Chemical Process Safety
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Lecture 52
Seveso Accident
July 10, 1976

Now welcome to the case study related to the toxicological aspect. Now here we will discuss the two cases, one is Soveso another one is the Bhopal. Now why these accidents are important? The reason is that unlike fire and explosion, these toxicological accidents they are having a long-term impact. So the impact is divided in two fold, one is the immediate impact, when few a couple of fatality or small amount of injury may take place and sometimes the injuries are not there because they may become the part (and the), the toxicant they may become the part and parcel of your body system through inhalation, dermal absorption etc and sometimes these toxicants they are having a very vital role because sometimes they may even change the (geno) gene character of body. So they may have a long term impact on the human.

Now as far as the environment is concerned then they may have a larger impact because the soil, air, water they may get contaminated over the period of time. So whenever those people, those who are using the soil may be in terms of growing the vegetables or vegetations etc or they are using the groundwater they may be get contamination over the period of time. So they are having the la long-term impact. So that is why these the toxicological accidents they should not be look into that how many fatalities are there, but they should be look into terms of that, how much impact they are giving to the environment as well as the human value. So prior to Bhopal the Seveso accident was termed as the most dangerous and disastrous accident in terms of toxicology.

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Now it was dioxin pollution and took place in Italy in 1976. So let us have a brief history about that particular plant and accident and then we will carry out the accident analysis in terms of case study. Now this is an extremely serious accident, this was an extremely serious accident occurred in 1976 in a small chemical plant located not far from Milan. Now it is known as The Seveso Disaster because Seveso was the most affected community at the point of time. Now this industrial plant was owned by a company called ICMESA sometimes referred as MESA, now Industrie Chimiche Meda Societa Azionaria. Now this is a subsidiary of an Italian company which in turn was a subsidiary of Hoffmann-La Roche the plant was built many years before the accident and it was involved in the manufacturing of dioxins.

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So the, due to a mechanical failure the temperature rose to around 300 degrees Celsius and the relief valve eventually opened and 6 ton of material this including 1 kilogram almost 1 kilogram of TCDD that is called Tetrachlorodibenzodioxine, they were all content for release to the atmosphere and they spread around 18 kilometers square, square kilometer area. So these (dogs) dioxins are extremely dangerous to mankind. So these they first came to widespread public notice during the Vietnam War when it was identified as a component of the defoliant Agent Orange and previously the substance had been banned from agricultural use because of its alleged toxic effect on humans. So people were very much aware about the severity of that particular chemical.

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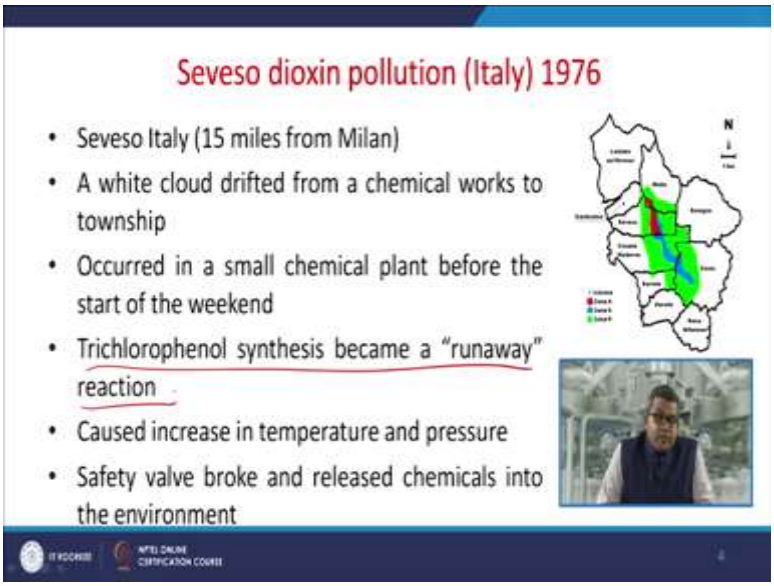

Now this Seveso Italy, it is 15 miles from Milan. Now a white cloud drifted from the chemical site work to the township. So that depends on the wind direction at the time of the release, now they occurred in a small chemical plant before the start of the weekend and Trichlorophenol synthesis become the runaway reaction. So it is some sort of thermal runaway reaction. This caused the increase in the temperature as well as the pressure and just to relieve the system the safety valve broken down and release the chemical into the environment.

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So this particular substance was TCDD 2, 3, 7, 6 tetrachlorodibenzoparadioxin. Now again, there was a lack of communication between the plant officials and local authorities. So they first notice when the animal tend to die and people fell in. However, please remember that there was no death directly attributed to TCDD. So, if you recall the previous statement made by me (in) at the start of this lecture, they may not have a immediate effect in terms of a fatality, but it may have some sort related to the occupational illness or illness and they may have a long term impact to the society. So coming back to the nothing, the product was hexachlorophene, a bacteriocide which trichlorophenol produced as an intermediate.

