Chemical Reaction Engineering - II
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Lecture – 43
Fluid-Solid Non-Catalytic Reactions I

Friends let us look at fluid solid non catalytic systems. In the next 3 lectures we are going to look at what are the different aspects related to fluid solid reactions in non-catalytic systems and how to appreciate the reaction process which is occurring in the solid in non-catalytic systems and how to model these systems.

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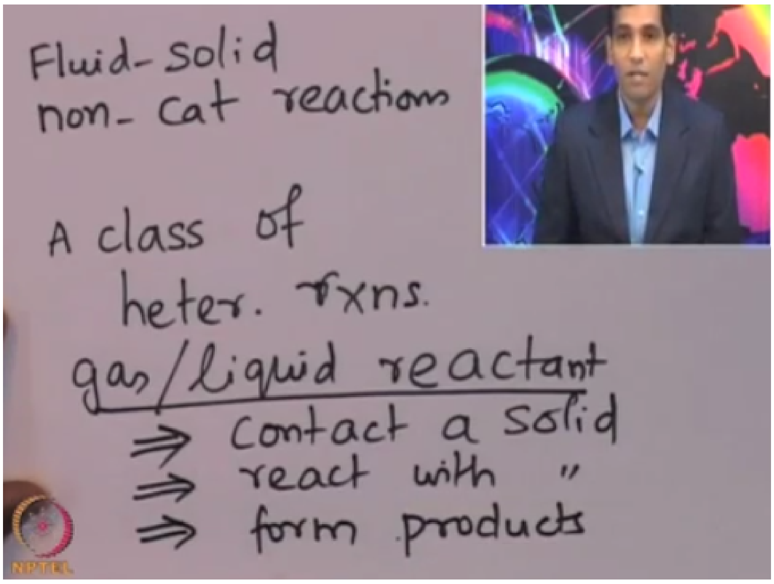

Fluid-solid
non-cat reactions

A class of
heter. rxns.
gas/liquid reactant
⇒ contact a solid
⇒ react with "
⇒ form products

So the fluid solid non-catalytic reactions, fluid-solid non-catalytic systems, so these are essentially heterogeneous reactions which where the gas or the liquid they actually come in contact with the solid and then they react with the solid and then they transform the reactants into a products okay, so these are a class of heterogeneous reactions where the gas or a liquid which is essentially a reactant.

A gas or a liquid reactant they come in contact with the solid, they contact a solid and then they react with the solid and then form products. So this is very common in many industrial settings and we are going to see several examples of these today and also to look at how to model these systems.

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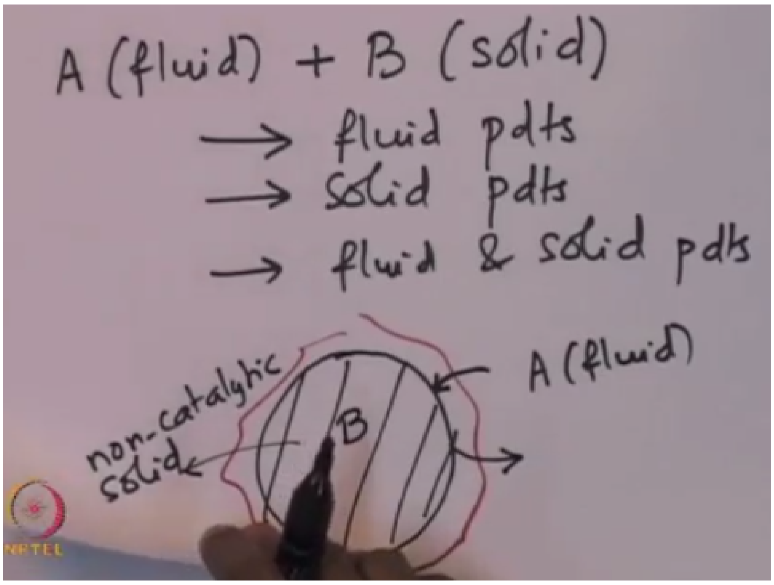

So suppose if the reaction is in general if suppose there is a fluid A, which is a fluid, it may react with a solid B to form various types of products. So there are various possibilities, one is the product might be a fluid, so it might be fluid products, so the fluid reacts with the solid B and then it forms a fluid product or it might form a solid product or it might form a combination of fluid and solid products together.

