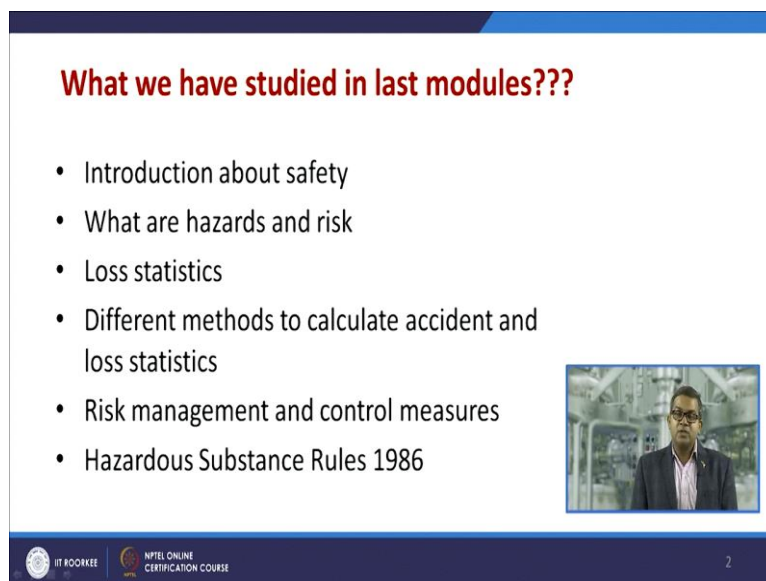


Chemical Process Safety
Professor Shishir Sinha
Department of Chemical Engineering, IIT Roorkee
Lecture 03
Nature of Accidents & Disasters


Welcome to this third module, in this particular module we will study the different type of accidents, nature of those accidents and various disaster, now the major, we are going to discuss four major disasters in brief, the reason is that prima facie must know that what was the problem and what are the different theories involved prior to the study of proper theories?

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What we have studied in last modules???

- Introduction about safety
- What are hazards and risk
- Loss statistics
- Different methods to calculate accident and loss statistics
- Risk management and control measures
- Hazardous Substance Rules 1986




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Now upto now we have studied in different modules about safety, what are the different types of hazard and risk at workplaces? We have performed the analyses of loss statistics, different methods to calculate the accident and loss statistics, we have studied about the concept of risk management and what are the different control measures to have this particular concept of risk management, we have a brief glimpse about the hazardous substance rules, 1986 and factories act 1948.

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What we will study in this lecture...

- Nature of Accident
- Introduction of Four significant disasters of world.
 1. Flixborough
 2. Seveso
 3. Bhopal
 4. Jaipur



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Now in this particular chapter we are going to study about the nature of accident, basically we will discuss three different kind of nature, fire, explosion and toxic release and based on that particular thing the introduction of four significant disasters of world Flixborough, Seveso, Bhopal and Jaipur because these four accidents, these accidents are landmark accidents and these accident gave a very important information about the chemical process safety.


Now there are three most common types of accident fire, explosion and toxic release, now in detail, we will discuss all three aspects in subsequent models, now basically because at this particular point of time, we must know the different type of accidents plus what are the major hazards? So what went wrong for those particular hazards?

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Types of Chemical Plant Accident

Type of Accident	Probability of Occurrence	Potential for fatalities	Potential for economic loss
Fire	High	Low	Intermediate
Explosion	Intermediate	Intermediate	High
Toxic Release	Low	High	Low

With respect to fatalities, accident because of toxic release having the greatest potential for fatalities.



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Now in this particular table, we find that the type of accident fire, the probability of occurrence is on the higher side and potential of fatalities is on the lower side and the potential for economic loss is in between high and low, now will discuss why all this things happened, the explosion because of the release of large quantum of energy, the potential of economic losses is on the higher side, it may not lead to the fatality on the larger segment, it may be in the range of intermediate and the probability of occurrence is intermediate, the toxic release, the toxic release, the probability of occurrence is extremely low or low, but the potential for fatality is on the higher side and economic losses are on the lower side.

Now you can see by the evidence because in the subsequent slides, when we go through all kind of accident in brief, you will find that the fatalities in terms of toxic release with respect to Bhopal gas tragedy was on the higher side compare to the fire in the Flixborough or a Jaipur or explosion in case of Seveso, with respect to fatalities accident, maybe because of toxic release having the greatest potential, may be sometimes the fire may lead to an explosion and sometimes explosion may lead to fire.