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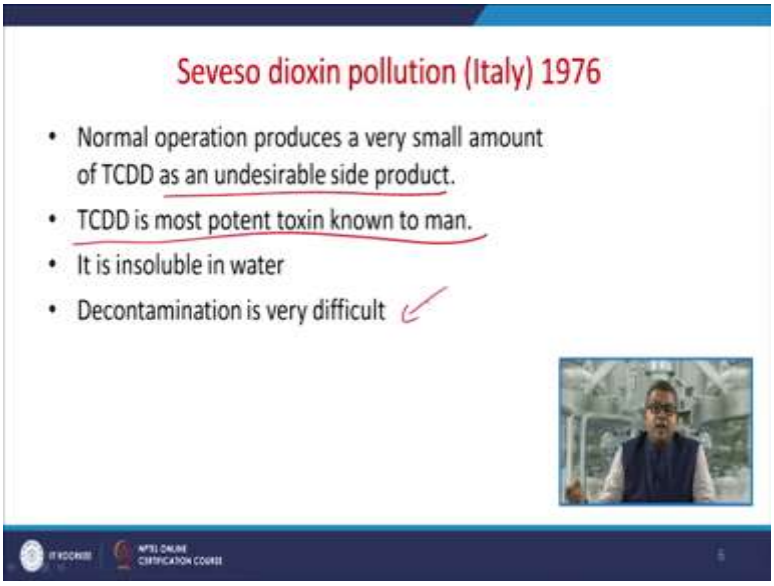

The when you are having a very controlled things in your in your hand and you are strictly following the chemical kinetics suggested by the engineers so, normal operation it produces a very small quantity of TCDD as an undesirable side product. Now this is the TCDD is the most potent toxin known to man. It is (unsol) insoluble in water and (decom) decontamination is extremely difficult. Now in the subsequent side, we will discuss that how we can decontaminate this particular TCDD from any process plant.

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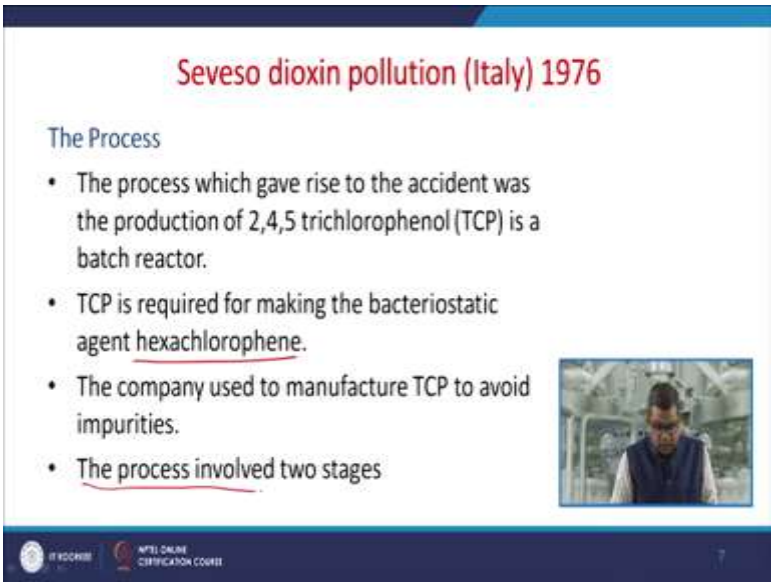

Now let us have a discussion about the process, the process which gave rise to the accident was the production of 2, 4, 5 trichlorophenol TCP is in a batch reactor. Now, this trichlorophenol is required to for making the bacteriostatic agent called hexachlorophene . Now the company used to manufacture this trichlorophenol to avoid any kind of impurities. Now this process involved two stages.

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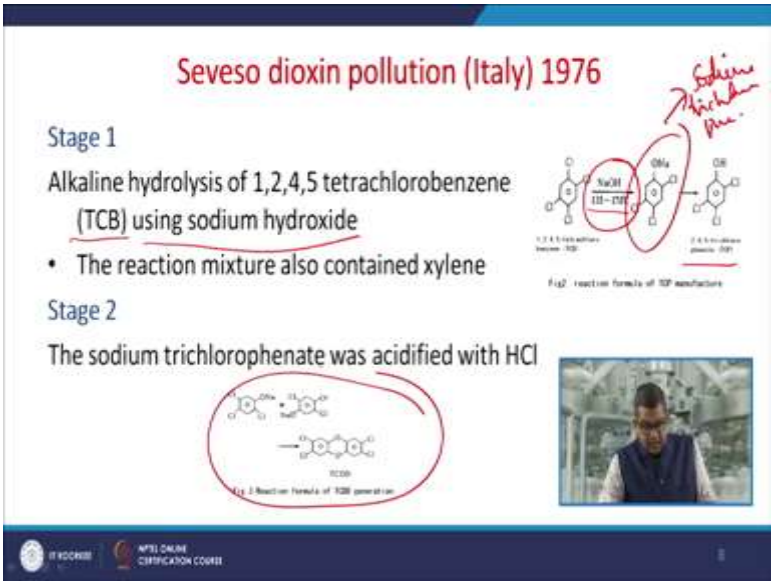

The stage one, the alkaline hydrolysis of 1, 2, 4, 5 tetrachlorobenzene referred as TCB using sodium hydroxide environment. Now the reaction mixture also contains some xylene so you can see this, this is the reaction mechanism 1, 2, 4, 5 tetrachlorobenzene in presence of NaOH the temperature of 135 to 170 degree Celsius. It gives rise to this, then the second stage the sodium trichlorophenate, this was the sodium trichlorophenate, (sodium tricehlorophenate) this was acidified to with HCL to give the trichlorophenol TCP. So this is the reaction formula for the generation of a TCDD.

