Chemical Process Safety
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Module 11
Lecture 51
The Flixborough UK Cyclohexane Disaster
(June 01, 1974)

So the first in this particular line is The Flixborough UK Cyclohexane Disaster which took place in 1st June 1974. Now this particular accident is most disastrous accident in terms of fire and explosion. So, let us have a look about this particular accident, now before we start this particular accident in terms of case study, we will have an introduction of the plant then we will discuss about the process protocol or process methodology then what were the shortcomings and to the best of our effort we will try to give a proper accident investigation.

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So let us have an introduction about this Flixborough plant, this was an explosion at a chemical plant that was owned by Nypro UK Limited and occurred in Flixborough, England on Saturday 1st of June 1974 about 4.53 pm. Now this particular plant was in operation since 1964.

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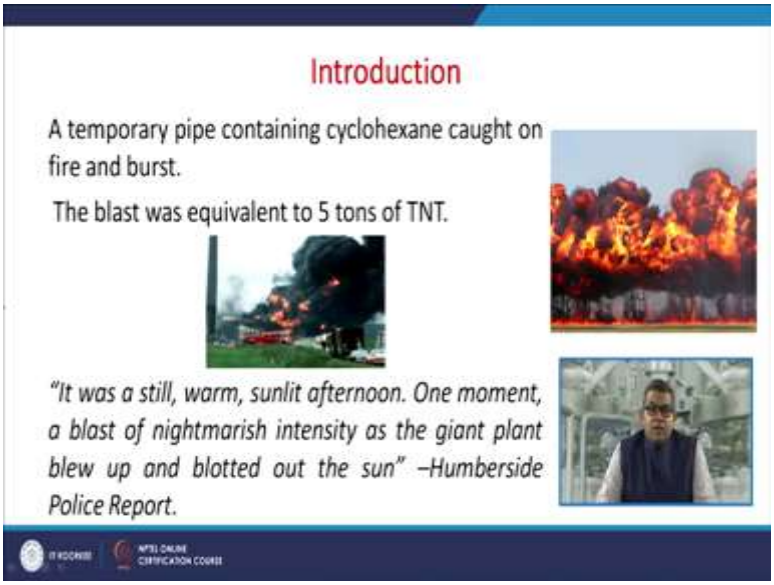

So why this particular accident took place we will go into the detail in due course of time but a temporary pipe which containing the cyclohexane caught on fire and burst and that blast was equivalent to almost 5 tons of TNT. So it was a still, warm sunlight afternoon, one moment a blast of nightmarish intensity as the giant plant blew up and blotted out the sun, that was the Humberside police report. So you can see these are the some of the photograph of at that particular time.

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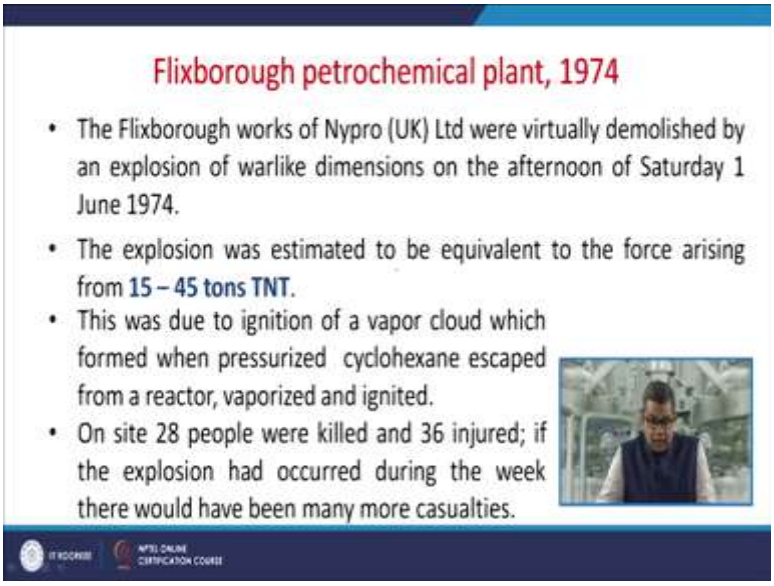

Now let us have a look about the Flixborough petrochemical plant, the Flixborough plant was owned by Nypro Limited which was virtually demolished by an explosion of warlike dimensions on afternoon of 1st June 1974. This explosion was initially estimated to be equivalent of to the force arising from 15 to 45 tons TNT. Later on it was turned as 5 ton, 5 TNT. So this was due to ignition of a vapor cloud which formed when pressurized cyclohexane escape from a reactor and vaporized and subsequently it was ignited. So, on site 28 people they were killed and 36 injured. Now if, remember, if the explosion had occurred during the week there would have been many more casualties because during the working hour there may be certain people in the offices and other general shift.

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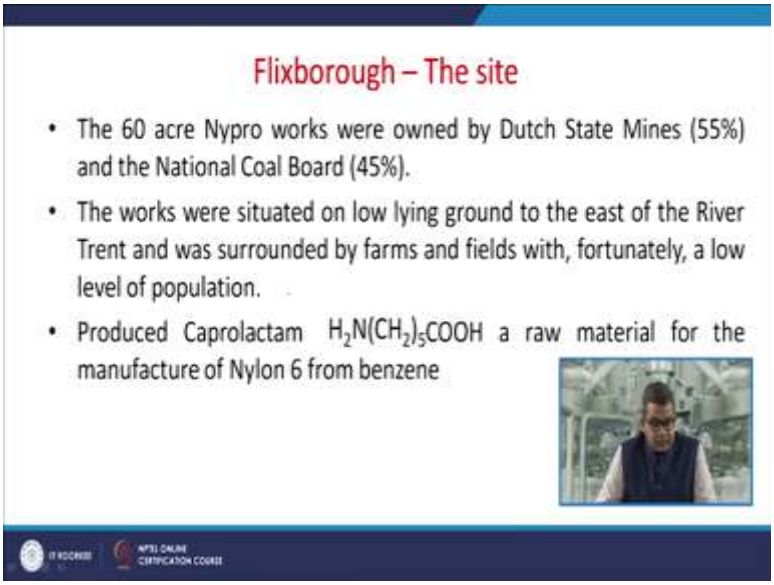

Now let us have a look about the Flixborough site, this was a 60 acre Nypro plant was owned by Dutch State Mines, 55 percent and National Coal Board, they were having the stake of 45 percent. Now this work was situated on a low lying ground of to the east of the river Trent.

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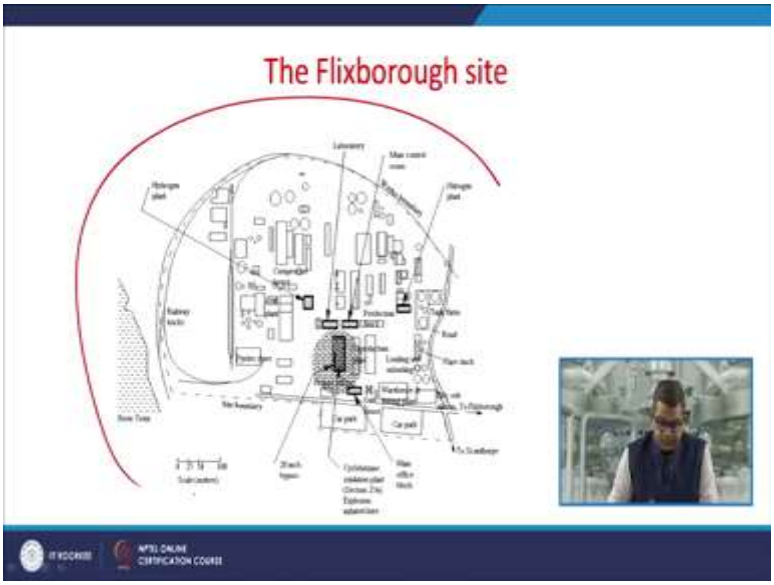

Now this is the Flixborough site and was this particular plant was surrounded by farms and fields with fortunately a low level of population.

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Now this particular plant involved in production of caprolactam that is H2N(CH2)5 COOH this is a raw material for the manufacturing of Nylon-6 and that is from the benzene.

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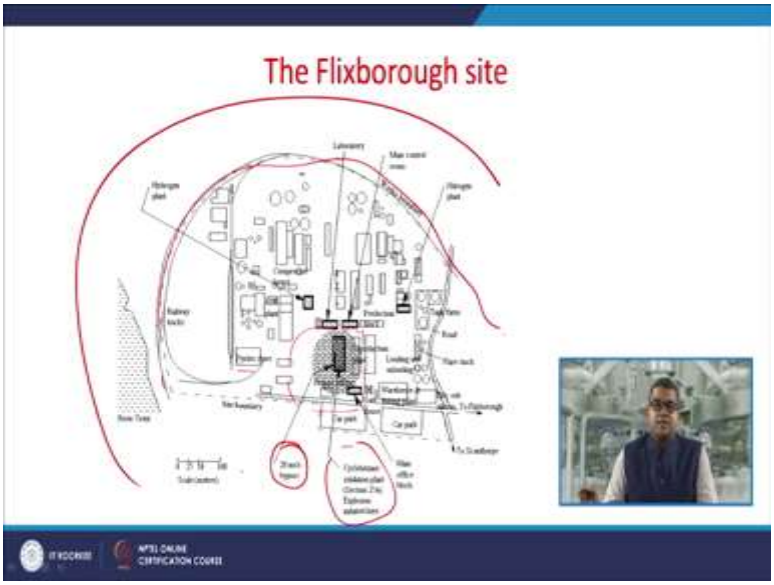

So this is the Flixborough site, here the main problem took place, this was the caprolactam plant, there was a certain loading-unloading operation the production arena, acid plant, pyrites sites, laboratory, main control room and that was the work boundary you can see and this was the cyclohexane oxidation plant, bypass line etc.

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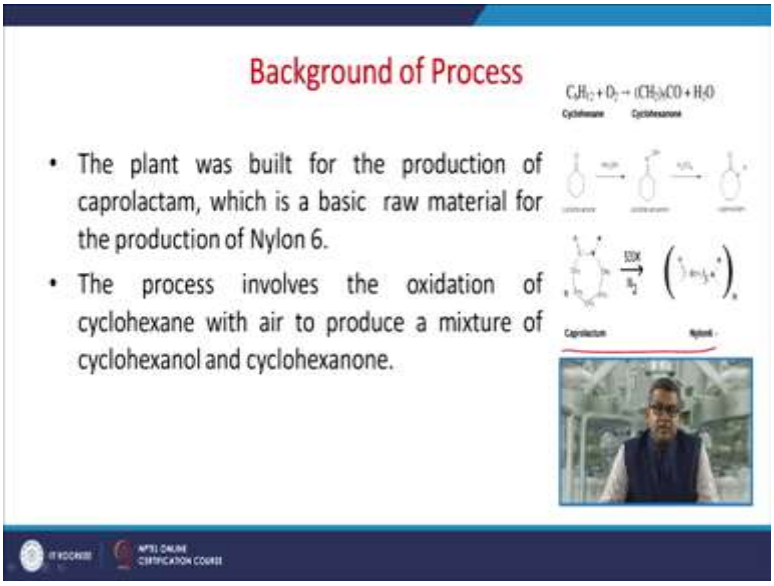

Now let us have brief discussion about the process. The plant was built for the production of caprolactam which is basic raw material for the production of nylon-6. Now the process involves the oxidation of cyclohexane with air to produce a mixture of cyclohexanol and cyclohexanone

and then this caprolactam is in situ converted into caprolactam which in turns produces nylon-6, we will discuss the reaction methodology later on.

