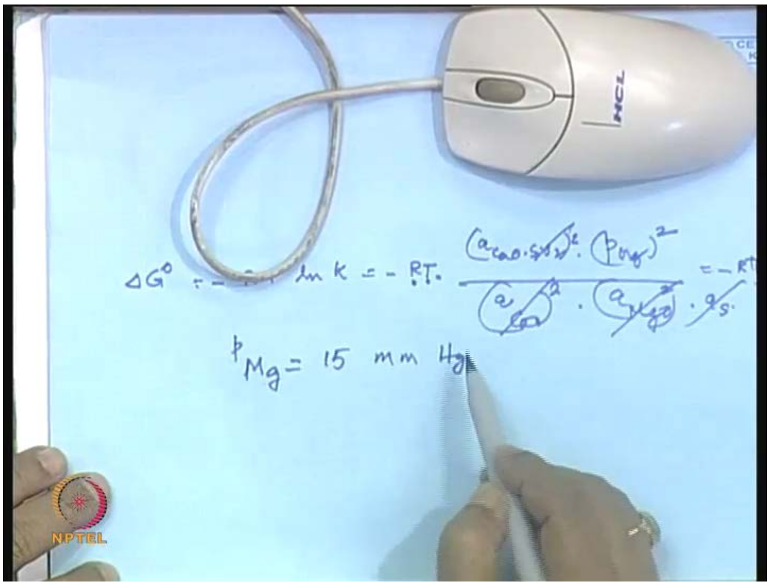

$$\Delta G^0 = - \ln K = - RT \cdot \frac{\cancel{(a_{CaO \cdot SiO_2})^2} \cdot (p_{Mg})^2}{\cancel{(a_{CaO})^2} \cdot \cancel{(a_{MgO})^2} \cdot \cancel{a_{Si}}} = - RT$$

$$p_{Mg} = 15 \text{ mm Hg}$$

Delta G naught will be minus RT lawn K; equilibrium constant K is activity of CaO SiO 2 square into PMgO square divided by activity of CaO square, activity of MgO square. Now, they are in pure states plus there is also activity of silicon. Now, they are in pure state. So, forget about all this. Basically it comes to minus RT P Mg square. We can put values of R and kilo calories T is T to the power. If we calculate for 1200 degrees, pressure of magnesium would be 15 millimeter Hg. So, if it is less than 15 millimeter Mg, this reaction will be possible; that means if you apply vacuum, so that the pressure of Mg is less than 15 millimeter. Then this reaction which we are trying to analyze the 2 MgO 2 SiO 2 SiO 2, it will become feasible. We get the arrow like this. Is that clear?

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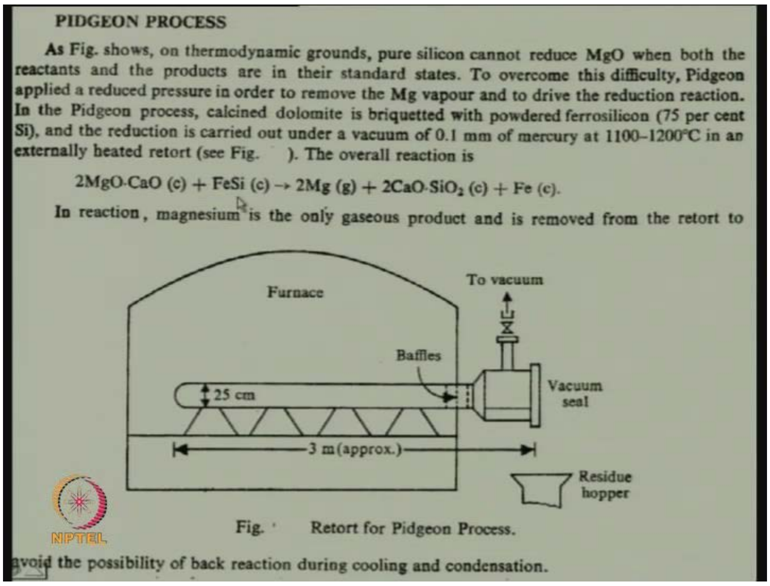

PIDGEON PROCESS

As Fig. shows, on thermodynamic grounds, pure silicon cannot reduce MgO when both the reactants and the products are in their standard states. To overcome this difficulty, Pidgeon applied a reduced pressure in order to remove the Mg vapour and to drive the reduction reaction. In the Pidgeon process, calcined dolomite is briquetted with powdered ferrosilicon (75 per cent Si), and the reduction is carried out under a vacuum of 0.1 mm of mercury at 1100–1200°C in an externally heated retort (see Fig.). The overall reaction is

$$2MgO{\cdot}CaO\,(c) + FeSi\,(c) \rightarrow 2Mg\,(g) + 2CaO{\cdot}SiO_2\,(c) + Fe\,(c).$$

In reaction, magnesium is the only gaseous product and is removed from the retort to

Fig. Retort for Pidgeon Process.

avoid the possibility of back reaction during cooling and condensation.