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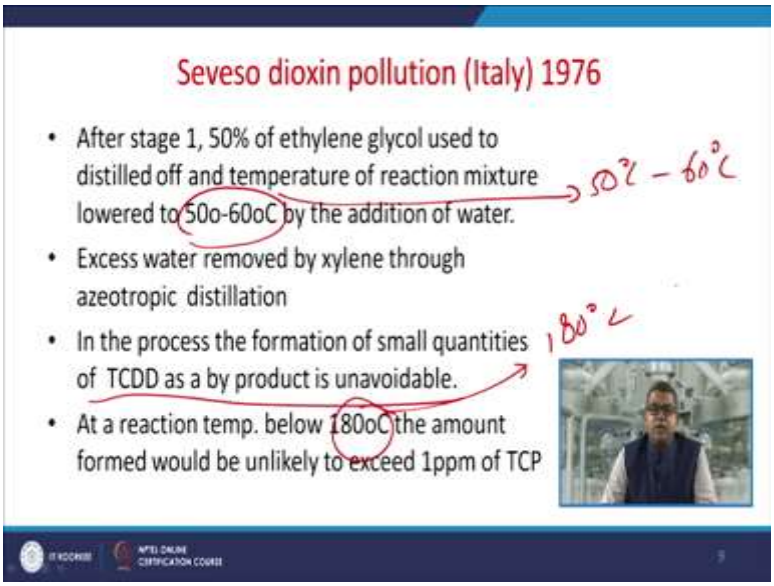

Now, there were certain mandatory steps involved in that particular production line. So after stage 1, that is this one stage this stage, after stage 1, 50 percent of ethylene glycol used to distill off and the temperature of the reaction mixture needs to lower down to 50 to 60 degree Celsius. It is 50 to (50 degrees) to 60 degree Celsius by the addition of water. Now excess water usually removed by the xylene through the azeotropic distillation. So in the process the formation of small quantities of TCDD as byproduct is unavoidable. So at a reaction temperature below 180 degrees Celsius, it is 180 degrees Celsius. The amount formed would be unlikely to exceed 1 PPM of TCP.

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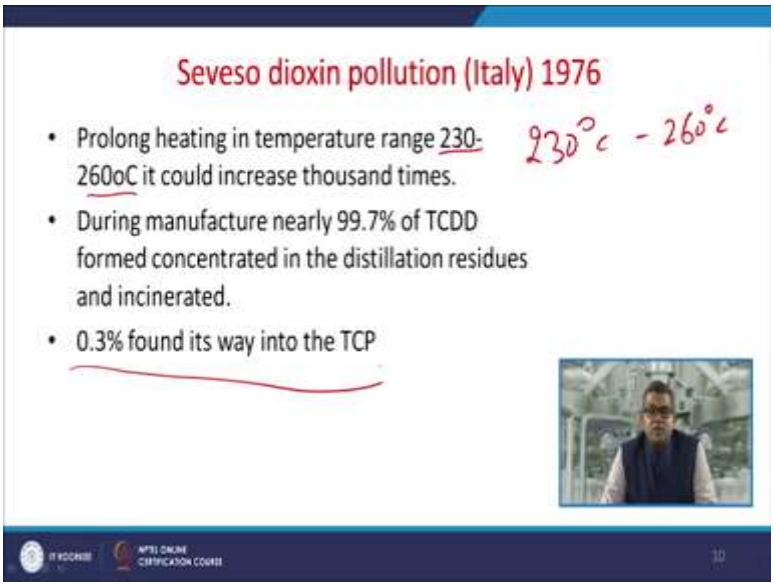

Now if you go on the prolong heating in the temperature range of 230 to 260 degrees Celsius, it could increase the thousand times. So, during the manufacturing or during the process nearly 99.7 percent of TCDD formed concentrated in the distillation residues and incinerated. Now only (1) 0.3 percent, 0.3 percent found its way into TCP.

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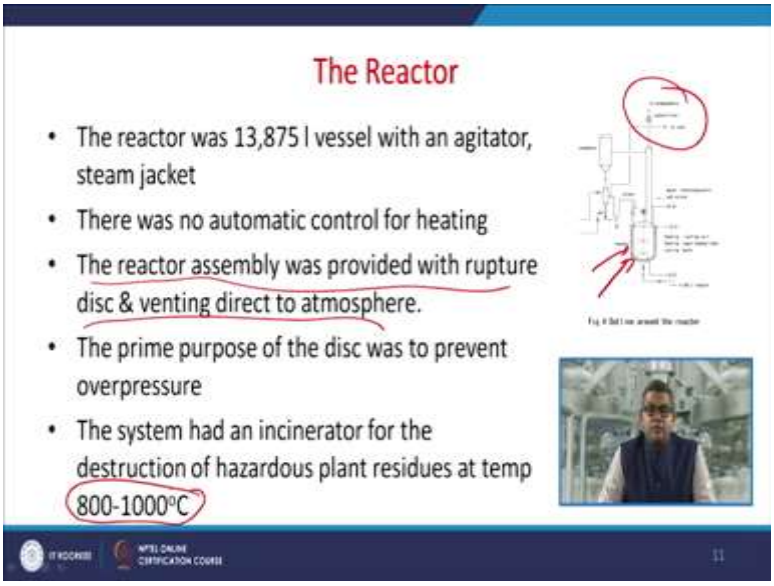

Now let us have a brief look about the reactor. The reactor was 13875 liter of vessel with an agitator and steam jacket and there was no automatic control for heating. The reactor assembly

was provided with the rupture disc and venting direct to atmosphere. So that was you can say, lacuna in that particular process. So this is, you can see the rupture discs and which is exposed to the atmosphere. The prime purpose of disc was to prevent the overpressure. Now the system had an incinerator for the destruction of hazardous plant residue at temperature (80) 800 to 1000 degree Celsius.