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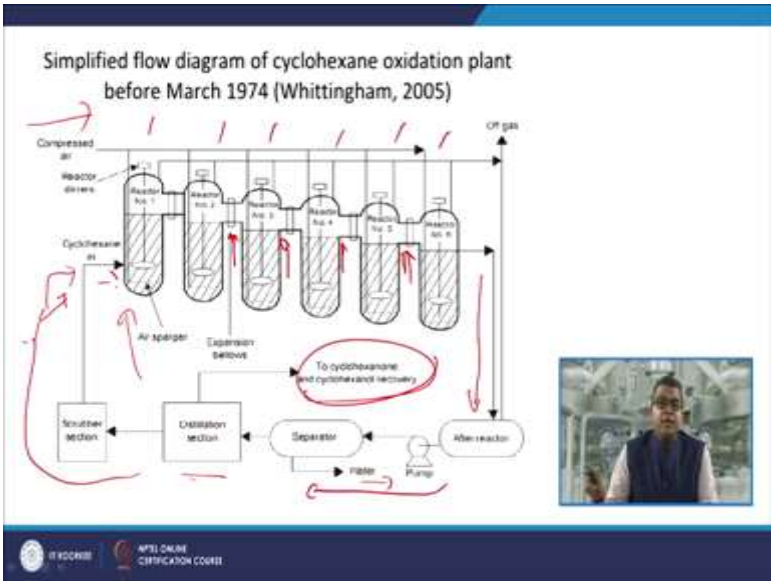

Now this is the simplified diagram of cyclohexane oxidation plant, here they were having 6 different reactors 1, 2, 3, 4, 5 and 6 and the cyclohexane, they were injecting from the first plant with the help of an air sparger and the compressed air was supplied from the air supply utility line and they are, these reactors are connected in series. Now, whenever there is a problem then what they used to do, they used to draw one reactor from problematic reactor from the main battery and then they used to repair and then they re-insert it.

So there are certain every reactor was connected with the expansion bellows like this to overcome any kind of pressure imbalance. Now the product whatever product they coming out from the after reaction they used to the pump and then separator water is separated and they send to the distillation section and this is subjected to the cyclohexanone and cyclohexanol recovery and whatever left behind this unreacted cyclohexane, it is sent back to after scrubbing it is sent back to the main reactor battery.

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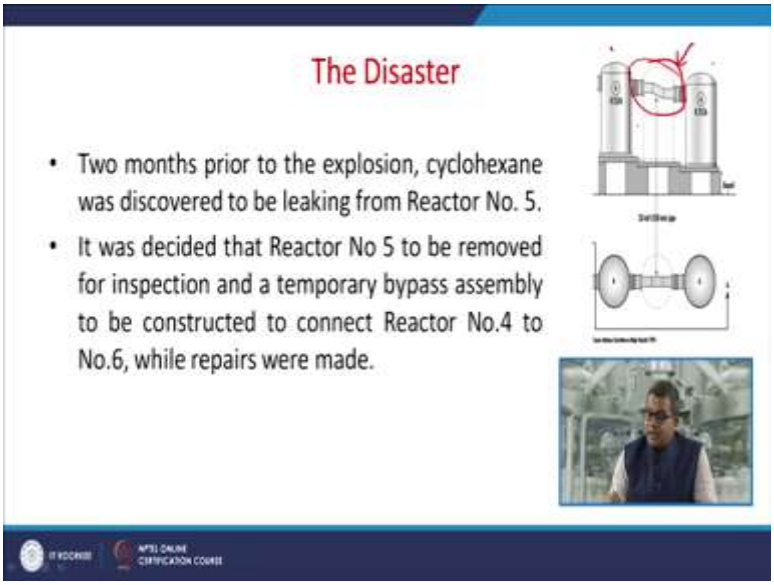

Now the disaster, the disaster took place among just you can say whatever they were misses or the some faulty operations, so we have enlisted all those things in these particular slides, so 2 months prior to the explosion the cyclohexane was discovered by leaking to the reactor number 5, this was the main problematic reactor so the cyclohexane and they were discovered from to be leaking from reactor 5. So it was decided that the reactor number 5 is to be removed for inspection and a temporary bypass this, was the temporary bypass, the temporary bypass assembly to be constructed to connect the reactor number 4 to reactor number 6, while repairs were made. So this is the basic repairing line or section being carried out.

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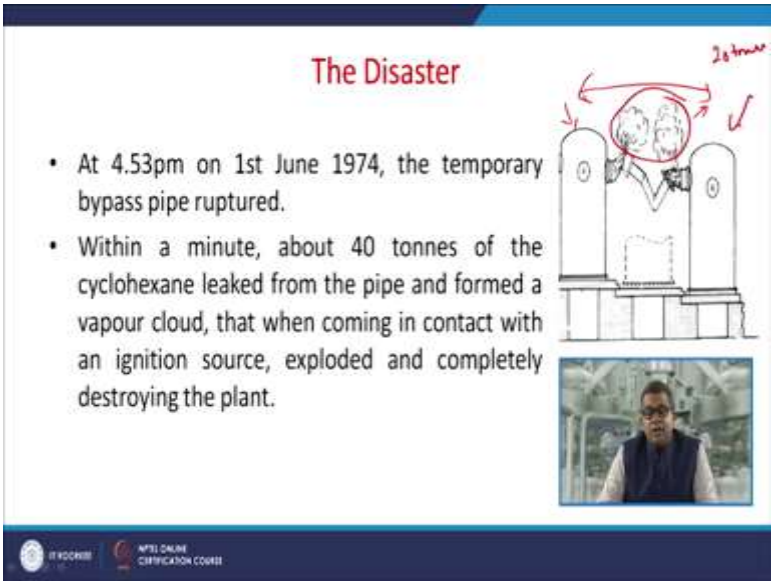

So on the 1st of June 1974 at 4:53 pm the temporary bypass line which was connected in between reactor number 4 and reactor number 6 was ruptured, so within a minute about 40 tons of, because of reactor was having the capacity of 20 tons each, so within a minute about 40 tons of the cyclohexane it was leaked from the pipe and formed a vapor cloud that when coming in contact in an ignition source exploded and completely destroying the plant because they were having high, they were having low boiling point (so in each) and the source of ignition was having the sufficient energy to ignite that particular vapor cloud and sometimes when this vapor cloud usually it is termed as unconfined vapor cloud, so whenever this type of scenario happens then practically the ignition source they are supposed to be available everywhere.

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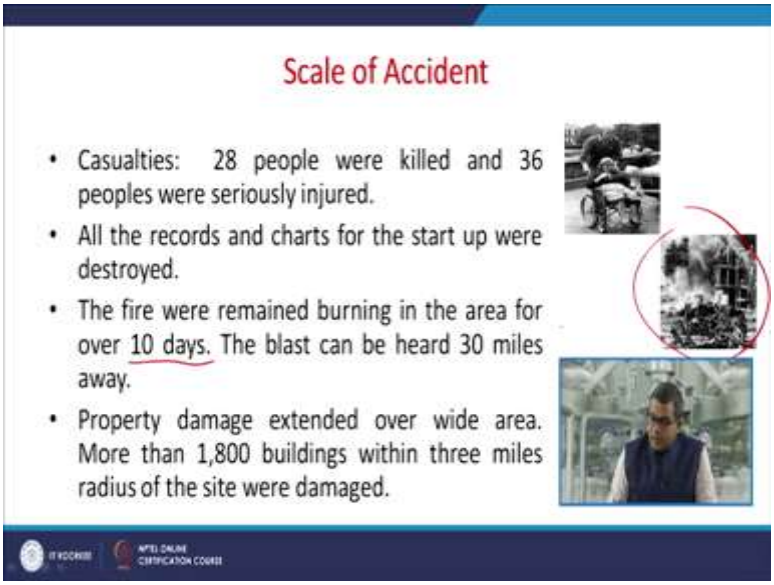

Now let us have a discussion about the scale of accident, so total casualties 28 peoples they were killed and 36 people were seriously injured. All the records and the charts for the startup were destroyed and the fire were remained burning in the area for over 10 days, so you can imagine that how much inventory was there in that particular plant, because they were practically unable to extinguish the fire for almost 10 days. So the blast was having so much impact that it can be heard for 30 miles away. The property damage, they extended over wide area and that is more than 1800 buildings within 3 miles radius of the site was damaged. So these are again couple of photographs of that particular time.

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Now you can see that the various newspaper clipping and accident sites in these figure. So this is the scenario of vapor cloud explosion and the daily mail they reported that survivor return to a funeral pyre. So this was the whole scenario.

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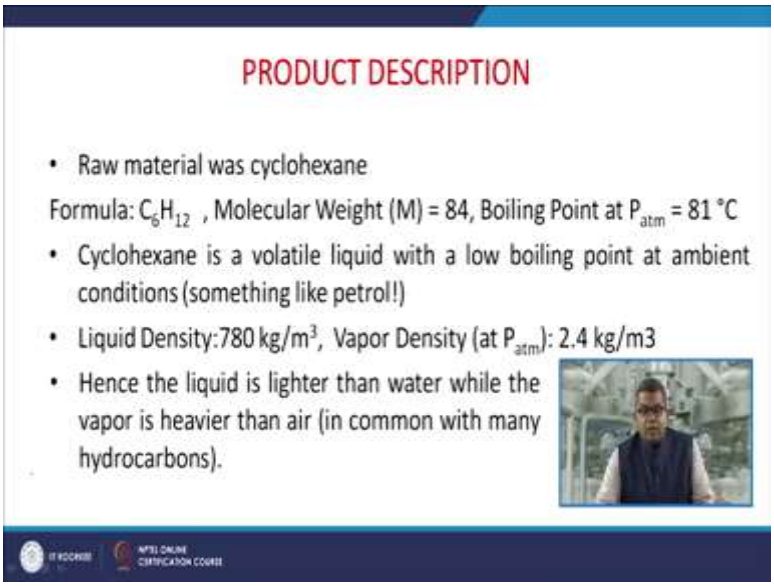

Now let us a Product Description, so the raw material for that particular caprolactam production was cyclohexane, it is having the formula of C6 H12 molecular weight 84 and boiling point is 81 degree Celsius. Now this cyclohexane is a volatile liquid with a low boiling point at ambient condition. It is something like petrol. It is having the liquid density, 780 kilogram per meter cube

and a vapor density is 2.4 kilogram per meter cube at atmospheric condition or atmospheric pressure. So the liquid is lighter than water while the vapor is heavier than air, in common with the many hydrocarbons, this is very common phenomena for many hydrocarbons.

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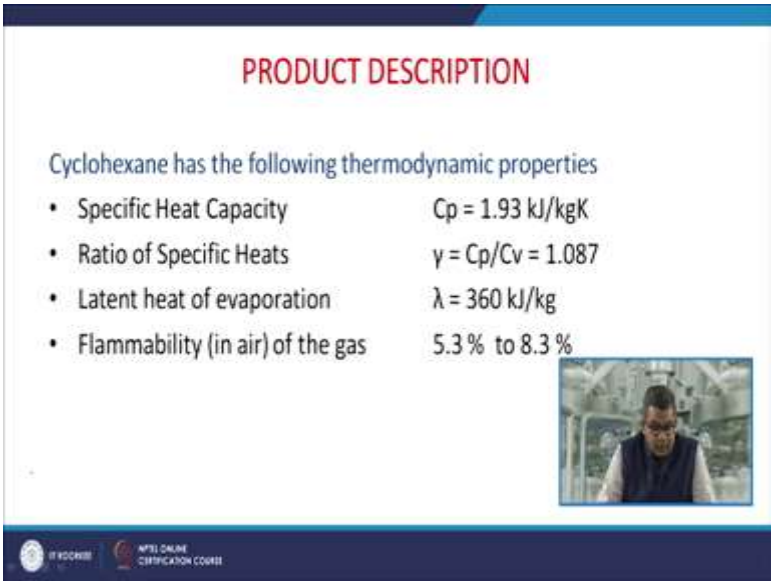

Now cyclohexane is having the following thermodynamic properties like specific heat is 1.93 kilo joule per kilogram kelvin, ratio of specific heat that is gamma is equal to 1.087, latent heat of evaporation is 360 kilo joule per kilogram and flammability in air of the gas is 5.3 to 8.3, in other words you can say the LFL and UFL.