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Most accidents follow a three-step sequence:

- **Initiation** (the event that starts the accident)
Example: Mr. A threw away a burned cigarette bud into dried bushes.
- **Propagation** (the event or events that maintain or expand the accident)
Example: A portion of dried bushes ignited, releasing thick smoke and hot flame.
Fire starts to progress to another part of bushes.
- **Termination** (the event or events that stop the accident or diminish it in size)
Example: Consumption of combustible materials in process, fire extinguisher.



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Now most accidents follow three-step sequences as we discussed in module 1, the initiation, the event that starts the accident, for example, somebody threw away a burned cigarette bud into the dried bushes, now in that particular case, sometimes propagation may lead, the event or events that maintains to expand the accident, a portion of those dried bushes ignited and release the thick smoke and hot flame, fire starts to progress to another part of bushes and the termination, the event of or event that stop accident or diminish it in size, the consumption of combustible material in process or sometimes fire extinguisher.

Now remember, I talked about the Jaipur incident, IOCL depot caught the fire and that particular accident followed the three, initiation, propagation and termination steps, we will discuss this thing in subsequent slides.

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Inherent Safety


The major approach to inherently safer process designs is divided into the following categories:

- Intensification
- substitution
- attenuation
- limitation of effects
- simplification/error tolerance

Four words to describe inherent safety:

- minimize (intensification)
- substitute (substitution)
- moderate (attenuation and limitation of effects)
- simplify (simplification and error tolerance).

KISS



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Now that is inherent safety, the major approach of to inherent safe process design divided into four, five different segments intensification, that means you need to intensify the process, so that the chances for any kind of fire, explosion or toxic release may be diminished, you must be in a position to substitute with the help of suitable chemicals which are those who are less toxic, those who are less inflammable, you must give a proper attenuation, limitation of effect, you must analyse and you need to simplify the process or you need to simplify the error or tolerance.

The four buzzword to describe the inherent safety the minimize, the substitute, you must substitute, moderate conditions, maybe use of low-temperature or low pressure, sometimes may, of course it may give you low yield or low conversion but sometimes your expenditure on the safety may be on the lower side, simplify, you must follow the concept of KISS, keep it simple and safe.

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The Flixborough, UK, Cyclohexane Disaster, 1 June 74

A Vapor Cloud Explosion (VCE) Case




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Introduction



- Flixborough disaster was an explosion at a chemical plant owned by Nypro (UK) Ltd.
- Occurred in Flixborough, England on Saturday, 1st June 1974 at about 4.53pm.
- The plant has been in operation since 1967.



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Now before we go into detail of fire, toxic release and explosion, we must have a brief idea about the different accidents, those landmark accidents, the first one is the Flixborough, UK cyclohexane disaster took place on 1st June, 1974, this was purely based on the vapour cloud explosion, this Flixborough disaster was an explosion at a chemical plant owned by Nypro UK Ltd and this occurred in Flixborough, England on Saturday 1st of June, 1974, at about 4:53 PM, this particular figure is taken just immediately after the accident.

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PRODUCT DESCRIPTION


Raw material was cyclohexane

Formula	C_6H_{12}
Molecular Weight	84
Boiling Point	81 °C

Cyclohexane is a volatile liquid with a low boiling point at ambient conditions (something like petrol!)

Liquid Density	780 kg/m ³
Vapour Density (at P _{atm})	2.4 kg/m ³

Hence the liquid is lighter than water while the vapour is heavier than air (in common with many hydrocarbons).



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Now before I give you a brief description about accident, let us have a product description, the raw material was cyclohexane, the formula C_6H_{12} , molecular weight 84, and boiling point 81, now this is a very vital information and you can have this particular information from material safety data sheet for each and every component, now cyclohexane is a volatile liquid with a low boiling point at ambient conditions something like petrol, now it is having a liquid density of 780 kg/m³ and a vapour density is 2.4 kg/m³.

Now this particular aspect is essential, the liquid is lighter than water, while the vapour is heavier than air, this is common with the many kind of hydrocarbon, now this is again a very important information because for every accident you need to go for accident investigation, so that it cannot occur in near future for a same type of scenario, so this particular information, all this information, you can have it from material safety data sheet.