So they properly knew the fact that this TCDD is having problematic approach. So (they were) the plant was equipped with the (destruct) destruction facilities, which was maintained at 800 to 1000 degree Celsius.

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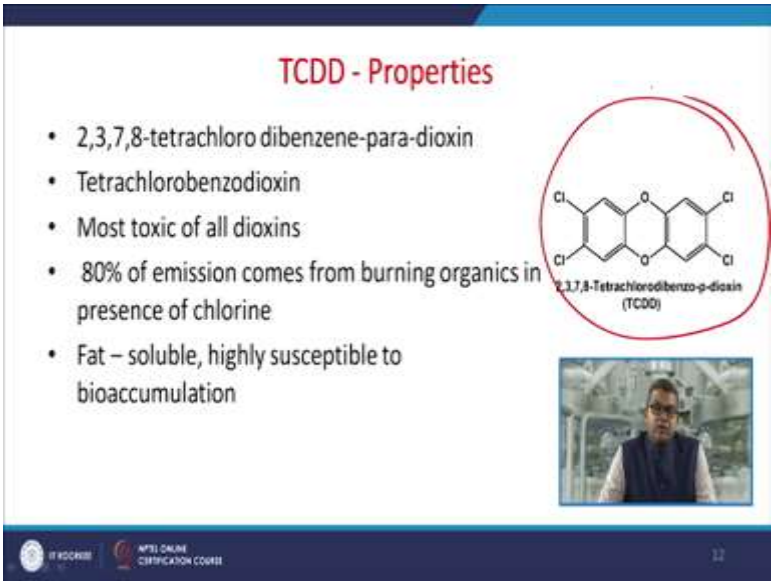

Now, let us have a look about the abridged MSDS of this TCDD. Now this is 2, 3, 7, 8 tetrachloro dibenzene-para-dioxin having the formula like this. This is most toxic of all dioxins so 80 percent of emission comes from burning organics in presence of chlorine. Now this is a fat-soluble, highly susceptible to bioaccumulation. So sometimes it may deposit in the fatty tissues of your body. So that is why I am saying that this is the problem may come later on. You may not observe the immediate problem, but the health issues may come on later on because this is fat soluble and highly susceptible for the bioaccumulation.

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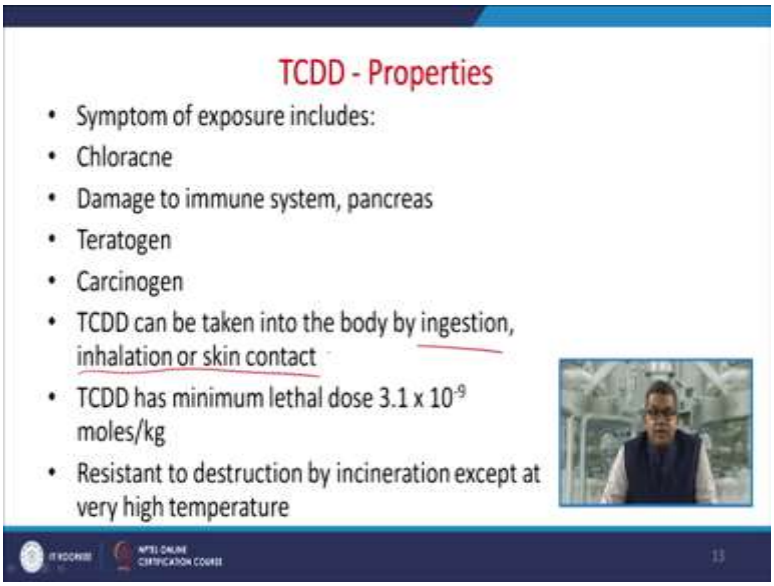

Now there are certain symptoms of exposure, this includes the Chloracne, the damage to the immune system, pancreas etc because it is a fat-soluble tissue. A Teratogen, sometimes it may lead to the carcinogenic ability then, this TCDD can be taken into the body by ingestion, inhalation or skin contact. So which we had a discussion in the industrial hygiene chapter. Now this TCDD has the minimum lethal dose of 3.1 into 10 to the power minus 9 moles per kilogram. So you can see that how dangerous it is. Now this resistant to the destruction by the incineration except at a very high temperature, that is why they maintained the destruction temperature at 800 to 1000 degree Celsius.