So any of these 3 possibility, any of these 3 can occur because of a fluid solid non-catalytic reaction. So now if we look at what happens exactly. Suppose if there is a catalytic core okay. Suppose if there is a solid and it is a non-catalytic solid core which is present then suppose if this is B, B is that particular reactant and there might be A, which is in the fluid stream, which might be present around this particular solid, it might be present around the solid.

And the species A now moves into the solid and then it reacts with the particular species B and then the product is now removed from this B, from this particular species. Remember that it is a non-catalytic system. So now there are 2 possibilities or 2 different classes of such type of fluid-solid non-catalytic systems.

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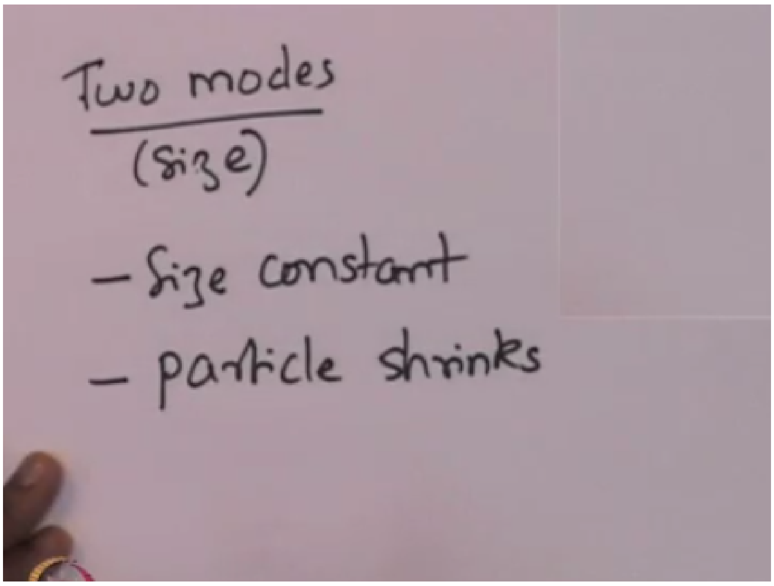

Two modes
(size)
- Size constant
- particle shrinks

So I call it 2 modes, there are 2 modes that are possible, 2 particular modes and this classification is based on the size of the solid core which is actually participating in the heterogeneous reaction. So one mode is where the size remains constant, one mode is where the size of the solid core which actually remains constant, another one where the size actually shrinks that is the particle actually shrinks.

So there is a change in the size of the solid particle, so there are 2 modes based on the classification based on size. One is the, one is where the size remains constant, the other one is where the size actually shrinks. Here it is assumed that the density of the solid reactant and product are not very different, it should be noted that if the densities are different then the particle can also expand.

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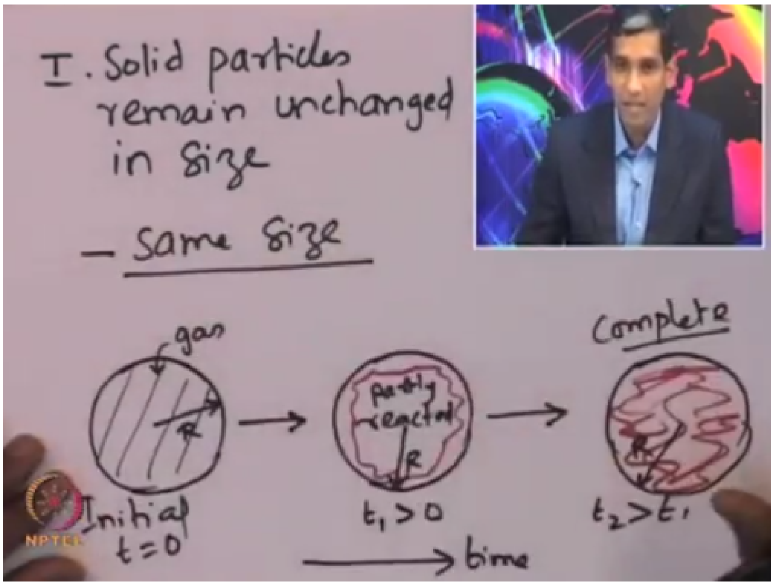

I. Solid particles remain unchanged in size
- Same size

So let us look a little bit more deeply into these 2 modes. So the first mode is where the solid particles remain unchanged in size, this remain, so the size remain same which means that it is a same size all through the reaction is being conducted. So now suppose if I have a solid, suppose if I take a spherical particle now this is the initial unreacted solid core. So let us say at time T = 0.