We have just consider one reaction and calculated the partial pressure of magnesium and we have come to the conclusion that it has to be less than 15 millimeter MgO. This is exactly what was done, what was accomplished by gentlemen called pidgeon with some of his associates during the Second World War.

Incidentally l m pidgeon after the war became the head of the department of metallurgy at university of Toronto, and when I joined university of Toronto as a graduate student, he was the head. The very kindly old gentleman totally British, but he was very famous boy at that and he was also decorated by the British, because he made it possible for England to produce during the war magnesium metal which were required urgently not only for alloy making, but many explosives and other things.

His method was basically this. He actually took this decomposed dolomite reduced it by ferrosilicon. Here, the word c means solid many books write c as crystal. I have taken it from my own book I have been using writing the word c but its s. Magnesium vapour 2CaO SiO 2 solid iron solid. So, again I will read what is written here. On thermodynamic grounds, pure silicon cannot reduce MgO when both the reactants and products are in the standard states.

To overcome this difficulty, pidgeon applied a reduced pressure to remove the magnesium vapour to drive the reaction reduction reaction to the right in the pidgeon's process. Calcined dolomite is briquetted with powdered ferrosilicon 75 percent silicon, 25 percent iron and the reduction is carried out under vacuum of 0.1 millimeter mercury.

So, 15 millimeter would make it feasible 0.1 millimeter mercury at 1100 to 1200 degrees in an externally heated retort as I shown here. Now, this is a retort which is in a furnace. The retort is protruding out because magnesium vapours will come and there are baffles here. Magnesium vapours will come, and by the time they are coming here, temperatures has come down. It is almost outside the furnace. They will solidify there; they would not escape through right here.

And they can be taken in to the, it can be removed, and later on, the magnesium metal can be removed. It is about 3 meter approximately is the length. Now, two things happen here. First of all, you get your solidifying magnesium vapours, and once they get solidified, there is no chance of any back reaction between magnesium and any residual oxygen whatever that can be its not possible.

Now, in theory, this is very simple, but this reaction also raises some questions. I have always been emphasizing this is not a coursing chemistry that we write a reaction. We always think of the mechanism. How does the reaction take place, because once you understand the mechanism, you can manipulate the reaction. Firstly, you understand the weight is written is solid calcined dolomite reacting with solid ferrosilicon.

Now, any solid solid reaction is not a very efficient reaction, because solid solid reaction means the there must be in touch, and if you put a whole lot of solids together, you will find the touch only at certain points. They do not get compacted to each other. So, their interfacial contact areas are very small. Now, I will ask the question suppose you had put one solid here, another solid here, will the reaction take place? It will not take place because they are in not in contact. If they just happen to touch each other, reaction will take place, but it will a very slow reaction. Kinetic should be small because there is not in a surface area for reaction. So, many people have suspected that although you are writing the reaction like that, this is not the mechanism of the reaction because it implies solid solid reaction which it is really not.

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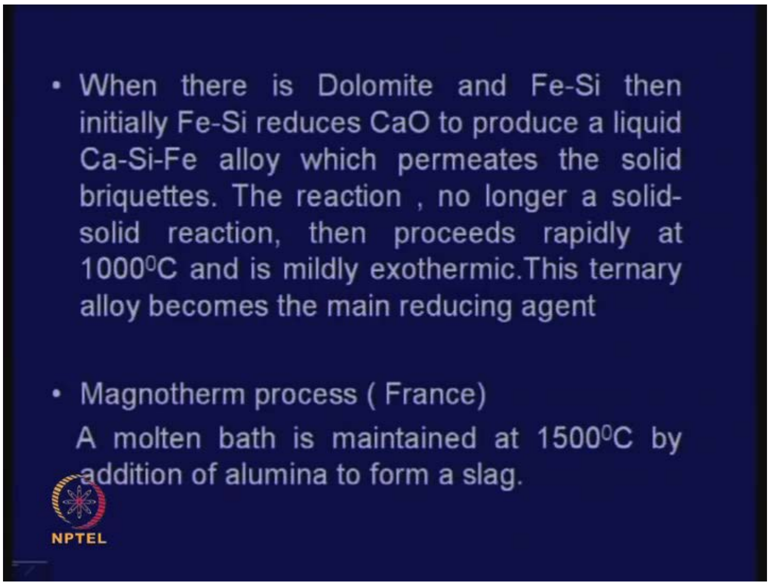

- When there is Dolomite and Fe-Si then initially Fe-Si reduces CaO to produce a liquid Ca-Si-Fe alloy which permeates the solid briquettes. The reaction , no longer a solid-solid reaction, then proceeds rapidly at 1000^{0}C and is mildly exothermic.This ternary alloy becomes the main reducing agent
- Magnotherm process (France)

  A molten bath is maintained at 1500^{0}C by addition of alumina to form a slag.