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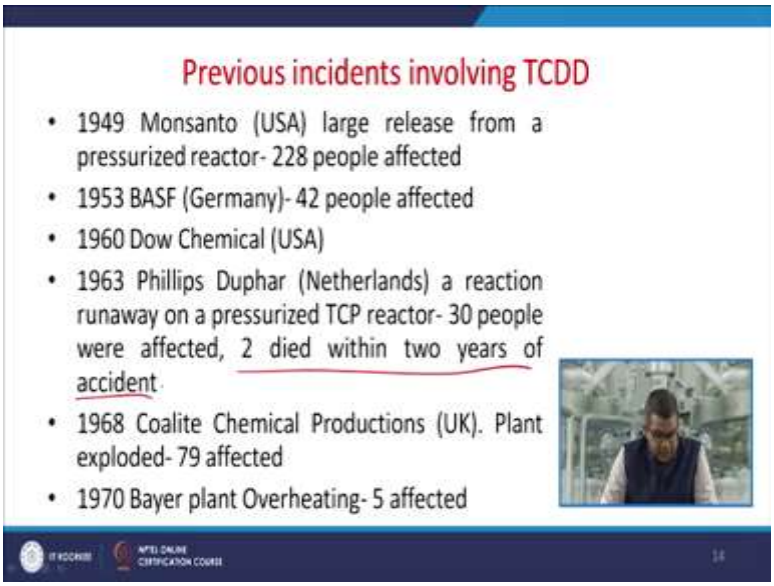

Now there were (severe) previous incident involved a TCDD, in 1949 Monsanto USA they had a large release from a pressurized reactor and 228 people they were affected. Remember we are talking about the immediate illness, immediate fatality etc. So (the) some of them may have the long-term problem, those might have reported or not that is a big issue. So in 1953 BASF the Germany they 42 people they were affected. In 1960 Dow chemicals, in 1963 Phillips Duphar Netherland a reaction run away on the pressurized TCP reactor and 30 people they were affected and 2 died within 2 years of the accident. So you can see that the result or of this body intake came after 2 years. So, in 1968 Coalite Chemical Production UK plant exploded and 79 affected. In 1970 Bayer plant overheating 5 people they were affected.

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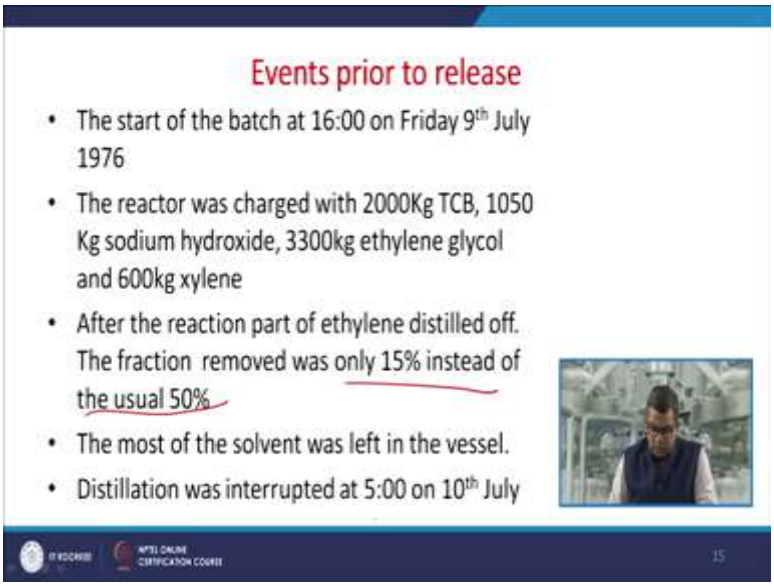

Now, let us have event of sequential event of this particular incident, the start of the batch took place at around 4 pm on Friday 9 July, 1976. The reaction was charged with 2000 kilogram of TCB, 1050 kilogram of sodium hydroxide, 3300 kilogram of ethylene glycol and 600 kilogram of xylene. So after the reaction part of ethylene distilled off, the fraction removed was only 15 percent instead of 50 percent which was desired. So that was the first instance when the people committed mistake. So, when you are having lesser number quantity of the material removed, then the most of the solvent was left in the vessel and distillation was interrupted at 5 am on 10thJuly, 1976.

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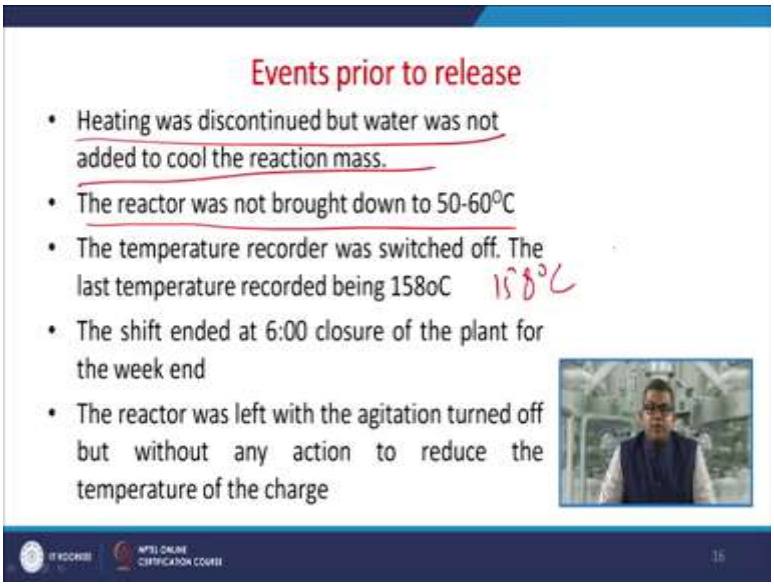

Now this heating was discontinued but water was not added to cool the reaction mass. Again that was a sheer negligence. So (the) because the water was not added so reactor was not brought down to 50 to 60 degree Celsius and the temperature recorder was switched off and the last temperature was recorded at 158 degrees Celsius. Remember the shift was ended at 6 am closer to the plant for the weekend and that is why lesser number of people were affected by this discharge. Now the reactor was left with the agitation turned off but without any action to reduce the temperature of the charge.