Now as the reaction proceeds suppose there is a gas which is present outside and the gas actually gets into the solid and there is a certain reaction which is happening and after a certain time what happens is let us say that there is in this particular case there is a, the size does not change and so there is some parts of the solid core which is actually undergone a reaction. So there might be, so it is basically partly reacted, so it is a partly reacted. Remember that the size does not change.

So if the radius of this core is R, the radius continues to remain as approximately the same size as the initial size of the particle. So this might be some time t1 which is > 0 and then as time further proceeds as the reaction proceeds to further conversion as there is more conversion of the reactants then one can see that suppose if this is the particle where remember that the size remains same, the size does not change in this particular mode; however, there is more amount of reactant which gets converted.

So this could be like a completely converted situation where t2, which is greater than t1. So as time proceeds so this might be a complete conversion, this might be a complete conversion situation. So as time proceeds slowly the gases will go inside and then the reaction will start occurring from the outer periphery and then it will start going into the reactants will go inside and the reaction will proceed inside and the complete conversion will occur; however, while the reaction occurs the size of the particle does not change.

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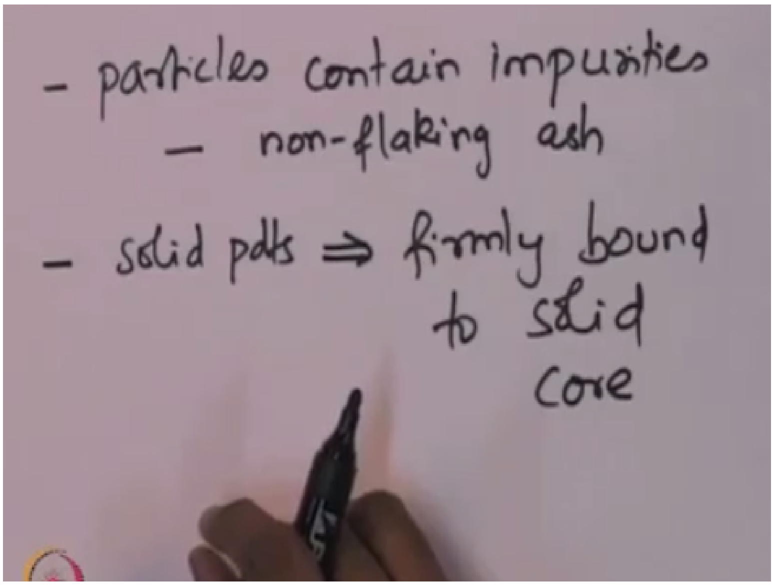

- particles contain impurities
  - non-flaking ash
- solid pdts ⇒ firmly bound to solid core

Now how is this possible this particular mode is possible when the particles they contain, particles contain lot of impurities. So these impurities are actually they are tightly bound to the solid core. So these impurities are tightly bound to the solid core and they remain as a non-flaking power ash. So what happens is these impurities after the reaction is actually being conducted.

So these impurities continue to stay inside the solid core and therefore it preserves the shape and size of the solid core and therefore these impurities they remain as a non-flaking ash as the reaction proceeds and the other possibility how this particular mode can actually occur is where the products are actually solid products. If solid products are formed they are firmly bound to the solid core.

So if the solid products form and they are very firmly bound to the core in which the heterogeneous reaction is occurring then the size does not change, it actually preserves the size and pretty much the shape of the solid. So this particular, this aspect actually helps the solid core to retain it is shape. So now let us look at a few examples of, few realistic examples of under what kind of systems this mode has been observed.