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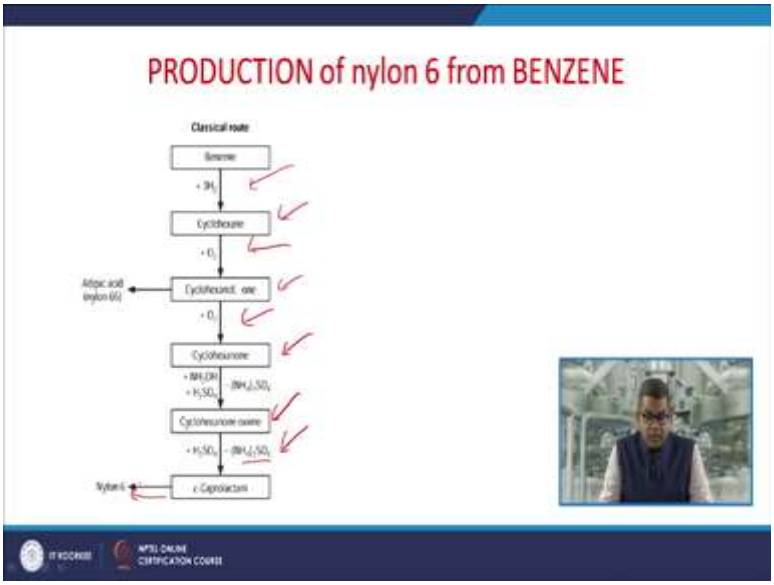

Now this is the production protocol of nylon 6 from benzene, this is the classical route and they were suppose to follow this classical route. Now benzene is hydrogenated to give the cyclohexane and this cyclohexane (in) is subsequently oxidized to give the cyclohexanol and this cyclohexanol is further oxidized to give the cyclohexanone and in presence of NH2OH (and) H2SO4 the cyclohexanone is converted into cyclohexanone oxime which is subsequently converted into caprolactam with H2SO4 and NH4 whole twice SO4 ammonium sulphate is byproduct and this caprolactam is converted into nylon-6. So this is the production stream of nylon-6 from benzene route and the plant was having substantial quantity of benzene within its periphery.

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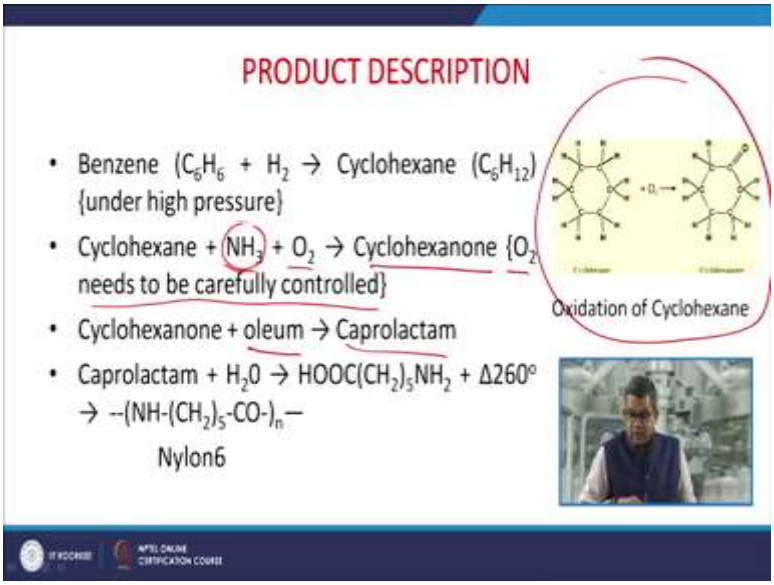

Now the benzene under high pressure gives the cyclohexane and cyclohexane with ammonia and oxygen the cyclohexanone, so ammonia is again used for the production of cyclohexanone and one advisory is that oxygen needs to be carefully control. Now why oxygen needs to be carefully controlled? The reason is cyclohexane is extremely flammable and you are supplying oxygen, so sometimes it may happen that the if you are not controlling oxygen, so that it can meet the minimum oxygen concentration demand and it is extremely you can say it may become the extremely disastrous. Then this cyclohexanone plus oleum H2SO4 gives the caprolactam and caprolactam upon hydrolysis it gives the nylon-6. So this is the basic stream and this is the oxidation of cyclohexane.

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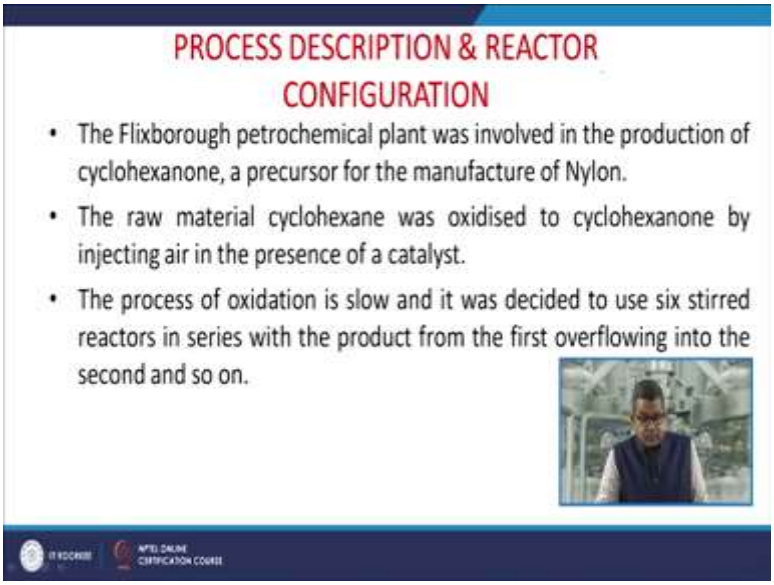

Now the Flixborough petrochemical plant was involved in the production of cyclohexanone, a precursor of the manufacture of nylon. The raw material cyclohexane, this was oxidized to cyclohexanone by injecting air in presence of a catalyst. So the process of oxidation is usually slow and it was decided to use the 6 stirred reactors in series with the product from the first overflowing into the second and so and so on.

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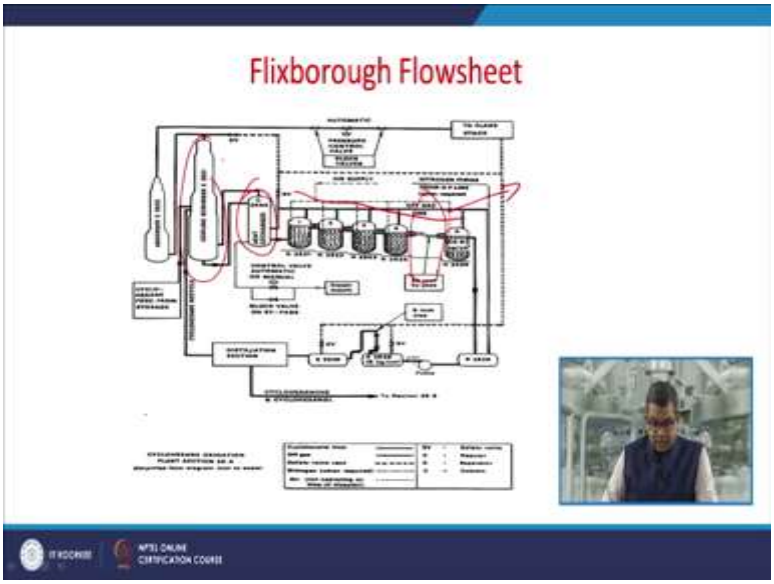

So if you recall, the production protocol, so these 6 reactors they were in series and the overflow of the previous reactor is subjected to the inlet of the next reactor inline and in such a way. So

this is (the) you can say the Flixborough flow sheet here (the) this was a cooling scrubber then there is heat exchanger, this 6 reactors they were in series they are connected with the 20-inch bypass line. Now here the reactor number 5 is out of the business because of the some repair and there are other previous sections just which we have already discussed.

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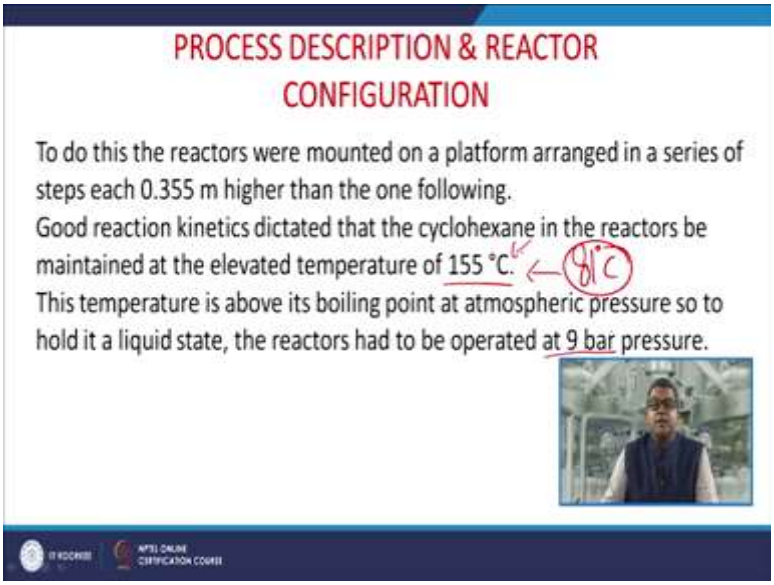

Now since to meet the reaction kinetics, they were having the 6 reactor in series. Now to do this the reactors they were mounted on a platform arranged in a series step such that each step is having the height difference of 0.355 meter with another one. Now, the good reaction kinetics, they dictate that the cyclohexane in the reactor be maintained at an elevated temperature of 155 degrees Celsius.

So, chemical kinetics plays a very vital role for any kind of fielder conversion things. Now this temperature is above the boiling point at the atmospheric pressure, so (it) to hold the liquid, to hold all the contents in the liquid state the reactor had to be operated at 9 bar pressure. Because remember the cyclohexane is having the boiling point 81 degree Celsius. Now since reactors they are operating at a temperature higher than this particular temperature and the operating temperature was 155 degrees Celsius so they need to be put at a higher pressure.