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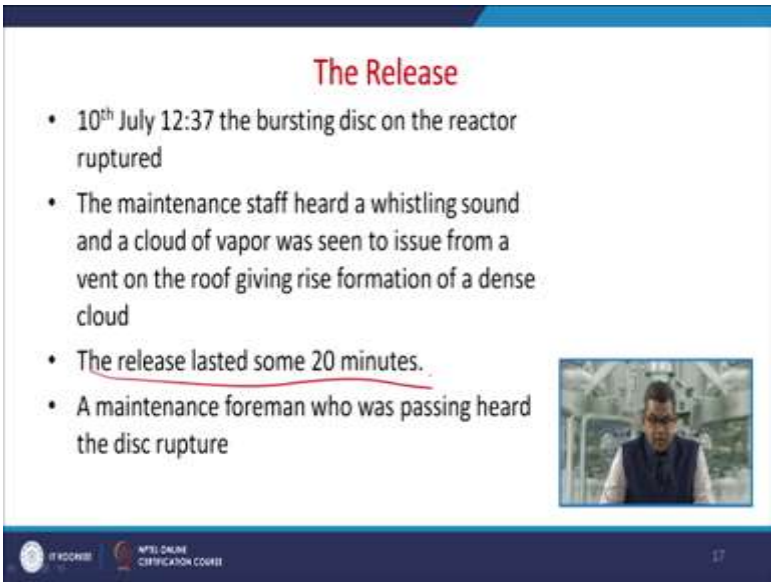

So on 10th July, around 12:30 pm the bursting disc on the reactor ruptured then the maintenance staff those who were present on site heard a whistling sound and a cloud of vapor was seen to issue from a vent on the roof giving rise to the formation of a dense cloud. So the release because the reactor was a very small size, so the quantity of the release was very small, so the release lasted for some about 20 minutes and then a maintenance foreman who was passing heard the disc rupture because a huge sound was there.

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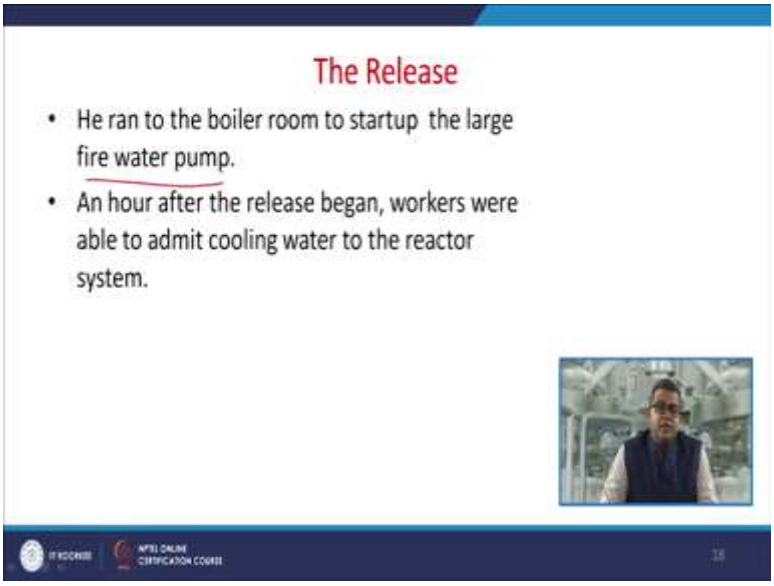

So he ran to the boiler room to start up the large fire water pump. So an hour after the release began the workers were able to admit the cooling water to the reactor system. Now since the reactant contents was not brought down to 50 percent, so thermal runaway reaction was promoting at the time of shift, when the shift was over. So that was the thing when why the pressure was continuously built up and the rupture disc was freed. And again (the) this was the main chemical kinetics who suggested the formation of minimum TCDD within the reactor mass.

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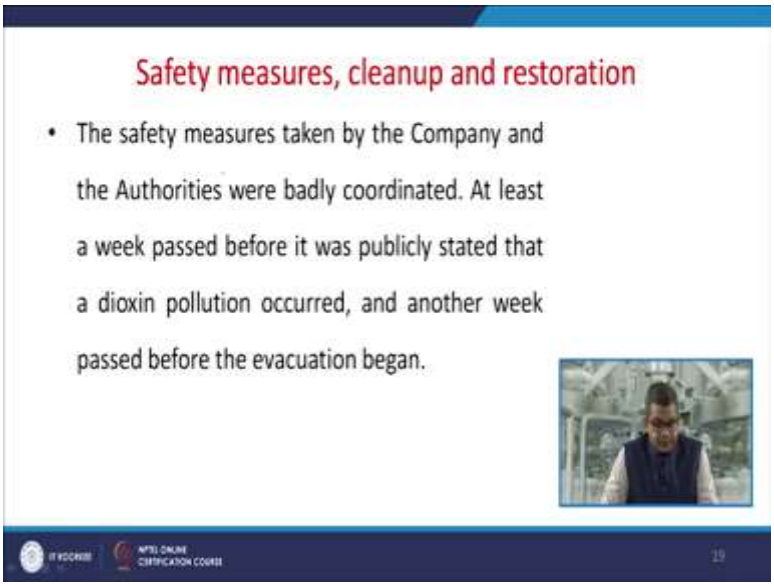