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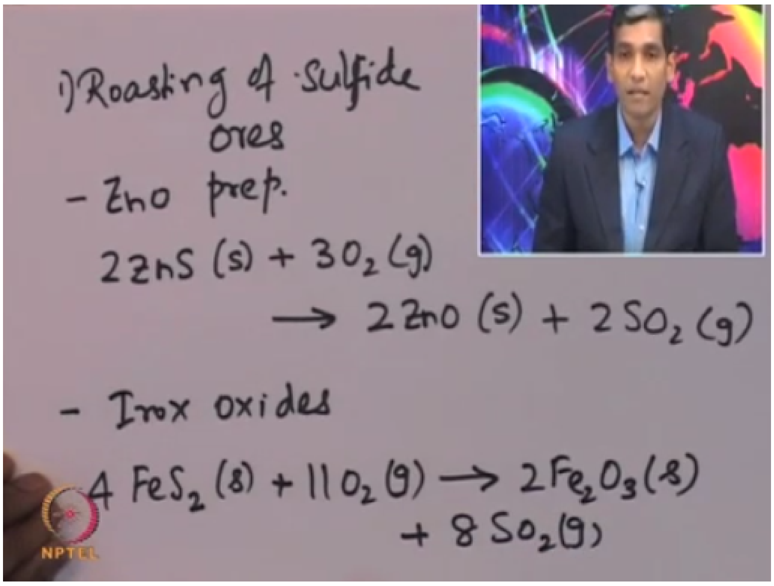

i) Roasting of Sulfide ores

- ZnO prep.

$2ZnS (s) + 3O_2 (g) \rightarrow 2ZnO (s) + 2SO_2 (g)$

- Iron oxides

$4 FeS_2 (s) + 11 O_2 (g) \rightarrow 2Fe_2O_3 (s) + 8 SO_2 (g)$

So one good example is where the roasting of sulfide ores. So roasting of sulfide ores is basically a sulfide form for example zinc sulfide and roasting process is where there is an oxidation reaction. So the oxygen is these zinc sulfide is exposed to oxygen under certain conditions and it lead to formation of the zinc oxides. So it is basically formation of zinc oxide from zinc sulfide.

And zinc sulfide is actually available in nature in solid form and the oxygen which is a fluid undergoes a non-catalytic reaction and it leads to the formation of the zinc oxide which also is a solid product. So therefore the nice example is where it is a zinc oxide preparation and the reaction scheme is 2 zinc sulfide and 3 oxygen molecules, they combine together to form 2 zinc oxide, which is again in the solid form and then it leaves out sulfur dioxide.

So that is the reaction scheme. So this particular example actually the reaction follows the first mode of fluid-solid non-catalytic heterogeneous reaction type where the size of the zinc sulfide particle, sulphide ore that was used does not change much in the size. So the actual industrial processes the ore is taken and then it is crushed and then it is sized into a certain size and then it is put into a certain type of reactor where the oxygen, the air is being fed and then it reacts with zinc sulfide and then forms zinc oxide which is a solid product.

Another example of that is the preparation of iron oxides and the way it is done is 4 times, 4 ferric sulfide in the solid form that reacts with 11 molecules of oxygen and that gives 2 Fe2O3 solid and 8 sulfur dioxide yes. So that is another example of heterogeneous reaction, which follows this first mode of fluid solid non catalytic reaction. Another example is where we have magnetite which is Fe3O4, which is actually being reduced for the formation of the metal ion.

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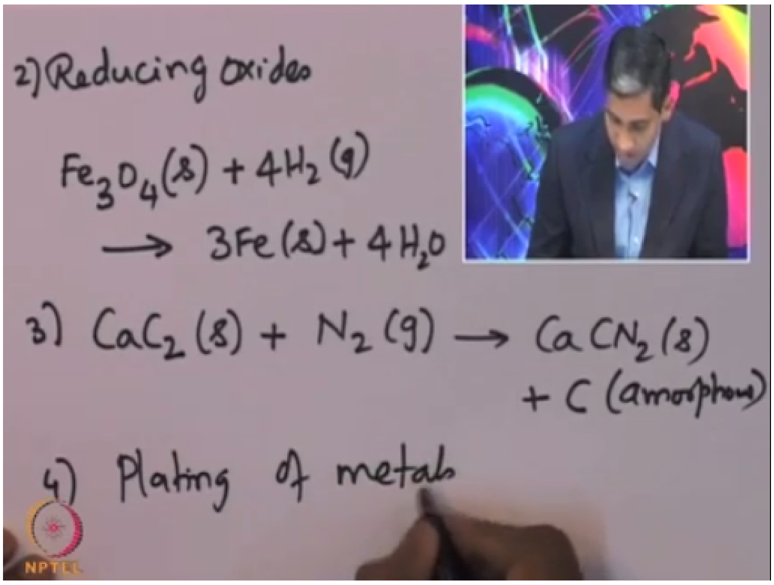