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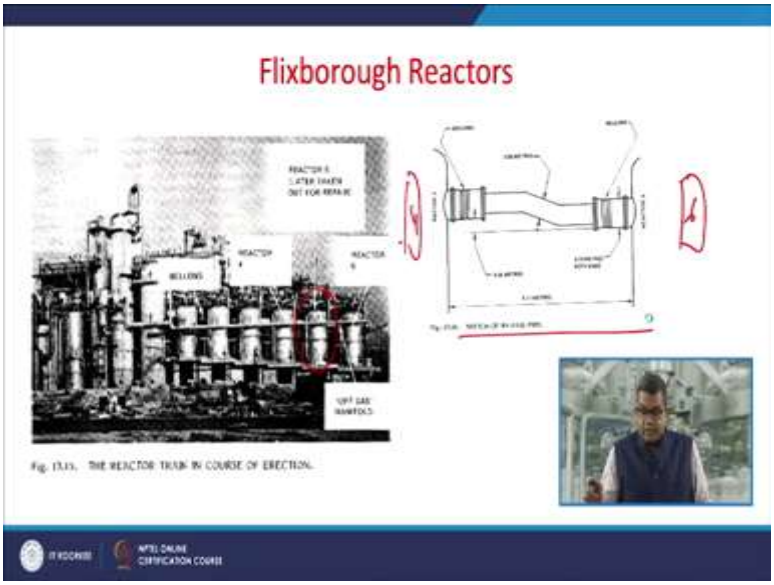

So this higher pressure and higher temperature, this is this was a main reason these two parameters were the main reason for this particular reactor apart from the mechanical or deliberated failure. Now, this is the actual photograph of the reactor train or reactor battery in the course of during the course of the erection. Now, this was the reactor which was taken out for the repair and this was the sketch of the bypass pipe. So there was a reactor number 4 and this was a reactor number 5, reactor number 6, so they were connected through this bypass pipe.

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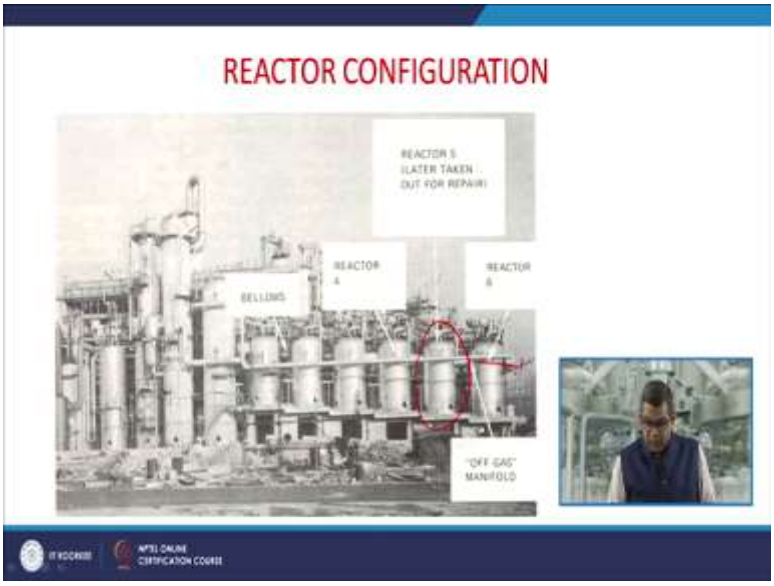

Now you can have a more closer look of this a particular reactor battery. So these were the 6 reactor and this was the off gas manifold and this was a problematic reactor.

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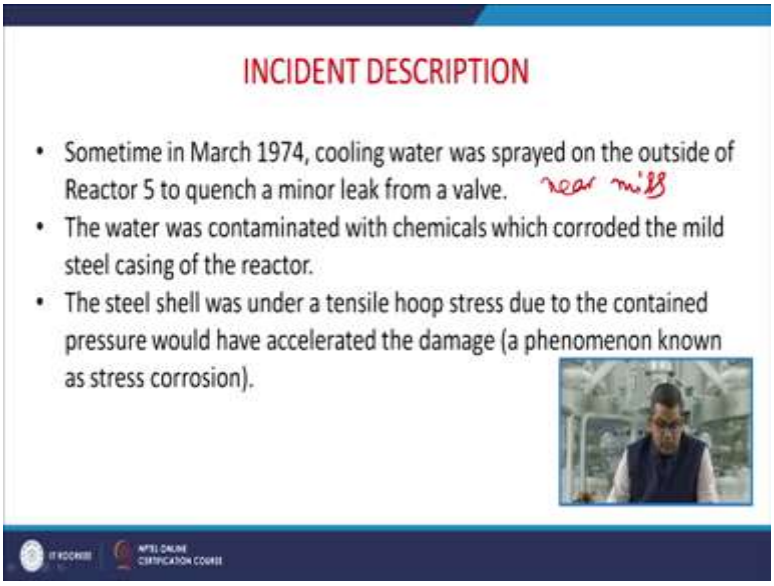

So sometimes in March 1974, the cooling water was sprayed on the outside of reactor number 5 to quench a minor leak from a valve. Now the water was contaminated with the chemicals which corroded the mild steel casing of the reactor. Now this problem you can say, this is the near miss. Now the steel shell was under a tensile hoop stress and due to this the contained pressure which would have accelerated the damage. Now this phenomenon is known as the stress corrosion.

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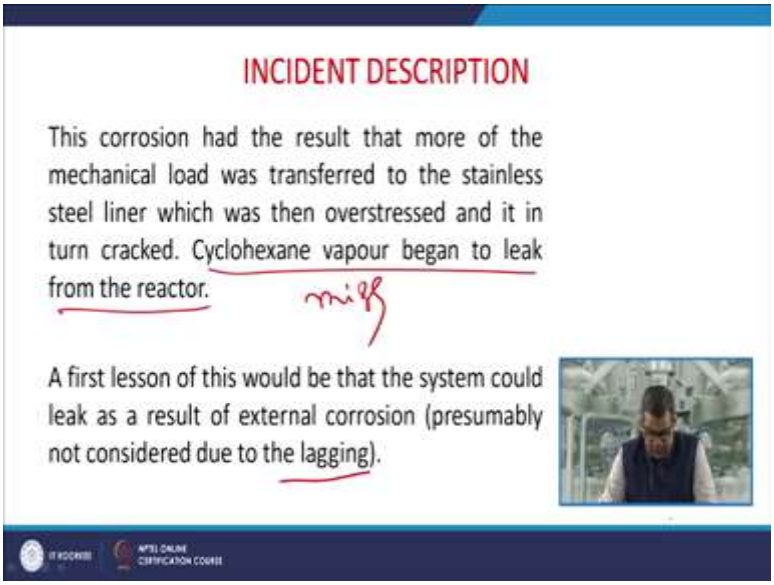

So this correction had to the had the result that more of the mechanical load was transferred to the stainless steel liner which was then overstressed and it in turns cracked. So cyclohexane vapors they begin to leak from the reactor, again you can say this is the miss. Now the first lesson of this would be that the system could leak as a result of an external corrosion that is presumably not considered to due to the lagging. So sometimes it may referred as that this is lagging but it is not.

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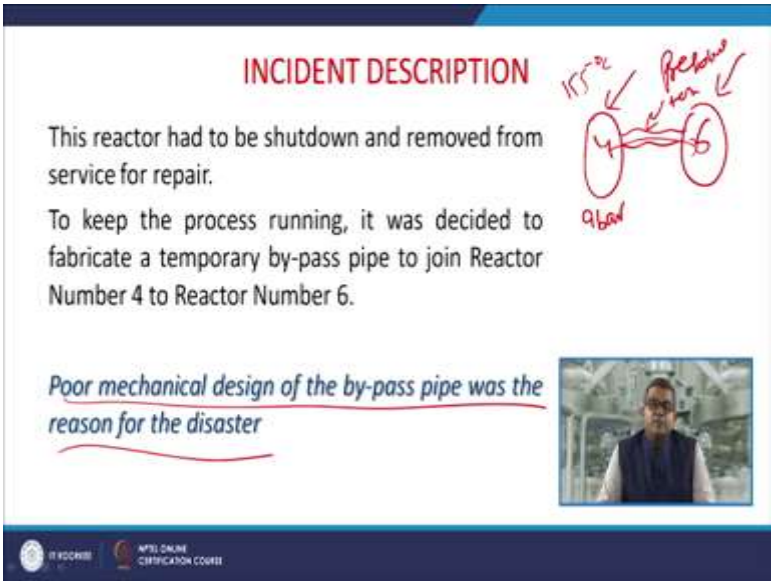

Now just because of this particular thing, this reactor had to be shut down and removed from the service for repair. Now to keep the process running, it was decided to fabricate a temporary bypass pipe to join reactor number 4 to reactor number 6. Now a poor mechanical design of the bypass pipe was a reason for that disaster. Now remember, both the reactors they were pressurized and they were at an elevated temperature, see remember the reactor temperature was 155 degrees Celsius and both of them were at 9 bar.

So whenever you are applying such kind of for modification you need to go ahead with the pressure test. So which was not performed because sometimes it may have (because) whenever the content moves from this place, this reactor to this one then there may be a chances of any fluctuation.

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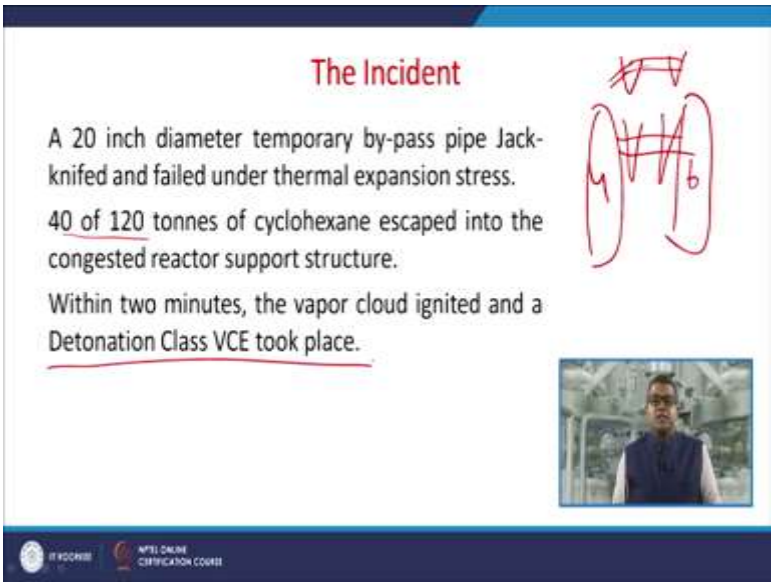

So a 20-inch diameter temporary bypass line or jack-knifed, this is like this where the pipelines they are supported, so jack-knifed and failed under the thermal expansion stress, now because both of the reactors they were operated at higher temperature. So again, the thermal (expression) expansion test or stress tests need to be performed. So, about 42 of 120 tons of cyclohexane escaped into the congested reactor supported structure. Now the jack-knifed were like this, so they approximated around 40 to 100 tons or 120 tons of cyclohexane they escaped into this arena. So within 2 minutes of the vapor, the minutes the vapor cloud ignited and detonation class of vapor cloud explosion took place.

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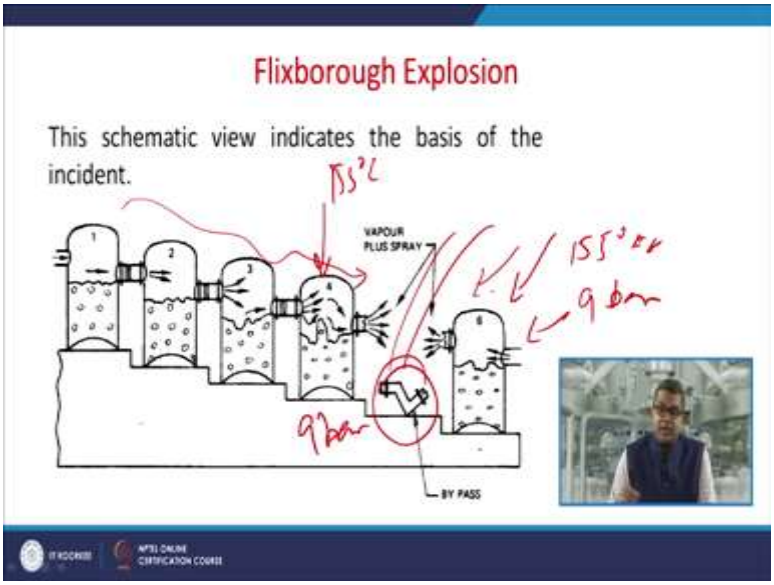

Now this is the schematic view of this indicate the basis of the incident. Remember this was running at 155 degrees Celsius and again the temperature of a (105) 55 degrees Celsius, 9 bar pressure and it is again having the 9 bar pressure. So the entire content and when this was broken, this bypass line was broken, then you may assume that the entire material they may come out because every reactor was running under pressure.