Then, once it was escaped or the there was a release of a TCDD then the people started the various safety measures, they started the cleanup activities and the restoration activities. So the safety measures taken by the company and authorities were badly coordinated, there was a lot of communication gap between these two bodies. So at least a week passed before it was publicly stated that a dioxin pollution occurred and another week passed before the evacuation began. So you can imagine that for almost 7 days, the people were continuously under the exposure of this TCDD.

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So within days a total 3300 animals were found dead and mostly poultry and rabbits then the authorities ordered the emergency slaughtering of those animals. Now they it was just to prevent the TCDD from entering into the food chain and in (19s) up to 1978 over 80,000 animals had been slaughtered. So you can anticipate or you can imagine that (how) what was the gravity of that particular incident?

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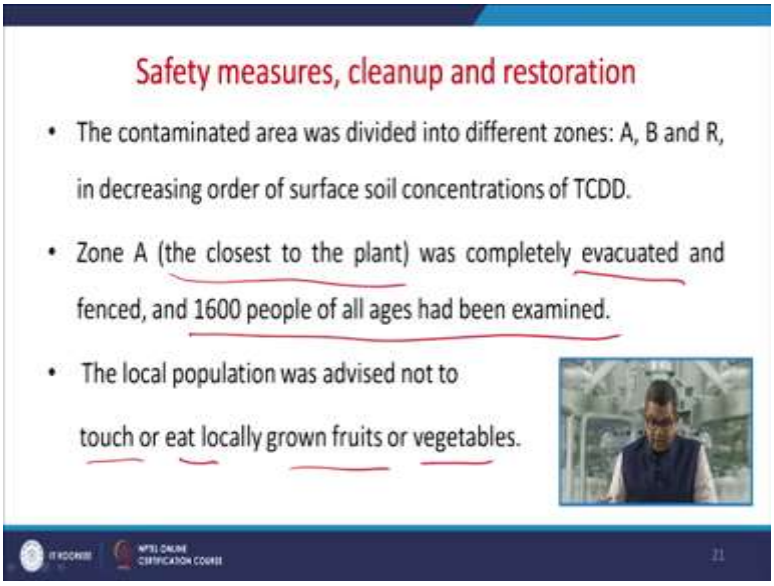

The contaminated area was divided into various zones like A, B and R in the decreasing order of surface soil concentration of TCDD. Now zone A that is the closest to the plant was completely evacuated and fenced and 1600 people of all ages had been examined. The local population was advised to not to touch or eat locally grown fruits or vegetable. So they have anticipated that the TCDD may enter into the fruits or vegetables also.

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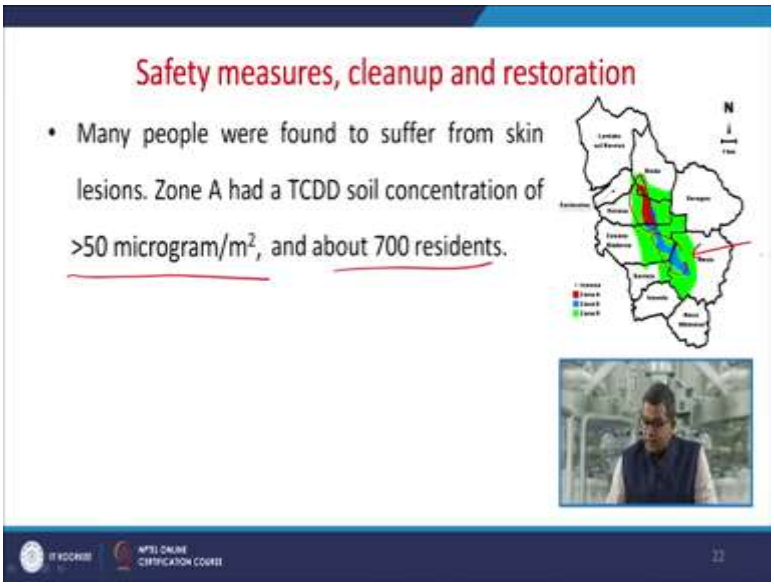

Now many people they were found to suffer from skin diseases. So zone A had a TCDD soil concentration of greater than 50 microgram per square meter and about 700 residents they were directly affected. So this is the zone A and this is the zone B and this one is the green colored is zone R.