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Flixborough petrochemical plant, 1974

- The Flixborough works of Nypro (UK) Ltd were virtually demolished by an explosion of warlike dimensions on the afternoon of Saturday 1 June 1974.
- The explosion was estimated to be equivalent to the force arising from 15 – 45 tons TNT.
- This was due to ignition of a vapor cloud which formed when pressurized Cyclohexane escaped from a reactor, vaporized and ignited.
- On site 28 people were killed and 36 injured; if the explosion had occurred during the week there would have been many more casualties.

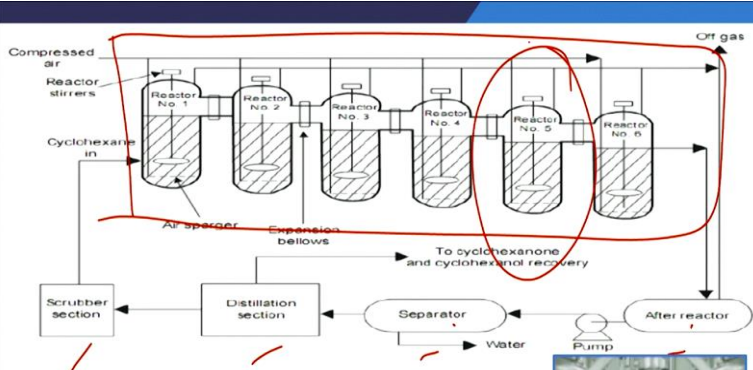


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Now the Flixborough works of Nypro was virtually demolished by an explosion of war like dimension on the afternoon of the Saturday 1974, the explosion was estimated to be equivalent to the force arising from 15 to 45 tons TNT, this was due to the ignition of vapour cloud which was formed when the pressurised cyclohexane escape from a reactor vaporised and ignited.

Now remember the initiation, propagation and termination these all three things took place in that particular accident, on-site 28 people were killed and 36 injured and if explosion had occurred during the week, there would have been many more casualties.

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Simplified flow diagram of Cyclohexane oxidation plant before March 1974 (Whittingham, 2005)



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Now what happen? Because this is the reactor battery and this Flixborough plant, they use to produce in this particular reactor battery, they used to produce cyclohexanenone from cyclohexane and this particular battery consisted of six different reactor having the capacity of 20 ton each and all these reactors were pressurised, so with the help of air, the cyclohexane is converted into cyclohexanenone, now there are four different segments through which they can get the purified cyclohexanenone, scrubber section, distillation, separator and after reactor.

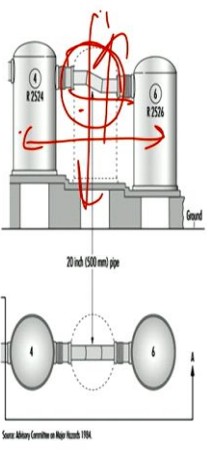
Now what happen? The reactor number 5 was faulty, so they sensed that this particular, something went wrong, so what they did? They bypass this reactor, this reactor number 5 and they just installed a flexible pipe to connect reactor number 4 with reactor number 6, no doubt, there was a very small amount of conversion loss because of the kinetics, but simultaneously, it is extremely dangerous in nature, we will go in detail when we discuss about this particular accident in detail of attributed to the accident investigation.

But without much loss in yield, they bypass the things and it took around 2 months, because 2 months prior to the explosion cyclohexane, they discovers that there is a leaking because of some variety of reasons, so they detected a leak and they decided to bypass like this.

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The Disaster

- Two months prior to the explosion, Cyclohexane was discovered to be leaking from Reactor No. 5.
- It was decided that Reactor No 5 to be removed for inspection and a temporary bypass assembly to be constructed to connect Reactor No.4 to No.6, while repairs were made.



The diagram shows a reactor battery with six vertical cylindrical reactors. Reactor No. 5 is circled in red with a red 'X' over it, indicating it is faulty. A red arrow points from reactor No. 4 to reactor No. 6, showing the bypass path. Below the main diagram is a detailed view of the bypass assembly, labeled '20 inch (508 mm) pipe', connecting two horizontal cylindrical vessels. A small inset video shows a man speaking.