2) Reducing oxides

$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O$

3) $CaC_2(s) + N_2(g) \rightarrow CaCN_2(s) + C$ (amorphous)

4) Plating of metals

So the second example is reducing oxides. So in the case of reducing oxides what happens is that the Fe3O4, which is actually present as in the solid form as a natural ore is actually, it is called the magnetite what is done is, it is actually crushed and then it is sized and then it is actually fed into a counter-current fluidized bed reactor, continuous counter-current fluidized bed reactor at the presence of hydrogen and this particular presence of hydrogen it gets reduced to forming the metal iron.

And so the reaction scheme is +4 H2, which is again in the gas form that leads to the formation of 3 times Fe + 4 times H20. So that is the reaction scheme which is used for reducing the oxides. Another example is the formation of calcium cyanamide where CaC2 which is basically the calcium carbide that is, which is again for present in the solid form and that reacts with the nitrogen N2 and that leads to the formation of CaCN2 which is again in the solid form and then it also leaves amorphous carbon as deposits.

So clearly in these examples there is a solid product which is formed which gets deposited onto the solid core in which the fluid-solid non-catalytic reaction actually occurs and this helps in preserving the size of the core. Another example is basically the plating of various metals. So for various purposes different metals are actually coated on to the surface using this method called electroplating.

And so in this plating where the original core does not change, but then the reaction actually occurs in the fluid-solid non-catalytic reaction actually occurs without changing the size of the original solid core. So the second mode is basically where the essentially the particles shrink.

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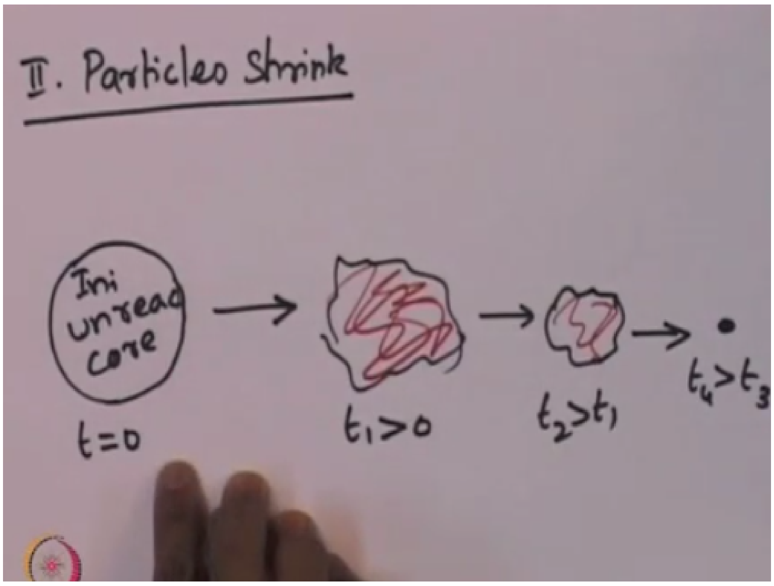

So there is a shrinking of the particles and in this particular case what happens is suppose if this is the initial unreacted core, so let us say at time t = 0. So as time proceeds the size of the particle changes because the solid is now being used and then it is converted into products and then it is being consumed. So there is a reduction in the size of the catalyst particle and that is said let us say time t1 >0.

And there is still unreacted core which is present inside, this is the unreacted core which is reduced in size and then as time further proceeds the size further reduces down. So this is let us say t2 > t1, at a further time and then as time proceeds further it gets reduced into, the solid core actually disappears. So this is because the solid which is present in the initial unreacted core is now almost completely consumed.

And so as time proceeds we can see that the core is slowly being consumed and then the core completely disappears. The particle can reduce in size even when there is a product layer around it. So there are several examples where this particular mode of heterogeneous reaction occurs and typically this occurs when there is reaction that involves carbonaceous materials.