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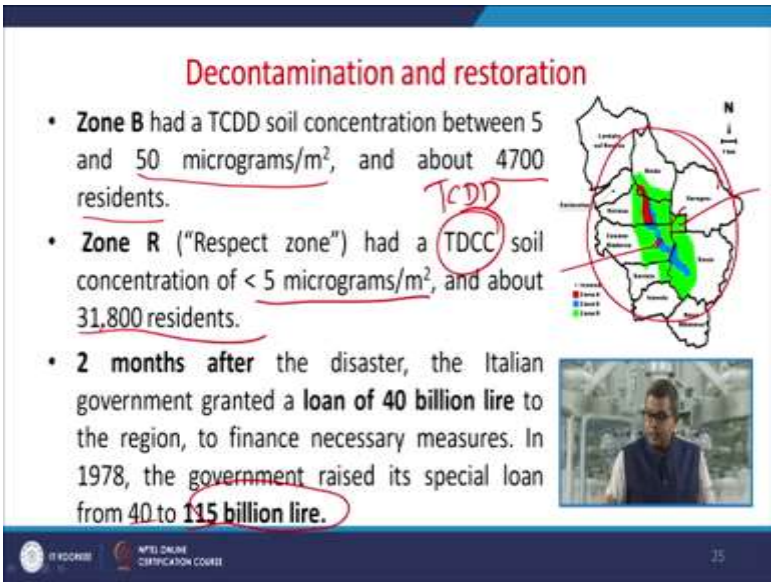

Now the zone B this one, this zone B had a TCDD soil concentration between 5 to 50 microgram per square meter and about 47 residents, 4700 residents they were affected. Now this green colored zone, this is called the zone R or sometimes this is referred as the respect zone this had a TCDD soil concentration of less than 5 micrograms per square meter and about 31,800 residents they were affected. Now 2 months after the disaster the Italian government, they granted a loan of 40 billion lire, lire the time when the incident took place was the (cut) name of the currency, which was there in Italy. Now it, nowadays it is a Euro. So they have sanctioned a loan to the region to finance the necessary measures in 1978 and government raised its special loan from 40 billion to 115 billion lire just to decontaminate and to perform the various restoration activities within this particular arena.

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Now 6 months after the accident the decontamination work began to enable the resumption of productive activities not within the plant but outside the other activities. So more than 1 year after the accident the decontamination work of zone A, this one was completed and government decided to demolish, demolish most heavily contaminated houses and rebuild. So the all the debris they were sent to some safe location to decontaminate them also.

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Now waste from the cleanup activities containing chemical residues and protecting cloth protecting clothings were stored in the containment tanks designed for the storage of nuclear waste. So you can imagine that how serious they were at the moment and just the seriousness was attributed just because of the fact that the TCDD is extremely dangerous to mankind. In 1982 several barrels of toxic waste left in that particular plant. So after a series of unclear event because there was so many events they are within the during the accident investigation, the investigator found there are so many events, they were practically not clear to them since no fatality, no proper illness, occupational illness was reported, so they left the things like unclear.

So after the series of these unclear events, 9 year after the disaster Roche which stated that the company wanted to take the responsibility of the safe destruction of the waste, they declared that the toxic waste had all been incinerated in Switzerland. So they transported all kind of toxic waste whatever leftover within the plant may be in terms of raw material, may be in terms of other contaminated debris, maybe in terms of product etc, they have taken and they have stored in the containment tanks and they disposed and they are incinerated the things in the Switzerland.

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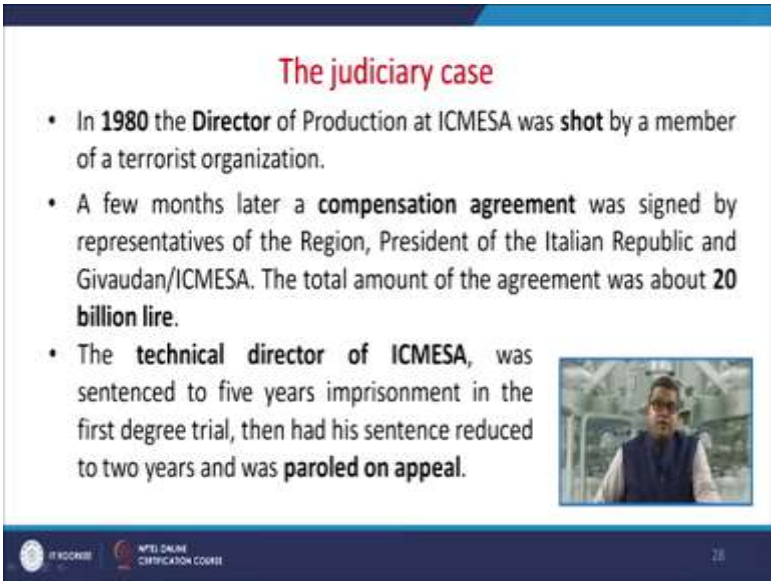

In so government of Italy, they initiated a Judiciary case against the directors of the company. So in 1980, the director of the production of the company was shot by a member of a terrorist organization because they thought that they have committed some illegal activities because it was a failure of (the) that the process protocol. So a few months later a compensation agreement

was signed by the representatives of the region, President of the Italian Republic and the company. The total amount of that agreement was about 20 billion lire. The technical director of the company was sentenced to 5 year imprisonment in the first degree trial and then had his sentence reduced to 2 years and was paroled on appeal.

In this particular module, we have discussed about the happening took place in the Seveso accident and prior to Bhopal, it was termed as the most dangerous, most devastating accident with respect to the toxicological studies. One of the major outcome of this particular incident was that they did not follow the process protocol and that outcome was that although they were having all kind of safety arrangements etc, but the most toxic dioxin was escaped to the atmosphere and the result was that the company led to the closure and it took around 4 to 5 years to decontaminate the things, though there was no fatality directly attributed to this one. Thank you very much.