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Now let us have a look about this the defective pressure vessel that is, the pressure vessel number 5. Now this failed pressure vessel taken out of the service. Now the cracked propagation near the flange square hold or where the material has been removed for examination.

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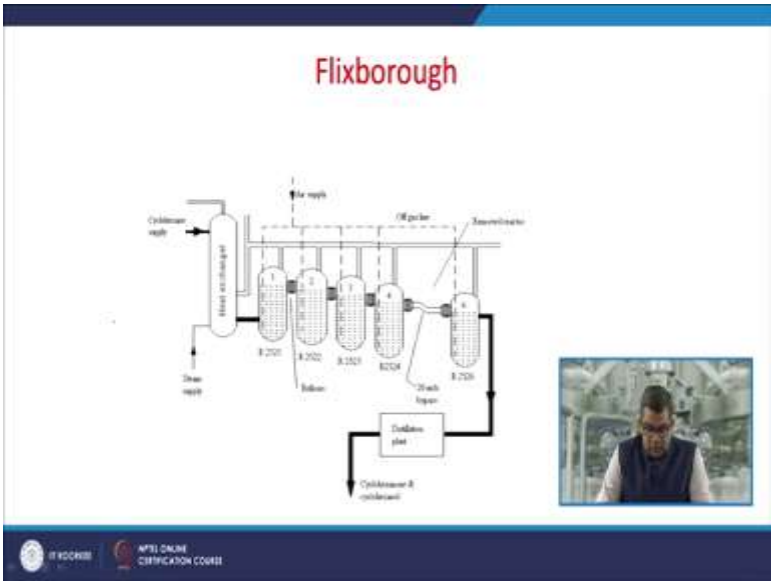

So this is again the original figure where this reactor number 5 was supposed to be there.

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Now this you can see that before the explosion the plant was having this type of thing and this is after the explosion.

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Now this is, you can see the view of the entire plant arena after the incidence, so this one is the main fire zone and you can see that the entire plant was destroyed at the moment.

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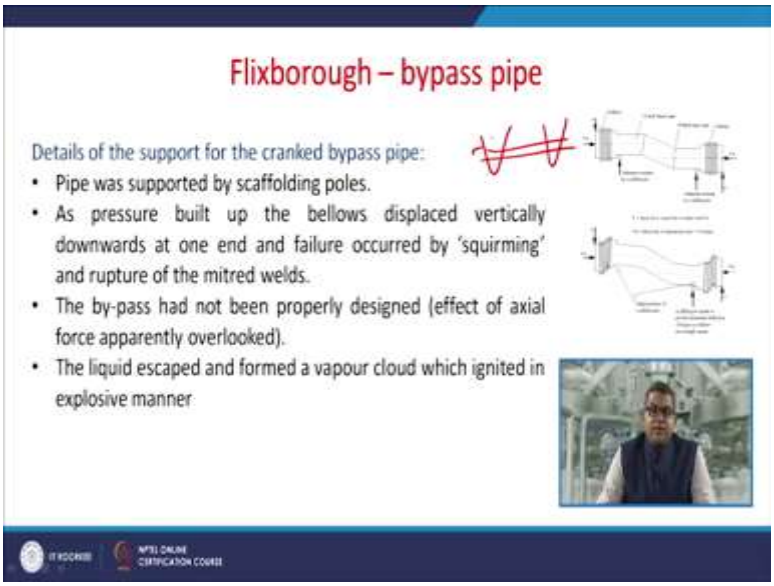

Now let us have a look about the bypass line because it was the main culprit of that particular incident. The details of the support of the cracked bypass pipe, the pipe was supported by scaffolding poles or you can say the jack-knife system. So, as pressure built up the bellows displaced vertically downward at one end and the failure occurred by squirming then the rupture of the mitred welds. So they just welded the things in a non-professional manner. So the bypass had not been properly designed and effect of some excel forces apparently they overlooked. The liquid escaped and formed a vapor cloud which ignited in the explosive manner.

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Now this is the reactor battery and they try to just extinguish the fire.

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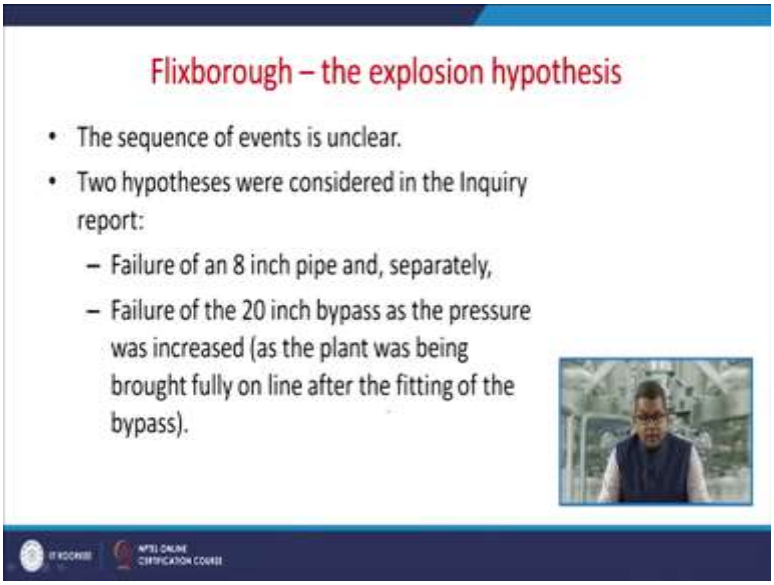

Now the explosion hypothesis, they suggested that the sequence of the event is unclear, still unclear. The two hypotheses were considered in the inquiry report because at as in this is an outcome of the accident investigation that was a failure of an 8-inch pipe and separately and then next is the failure of the 20 inch bypass as the pressure was increased, as the plant was being

brought fully online after the fitting of the bypass. So see again, it seems that the plant officials they were under stress.

So in case if you are removing any reactor then to meet out the reaction kinetics and to meet out the requirement of a conversion or a yield then they were forced to put the scenario to bypass the chemical kinetics things. Like now the original chemical kinetics, they suggest that you need to maintain the reaction temperature at around 155 degrees Celsius under 9 bar pressure. But whenever you are forcing towards the higher conversion, then that means you are compelled to alter all those process parameters.

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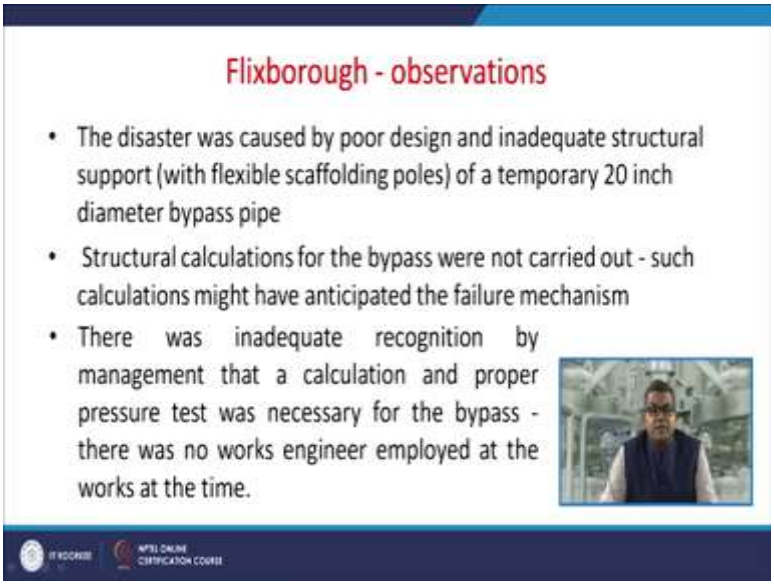

So this disaster was caused by poor design and inadequate structural support with the (flexible) jack-knife type of scaffolding of a (temperature) temporary 20-inch diameter bypass pipe. Now the structural calculation for the bypass were not carried out, such calculations might have anticipated the failure of mechanism. So again, they have, you can say they have missed this particular aspect, a very important aspect of the process.

Now there was inadequate recognition by the management that a calculation and a proper pressure test was necessary for the bypass because all the reactors they were under high pressure. So there was a necessity to carry out for the bypass and there was no work engineer employed at the work at the time.

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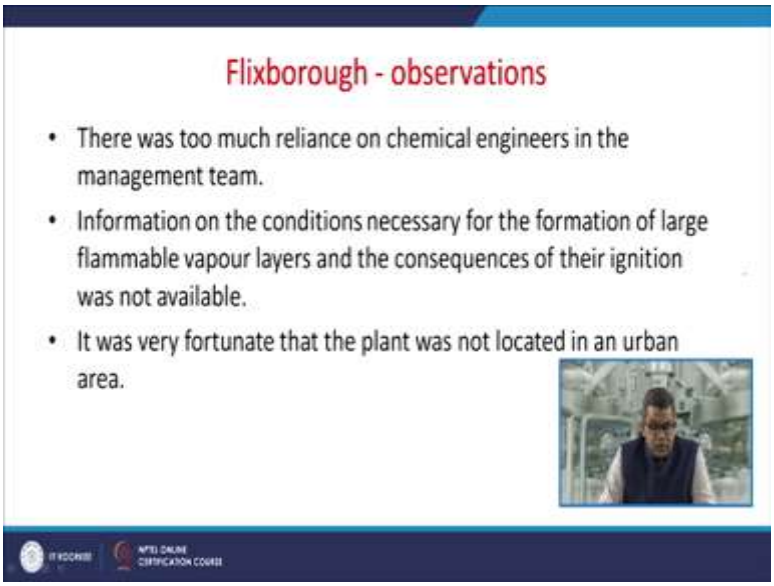

And there was too much reliance on the chemical engineer in the management team rather than the mechanical engineer. So chemical engineer they were just involved to alter the reaction kinetics or process parameters and they can, you can say, they were incompetent to carry out all kind of pressure temperature calculations for that particular pressure vessel. So the information on the conditions necessary for the formation of large flammable vapor layers and the consequences of their ignition was not at all available. So they did not carry out this type of analysis and it was very fortunate that the plant was not located in an urban area.

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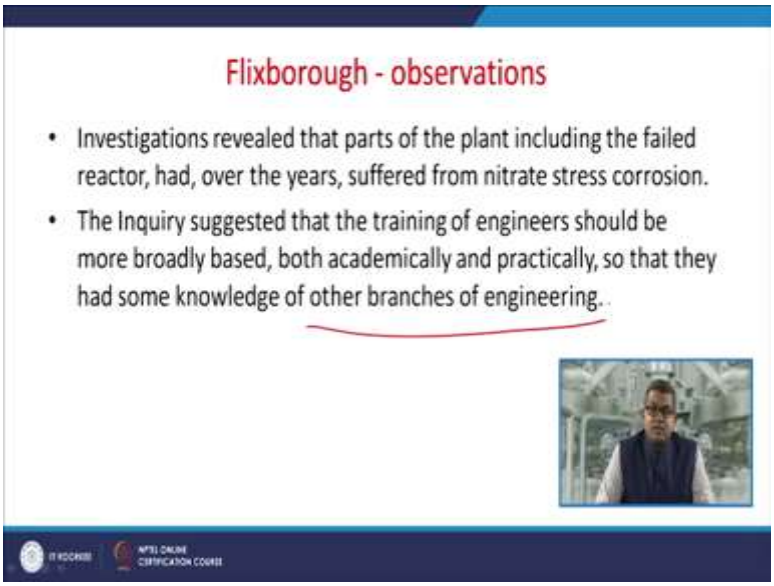

Now there are certain observations, the investigations revealed that the part of the plant including the failed reactor had over the years suffered from the nitrate stress corrosion. Now the inquiry suggested that the training of engineer should be more broadly based both academically and practically, so that they had some knowledge of other branches of engineering. Now this is very important had the chemical engineers they the knowledge of the stress test or the pressure imbalanced and (test) then they might have any position to compel the fabricators to perform such type of test to avoid such a scenario.