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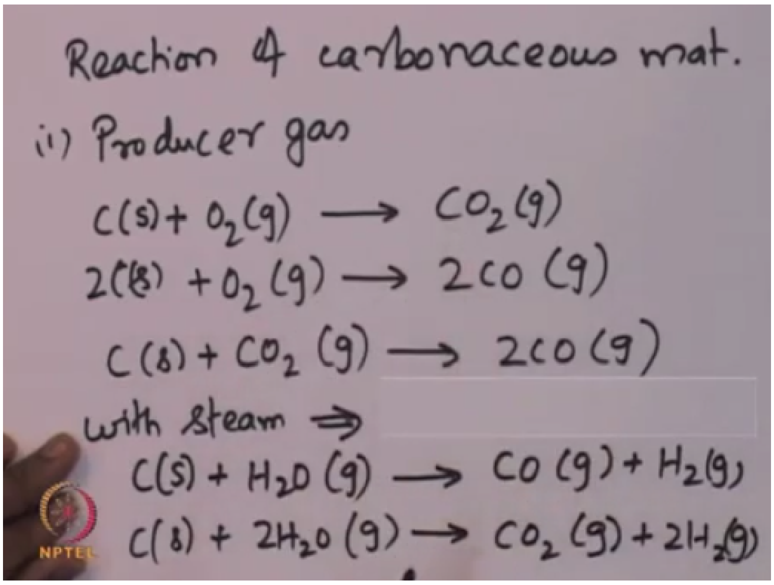

Reaction 4 carbonaceous mat.

(i) Producer gas

$C(s) + O_2(g) \longrightarrow CO_2(g)$

$2C(s) + O_2(g) \longrightarrow 2CO(g)$

$C(s) + CO_2(g) \longrightarrow 2CO(g)$

with steam ⇒

$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

$C(s) + 2H_2O(g) \longrightarrow CO_2(g) + 2H_2(g)$

So typically reactions that involve carbonaceous material, they generally follow this mode where the size of the solid core actually constantly decreases and then the core eventually disappears. So a nice example of that is the production of the producer gas and this is generally performed at a rare limiting conditions and so the reaction scheme is that carbon which is present in the solid form that reacts with oxygen which is in the gaseous form and that leads to the formation of CO2 in the gas form.

Now similarly in another scheme (()) (17:34) simultaneously is carbon it reacts with oxygen to form carbon monoxide this is again occur simultaneously along with the first reaction and then another reaction which also occurs with is carbon when it reacts with CO2, so CO2 which is also formed by this reaction it again interacts with the unreacted carbon which is present in the solid core and that leads to formation of 2CO.

So this is the reaction scheme for producer gas. Suppose if the reaction is conducted in the presence of steam then it leads to the formation of CO or CO2 and H2, which is the carbon gasification reaction and the scheme is the carbon and water. So steam is essentially the vapour form of water and that leads to CO and H2 and carbon in the presence of 2 water molecules that lead to formation of CO2 in the gas stream and 2 hydrogen molecules.

So both these reactions typically occur in a situation where the solid core which is basically unreacted carbon when to start with it is slowly being consumed and then the carbon eventually disappears. So that is basically the mechanism that has been observed for in the producer gas production. So similar process actually occurs in the manufacture of carbon disulphide.

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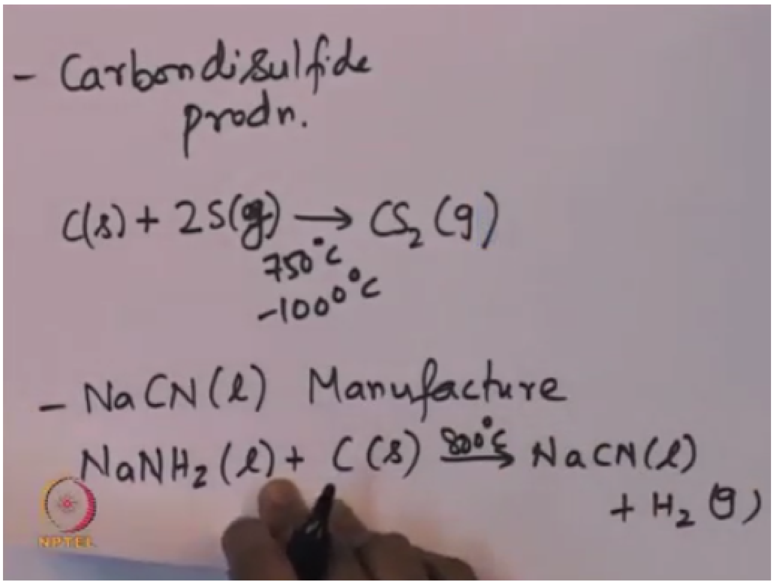