And then, further studies approved that the suspicion is correct. What happens is that, when you have dolomite and you have calcine to produce a powder which is actually calcium oxide, magnesium oxide and you are putting ferrosilicon. You can powder that also 75 percent silicon. Initially ferrosilicon reduces small amount of calcium oxide to produce a liquid calcium silicon iron alloy. Once you have done that, the nature of the reaction changes entirely; it is no longer a solid solid reaction.

Now, let us take it as a conjecture. Is it possible? Why should it not be possible? Silica can always reduce a small amount of calcium oxide and produce calcium metal and calcium metal silicon iron produces a low melting ternary which has a melting point lower than that of ferrosilicon. Once you have that, then in the briquettes that you have made by putting together calcine dolomite and ferrosilicon. Of course, you make a briquette. So, they bring the particles together to increase contact area of particles.

Now, in the contact area is no longer here. You have actually allowed a liquid metal to permeate also. So, we have now created a medium for easy reaction. So, the reaction is no longer a solid solid reaction, which it would have been had there been no alloy of any kind. The reaction would now proceed rapidly at 1,000 degrees because that liquid layer takes in reactants brings in products, takes in reactant, then it permeates the entire body and the nature of the reaction changes and this reaction is also slightly exothermic. So, it is an advantage.

This ternary alloy is now the main reducing agent. It is not ferrosilicon which is reducing. It is calcium, iron, silicon, ternary, alloy, which you get it is here. So, it is really not a solid solid reaction. Now, the idea of saying all this is it has nothing to do with thermodynamics. It has a bearing on kinetics. Like you know, you can say if you, supposing you have sugar to dissolve in water thermo dynamically dissolves, but if you make a big crystal of sugar, put it in water. It has only that much of surface area which dissolves which will take long time to dissolve, but if you take the sugar crush, it make fine powder surface area is very large.

So, at the same temperature, in the same kind of stirring same environment, it will dissolve much faster because you have much larger surface area. Similarly, in this case, it is no longer a solid solid reaction. It becomes a solid liquid reaction and a liquid permeates all surfaces of solids. So, it is not changing thermodynamics is changing kinetics this is the basis of Pidgeon's process, which was developed during the Second World War.

Now, there have been other developments in pedgion's process. One development is magnetherm process in France. In magnetherm process, they have answered this suspicion about solid solid reaction etcetera by going to a much higher temperature 1500 degrees. You do the same thing; you take ferrosilicon. You take calcined dolomite, take to 1500 degrees and add alumina in this to form a slag. So, you deliberately form a slag. So, what you are doing is you are producing now calcium, oxide, silica, alumina a ternary slag and you are producing an iron metal which is a vapour, and if there is ferrosilicon iron, that would go also go into the slag or it will remain as liquid iron.

Basically, the whole idea is to speed up the whole thing. First of all going to 1500 degrees means your kinetics is rapid. Severally, you just eliminate this question of solid solid reaction; bring in a low melting ternary that will permeate etcetera, nothing with that. Just go to 1500 degrees, make everything liquid. You have a liquid slag to make it facilitate, making a liquid slag put alumina and you can make a slag which will be useful elsewhere for cement making or whatever that iron may separate out depending on the atmosphere. If they reducing atmosphere, you are (( )) in a separate layer.

So, from ferrosilicon, you get the turn, but our main aim is that product which is coming out as a vapour. Incidentally, at that temperature, perhaps you will not need this kind of vacuum, because at that temperature, lot more than the cement come out. So, it will be easier to recover magnesium also. So, this is magnetherm process. So, let me summarize now. I have started a module 5 which is about extraction of metals from oxides by saying oxides are very common, because in earth’s crust, you have abundance of aluminum, silicon and oxygen. So, we have silicate, aluminous, alumina silicates.

In this oxides, many other oxides are also present, but there are also other deposits which are oxides, which do not have alumina or silica like magnesite or dolomite. Plenty of this deposits are available. From dolomite which is more abundant; by calcinations, we produce Mg MgO CaO. This is the main raw material for magnesium production. Calcined dolomite which will be calcined at about 6, 700 degrees without fusion. It will be reduced by ferrosilicon at around 1000 degrees. So, produce magnesium paper which will be condensed and collected.

Without application of vacuum, this reaction is not possible because our calculation show partial pressure is only 15 mm mercury. Vacuum apply this much much better than that. So, lots of magnesium can be produced this way. That is how it was produced during Second World War very successfully and a process continues. This was tried out in national metallurgical laboratory Jamshedpur and a pilot plant was also run for a long time. Unfortunately, for various reasons as I said, it may be good in r and d, pilot plant also worked, nut it wasn’t give commercial success some 10 years ago the plant was closed down then it remained close for many many years until some party bought the whole, whole, plant, but they have also failed to operate that plant. So, we are not producing magnesium in our country although attempts are going on. To modify the pidgeon’s process, many modifications possible; I need not go into that. Thank you very much.