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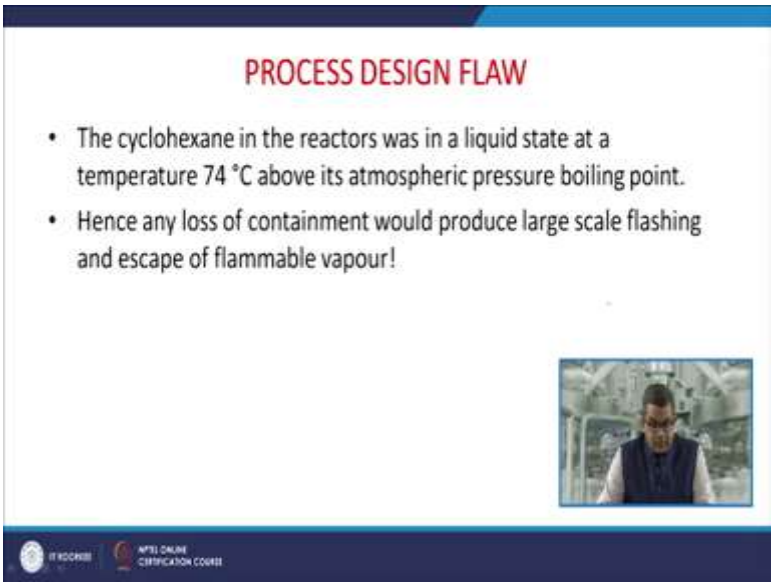

Now there are certain process design flaw, the cyclohexane in the reactor was in a liquid state at a temperature of 74 degrees Celsius above its atmospheric pressure boiling point. Hence any loss of containment would produce large scale of flashing and escape of flammable vapor. Now the cyclohexane and the benzene both of them they were stored in a large quantity, so inventory problem was also there in that particular thing.

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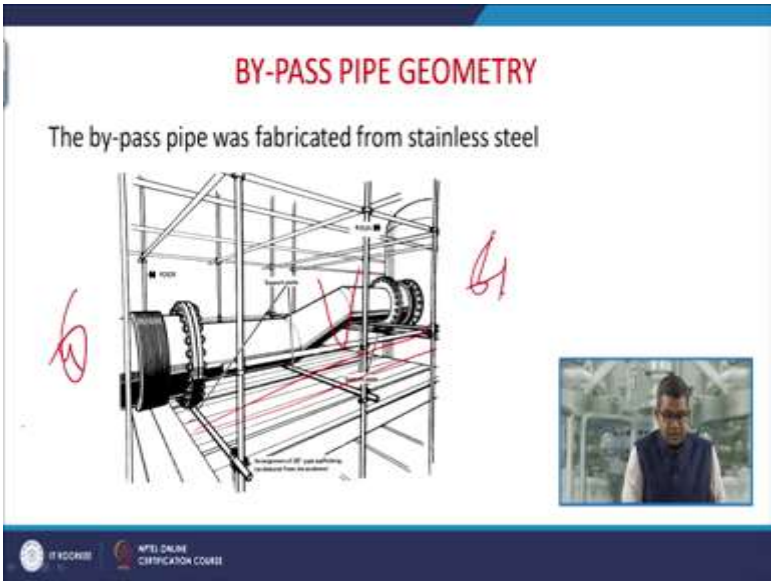

Now this was the structure of scaffold and this you can see the scaffold which was supported the reactor number 4 to reactor number 6.

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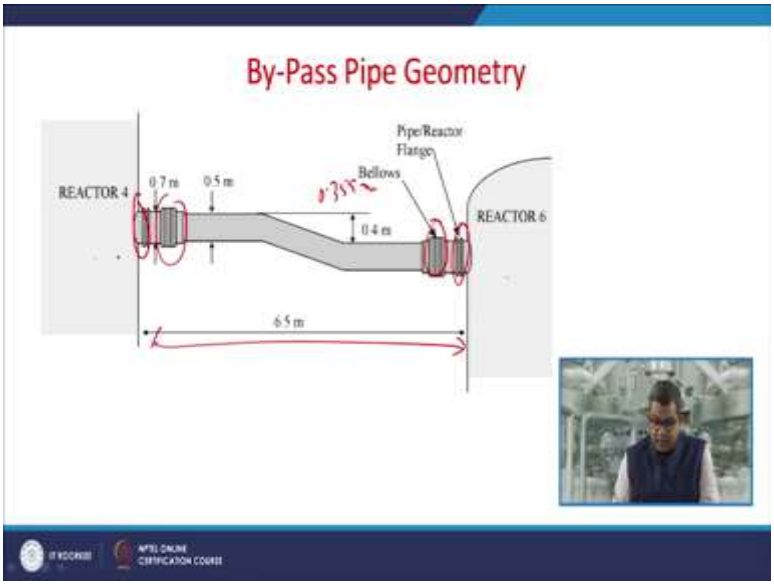

Now this was the bypass pipe geometry, this was a reactor 4 and this was a reactor 6, they were supported by these bellows and the pipe reactor flanges and the distance was almost 355 meter just to suggest that reaction kinetics and the distance of these two reactors, remember reactor 4 to reactor 6 was 6.5 meter.

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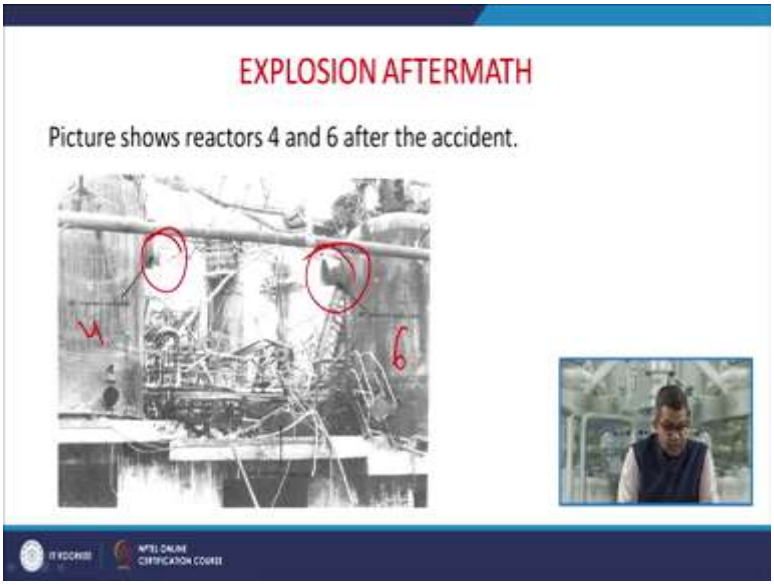

Now these are the pictures shows that a reactor 4 and 6 after the accident, so you can see these are the openings where the things were connected. So this was the (reaction) reactor number 6 and this was the reactor number 4.

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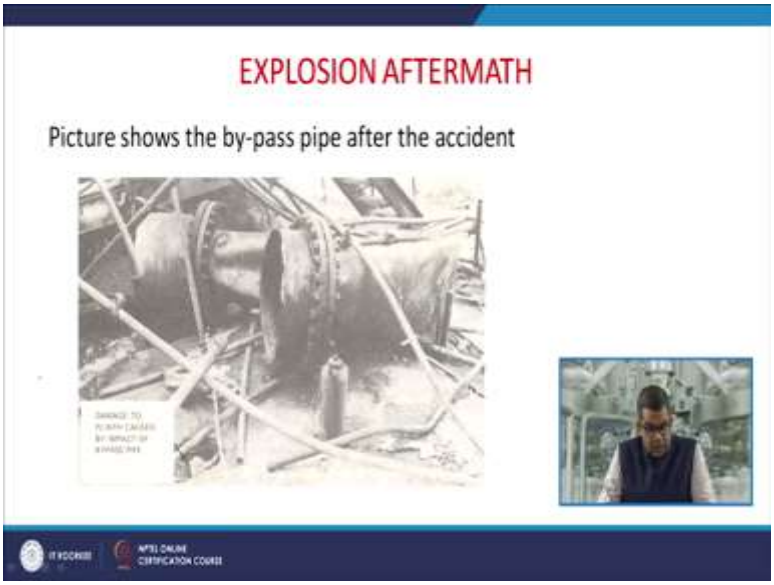

Now this is the bypass pipe after the accident, so you can see the damage over here.

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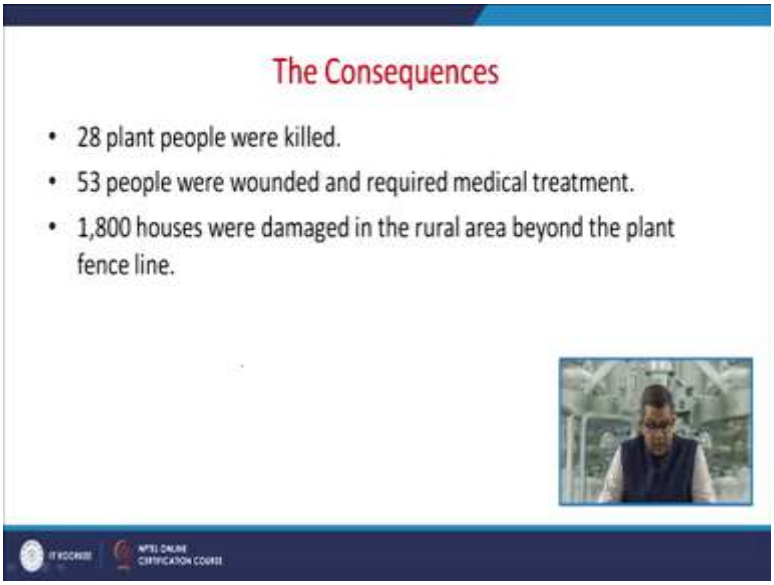

The consequences are 28 plant people they were killed, 53 people who are wounded and required medical treatment almost 1,800 houses they were damaged in the rural area beyond the plant fence line.

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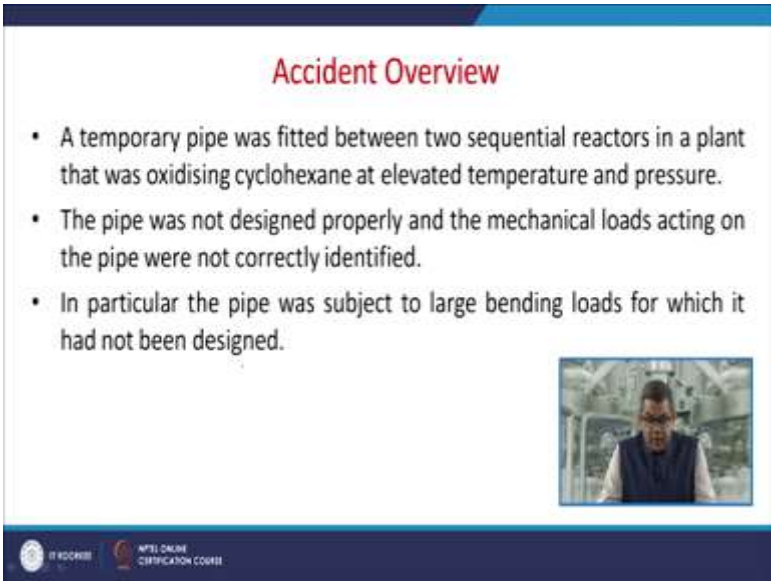

So when the accident investigation took place then team over viewed the entire scenario and they found out that a temporary pipe was fitted between two sequential reactor in a plant and that was oxidizing the cyclohexane at an elevated temperature under pressure. Now this pipe was not designed properly and the mechanical load acting on the pipe were not correctly identified. In particular the (ply) pipe was subjected to the large bending loads for which it had not been designed.