- Carbondisulfide prodn.

$$C(s) + 2S(g) \xrightarrow[750^\circ C - 1000^\circ C]{} CS_2(g)$$

- NaCN (l) Manufacture

$$NaNH_2(l) + C(s) \xrightarrow{800^\circ C} NaCN(l) + H_2(g)$$

Suppose if we look at carbon disulphide productions, then the reaction scheme is carbon in its solid form reacts with 2 sulfur molecules, which is again in the gas form and that leads to the formation of CS2 and this typically occurs at 750 degree to 1000 degree C, so that is at a very high temperature. So carbon in the solid form which is again present as a core, solid core and sulfur which is the gas stream it reacts to form this carbon disulphide.

And another example is the manufacture of sodium cyanide. So manufacture of sodium cyanide. Sodium cyanide manufacture and the reaction scheme is sodium NaNH2 in the liquid form it reacts with the solid carbon solid core and that leads to the formation of NaCN in liquid and it liberates hydrogen. So that is the reaction scheme and it is typically conducted at 800 degree C.

So that is another example where the core actually shrinks and eventually it disappears. So there are many other processes for which such mode of fluid-solid non-catalytic reaction have been observed. So now so let us attempt to model this system, model the fluid-solid heterogeneous reaction.

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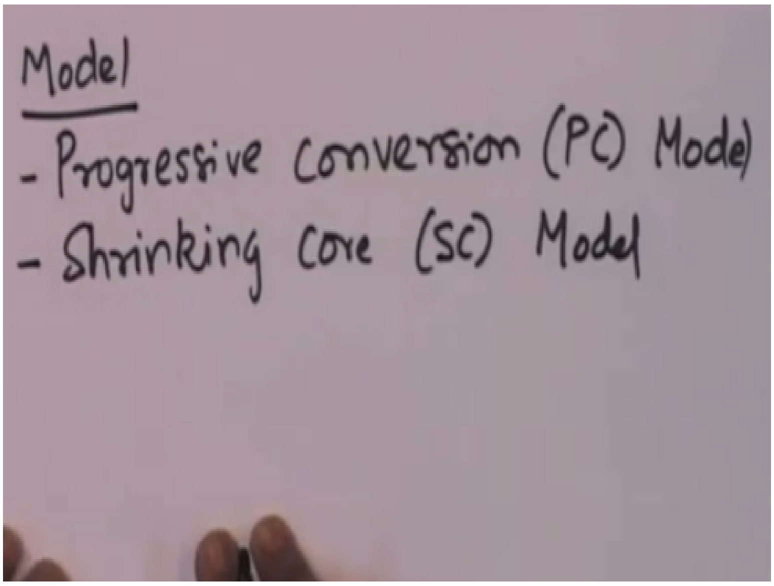

Model
- Progressive conversion (PC) Model
- Shrinking core (SC) Model

So there are 2 types of models that have been proposed. So the first model is called the progressive conversion model, I call it PC model. So the first model is called the progressive conversion model and the second model is called the shrinking core model. So the shrinking core model is much more well-known and more applicable to many systems than the progressive conversion model.

However, let us look into the details of what these 2 types of models are which to represent the fluid-solid non-catalytic heterogeneous reactions.

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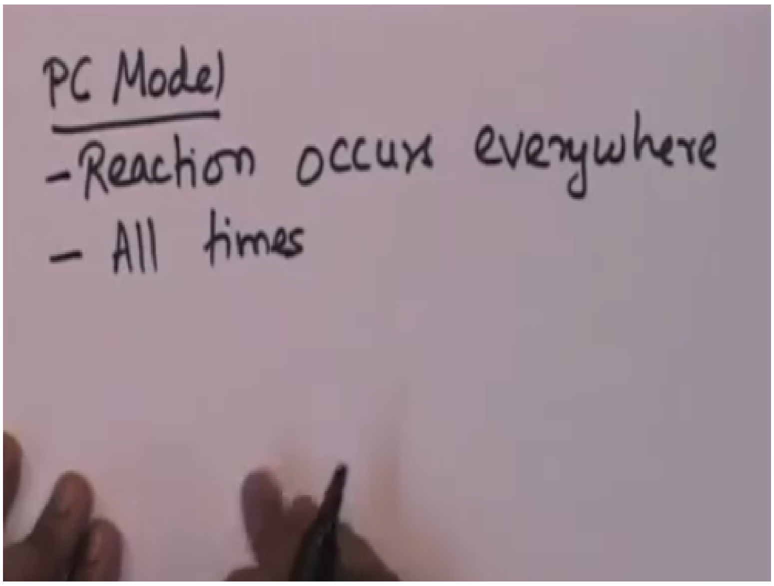