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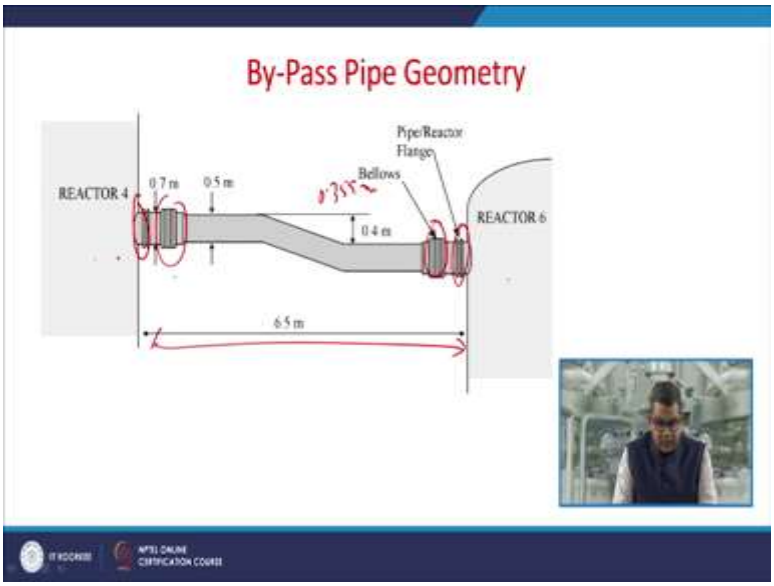

Now you can see in this particular figure that whenever the flow is transferred from this way. So the load would be on the higher side of this particular pipe junction.

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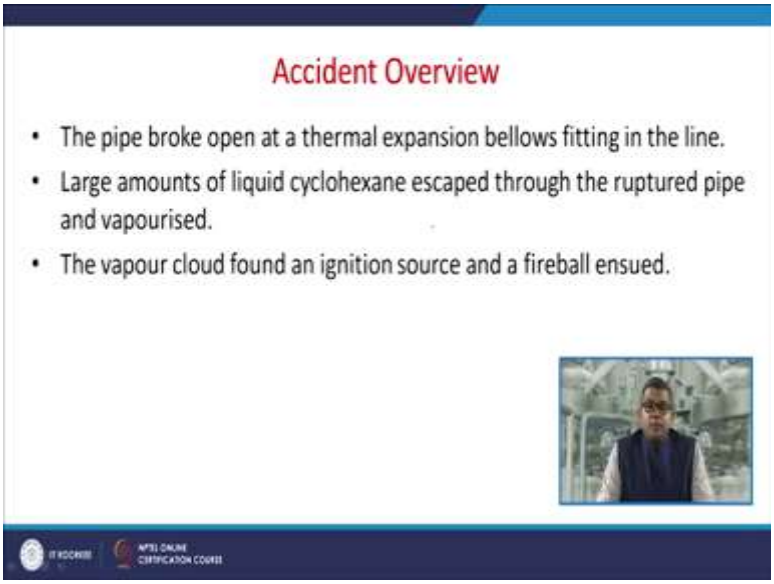

Now the pipe broken down, open at a thermal expansion bellow fitting in the line, the large amount of liquid cyclohexane escape to the atmosphere through the rupture pipe and vaporized because they were having the higher temperature and excess pressure. So the vapor cloud found an ignition source and a fireball in ensued.

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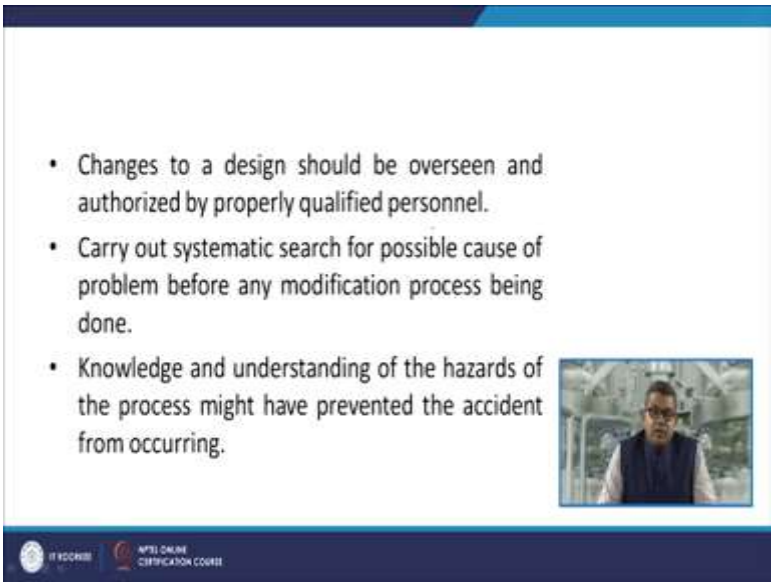

Now, so they recommended couple of things before they proceed further. The changes to a design should be overseen an authorized by the properly qualified person. Remember there was no mechanical engineer involved for carrying out any kind of pressure, temperature based calculation, so they suggested. Now there was an upmost requirement to carry out the systematic search for the possible cause of the problem before any modification process being done. Because the chemical engineers they were forced to carry out the higher conversion.

Now knowledge and understanding of the hazard of the process might have prevented the accident from occurring. Now this was again important point to note because they were having the large sized inventory and for all flammable materials like cyclohexane, benzene and because they were carrying out the oxidation reaction, so the source of oxygen was adequately available at the point of time. So in a synchronized manner the accident investigation team, they categorized the things in event leading to the incident.

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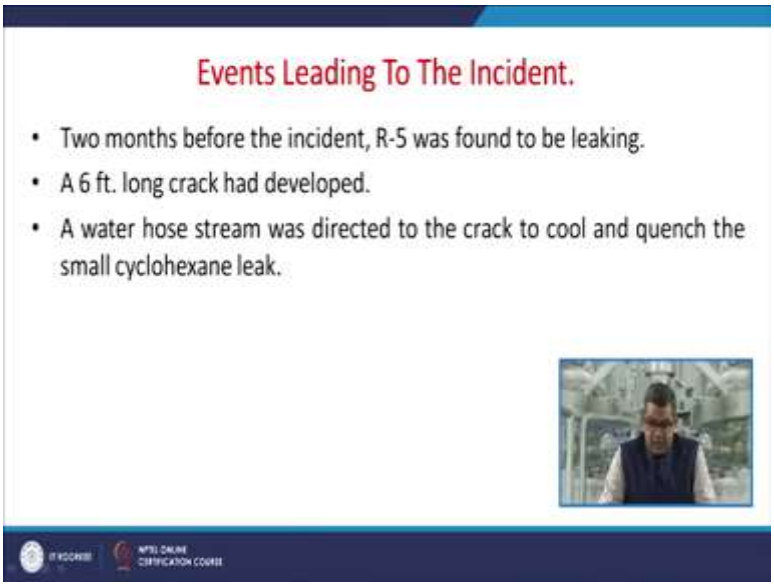

Now 2 months before the accident, the reactor number 5 was decommissioned and because they were founded to be leaking, a 6 feet long crack there in that particular reactor was developed, a water hose stream was directed to crack, to the crack to cool and quench the small cyclohexane leak.

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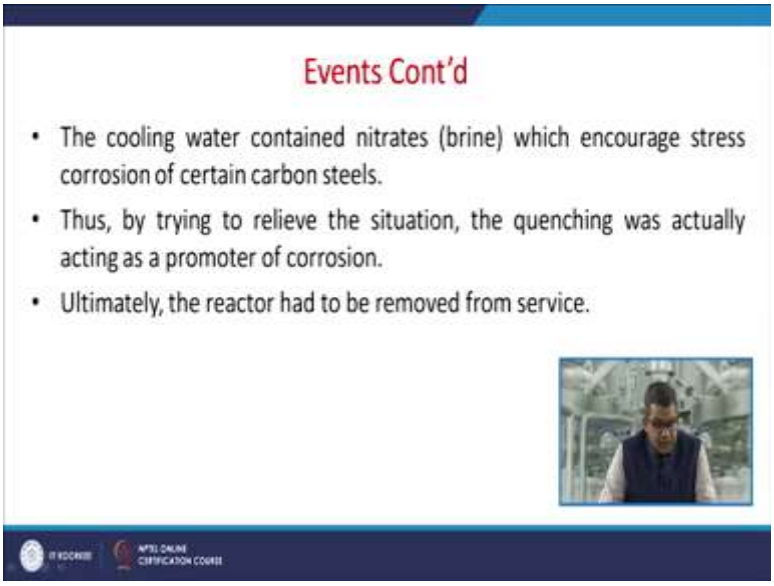

And this cooling water contained nitrates, brine just to have a thermodynamic calculation. So which (can) encourages the stress corrosion of certain carbon steel. So thus by trying to relieve

the situation the quenching was actually acting as a promoter of corrosion. So ultimately they were, they were decided to decommission that particular reactor from the service and they were trying to repair that particular reactor in due course of time.

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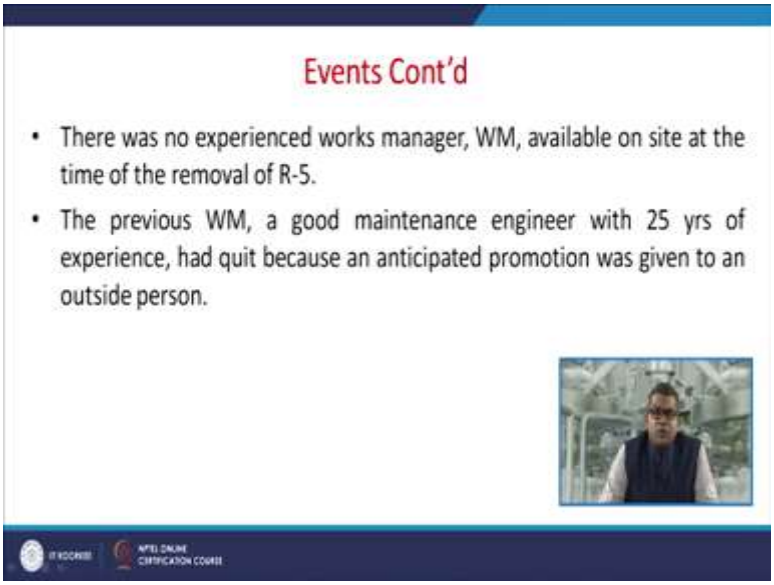

See there was no experienced worker, work manager available on the site to the time of removal of reactor number 5. The previous work manager, (which) who was a very good maintenance engineer with the 25-year experienced had quit job because an anticipated promotion was given to (an) another outside person. So this may be the reason when we were discussing about the accident investigation so human value point is there.