PC Model
- Reaction occurs everywhere
- All times

So let us start with PC model, the progressive conversion model. So progressive conversion model assumes that the reaction occurs everywhere and not just that it occurs everywhere, it occurs everywhere at all times. So it assumes that all the time till complete conversion the reaction occurs everywhere in the solid code. So suppose if we attempt to capture this assumption what it suggests is that suppose if there is an initial core.

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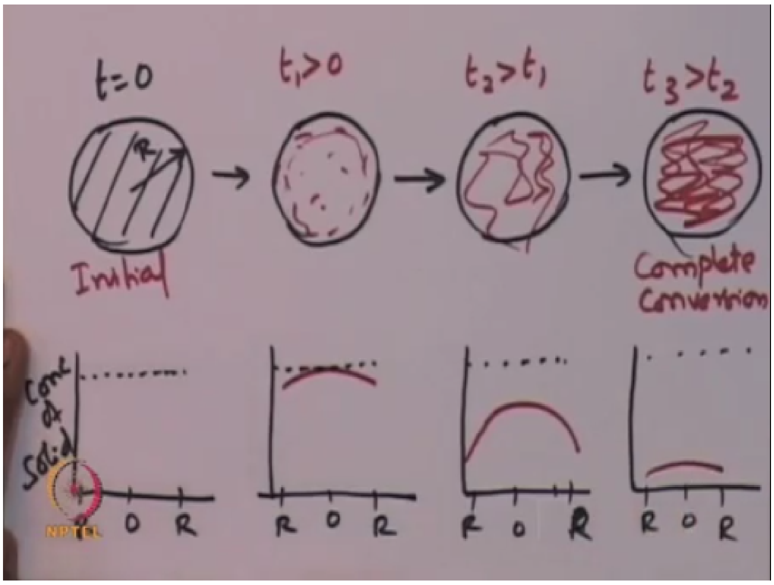

Suppose if this is the initial core that is at time t =0. So that is the initial core which is filled with the solid reactant. Now as time proceeds reaction occurs in the solid core everywhere and let us say at time t1, which is greater than 0 and then at a further later time what happens is that the reaction occurs further and suppose if this is the solid core reaction occurs further and more reactant is being consumed, more solid is being consumed.

Again the reaction is actually occurring everywhere inside the reactor; however, the rate of reaction that is occurring in different locations could in principle be different. So this might be at t2, which is greater than t1 and then at a further later time most of the reactants, which are actually present in the solid core have actually been reacted.

So suppose if the intensity of the red colour here suggests the extent of reaction at different times then at t3, which is greater than t2 one may assume that complete conversion has been occurred. So this might be the initials. Initially when the solid is actually present everywhere in the core and this is basically when the complete conversion has occurred. Now suppose if we attempt to sketch the concentration profile in each of these time steps.

So we can sketch it in the following way. Suppose if the radius of the particle is R and between 0 and R the concentration of the solid initially it remains, let us assume that it is uniform. So this is the concentration of solid, let us assume that it is uniform and then as time progresses at a later time let us say that this is the initial concentration, but because the reaction is occurring uniformly, reaction is occurring all through the particle it may be non-uniform because the rates may be different in different locations.

So we can sketch the profile in this way. So the concentration of the solids will attempt to decrease at every location inside the solid core and so let us say that at time t1, which is greater than 0 this is the kind of profile. Now at a later time, what happens is that because the reaction is occurring everywhere inside the solid. So the concentration of the solid would actually decrease it every location inside the solid core.

So therefore the kind of profile that one would expect is something like this where this is the end of the, this is basically R and at a much later time when the conversion is expected to be complete, so if this is the initial solid concentration and this is R then the concentration of the solid inside the solid core will be almost 0. So clearly you can see that there is a progressive decrease in the concentration of the solid all through the solid core. So this is an important assumption that is actually made by the progressive conversion model.