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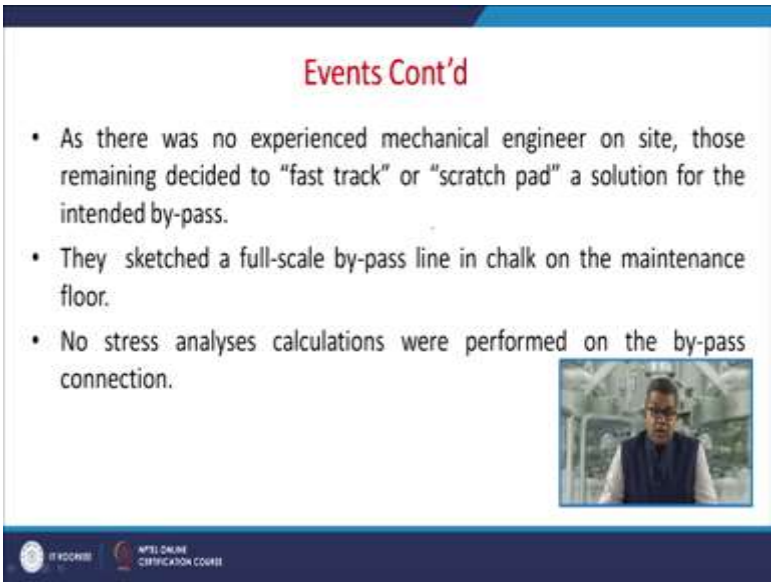

Now this event could not be happened as there was no experience mechanical engineer on site. Now those remaining decided to fast track on scratch pad type of solution to intent the bypass, so they just sketch the full-scale bypass line in chalk on the maintenance floor and that was highly undesirable because when you are having such a high sensitive plant with you. They were not carried out any stress analysis calculation on that particular bypass connection.

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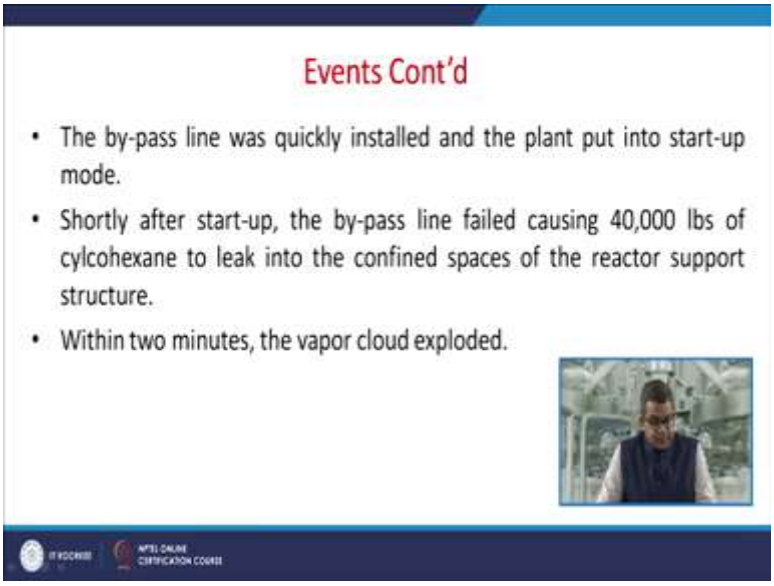

Now because they were so much under the stress, they the bypass line was quickly installed and the plant put into startup mode as quickly as possible. Now shortly after startup the bypass line failed causing forty thousand to hundred thousand pounds of cyclohexane to leak into the confined space of the reactor support structure. The reason was that initially the, the maybe the plant was having the low pressure and initially when they were raising the pressure, there was a pressure fluctuation that could have lead the rupture of that particular pipeline So within 2 minutes the vapor cloud that vapor cloud exploded.

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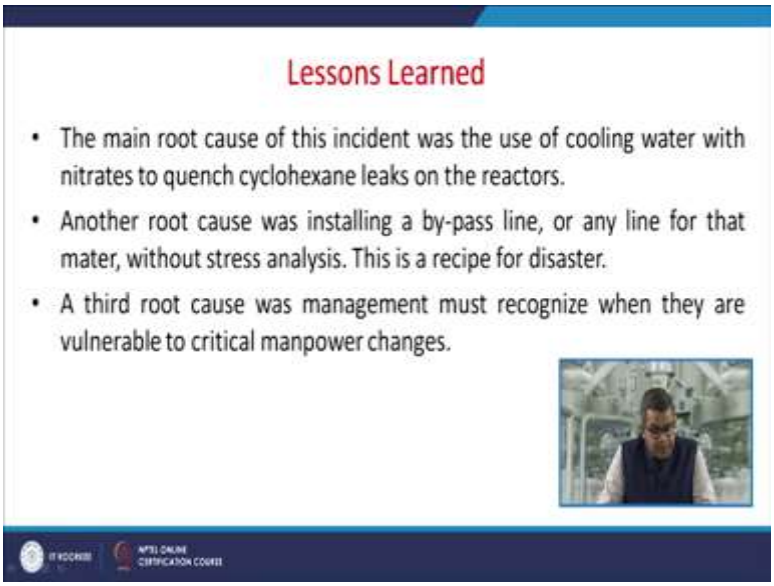

Now, we can learn a several lessons from this particular Flixborough explosion the main root cause of this incident was the use of the cooling water with the nitrates to quench cyclohexane leak on the reactor. So the, whenever you are compelled to use this type of cooling water carry out the stress analysis. Another root cause was installing a bypass line or any line for that matter, without any kind of stress analysis and that is the recipe of the disaster. The third root cause was the management must recognize when they are vulnerable to a critical manpower change. So if you recall the maintenance engineer, he was forced to quit the job because the promotion was given to some outsider. So that was a human value task.

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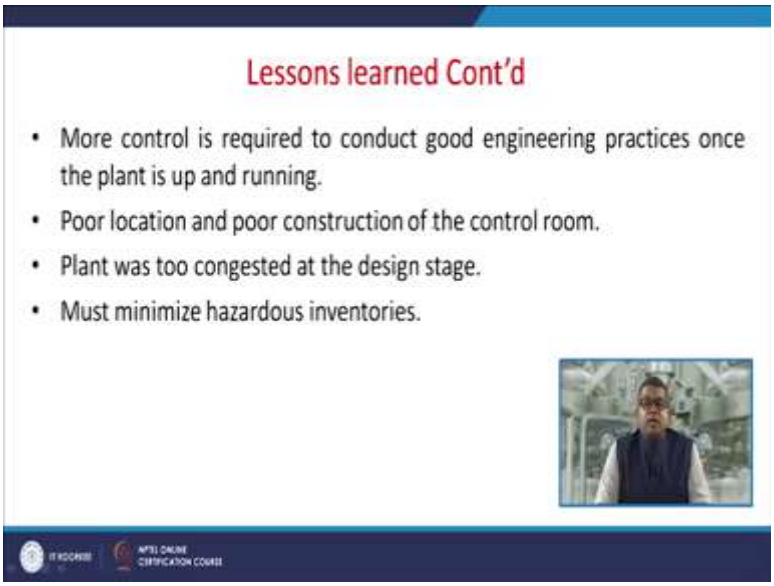

The more control is required to conduct a good engineering practices once the plant is up and running, that means the top at that particular point of time the workers, they were not well trained because they carry out all kind of bypass analysis through chalk on the maintenance floor. The poor location and a poor construction of the control room because it was collapsed at the time of vapor cloud explosion. The plant was too congested in that design (state) stage.

So if you can see the previous figure that was extremely congested because and remember the plant was having the involvement of a extremely highly dangerous flammable vapors. So they must minimize the hazardous inventories, at the time of accident they were having a very large quantity of hazardous inventories like acid, benzene, cyclohexane etc.

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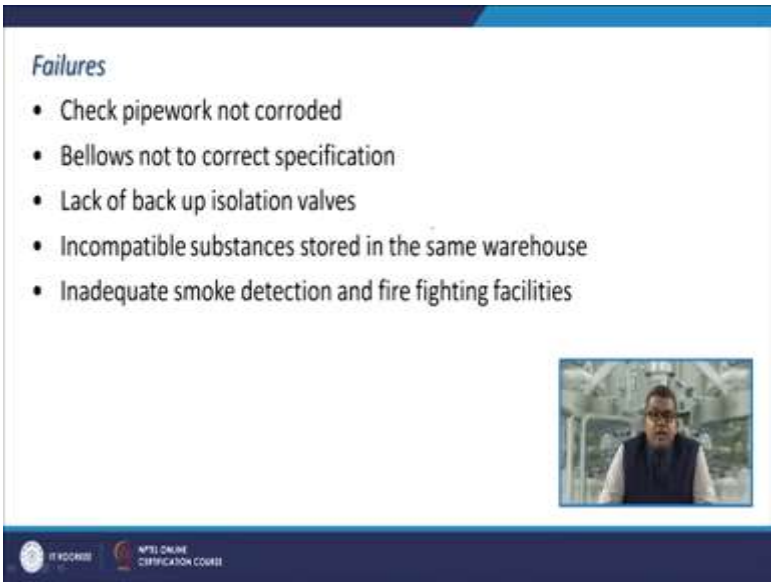

There were certain failure analysis need to be carried out like check pipework, which was not corroded, bellows they were not corrected specification because as a protocol whenever you are replacing anything and then the replacement should carry the same type of specification. So there was a lack of backup isolation valves, although it was not necessary at the time because all these 6 reactors they were connected in series. Incompatible substances stored in the same warehouse when they were not supposed to be there. Inadequate smoke detection and firefighting facilities were there at the time of accident in the Flixborough plant.

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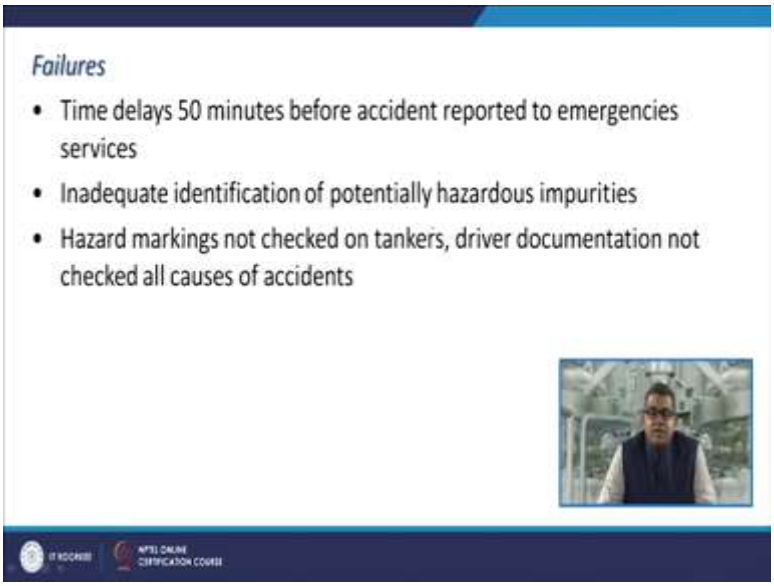

There was a time delay of 50 minutes before accident reported to emergency services. There was an inadequate identification of potentially hazardous impurities and hazard marking was also not checked on the tanks, driver documentation not checked, all the causes of accident. The reason was that because the source of ignition was unknown and it practically investigation team failed to find out the source of ignition from which that vapor cloud was ignited.

So in this particular module, we had a discussion about the Flixborough accident and a proper accident investigation and what was the failure of that particular Flixborough explosion. So in the subsequent slide, subsequent module, we will discuss about Seveso, that is related to the toxicological studies, Bhopal again, it was related to the toxicological studies and the Jaipur accident. Thank you very much.