Source: Ministry Committee on Major Hazards 1984

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Now what happened because of the pressure fluctuation, this particular pipe was dislocated and 80 tone of cyclohexane or mixture of cyclohexane and cyclohexanenone was exposed to the atmosphere and it created a vapour cloud and source of ignitions was enormous at that

particular time and somehow this particular vapour cloud got ignited and it is just like a fire cloud.

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Scale of Accident

- Casualties: 28 people killed & 36 seriously injured.
- Records and charts for the start up were destroyed.
- Fire remained burning for over 10 days.
- Property damage extended over wide area. More than 1,800 buildings within three miles radius of the site were damaged.
- Blast heard till 30 miles away.



The slide features three images: a man in a wheelchair, a destroyed industrial site with smoke, and a man in a suit speaking.

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So as a result 28 people killed and 36 seriously injured, the record and charts for the start-up were destroyed, fire remained burning for over 10 days because they did have a large quantity of inventories, in their store, warehouse large quantity in cyclohexane, cyclohexanone and other like products they are having the, other inflammable product they are having the large quantum of those inventories, property damage this extended over wide area, more than 1800 buildings within three miles radius of the side were damaged, blast heard till 30 miles away.

Now reason was the pressurised, vessels, they were exposed to the atmosphere and cyclohexane is extremely flammable in nature, now you can evident through the previous data given in the previous slides.

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Conclusion

- Changes to a design should be overseen and authorized by properly qualified personnel. ↩
- Carry out systematic search for possible cause of problem before any modification process being done.
- Knowledge and understanding of the hazards of the process might have prevented the accident from occurring.



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Now after accidental analyses, they found out there are certain points that is changes to the design should be overseen and authorized by properly qualified person, the carry out systematic search for possible causes of the problem before any modification process being done, because unfortunately they did not carry out any kind of pressure and temperature analyses for this particular modification, knowledge and understanding of hazard of the process might have prevented the accident from occurring.

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Seveso dioxin pollution (Italy) 1976 ↩



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Seveso dioxin pollution (Italy) 1976

- An extremely serious accident occurred in 1976 in a small **chemical plant located** not far from Milan. It is known as “Seveso disaster”, because **Seveso** was the most affected community.
- The industrial plant was owned by the company ICMESA (*Industrie Chimiche Meda Societa Azionaria*), a subsidiary of Givaudan which in turn was a subsidiary of **Hoffmann-La Roche**. The plant was built many years before the accident, and was manufacturing **dioxins**.



Another toxic release accident attributed to the Seveso dioxin pollution, it happened 1976, this was an extremely serious accident happened in the 1976 in a small chemical plant located not very much away from Milan, it is known as Seveso disaster and prior to Bhopal disaster, it was turned the most serious disaster in the toxicological studies, this industrial plant owned by a ICMESA company, a subsidiary of Givaudan, which is in turn was a subsidiary of Hoffmann-la Roche, it is a famous chemical company. The plant was built many years before the accident and was manufacturing dioxins, dioxins are more serious component to the human kind.

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Seveso dioxin pollution (Italy) 1976

- Due to a **mechanical failure**, temperature rose to around 300°C, and the relief valve eventually opened: **6 tons of material**, including 1 kg of **TCDD** (Tetra chloro-dibenzodioxin), were released over an 18 km² area.
- **Dioxin** first came to widespread public notice during the Vietnam War, when it was identified as a component of the defoliant Agent Orange. Previously, the substance had been banned from agricultural use, because of its alleged toxic effects on humans.




Now due to the mechanical failure, the temperature rose to around 300 degree Celsius and relief valve eventually opened, 6 tons of material, including 1 kilogram of TCDD, Tetra

chloro dibenzodioxin , this is more, extremely toxic in nature for the human being, it was released over 18 square kilometre area. Dioxin it first came into widespread public notice during the Vietnam War, when it was identified as a component of the defoliant Agent Orange, previously the substance had been banned from agricultural use because of its alleged toxic effects on human kind.

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Safety measures, cleanup and restoration

- The safety measures taken by the Company and the Authorities were badly coordinated. At least a week passed before it was publicly stated that a dioxin pollution occurred, and another week passed before the evacuation began.
- Within days a total of 3,300 animals were found dead, mostly poultry and rabbits. Emergency slaughtering started, to prevent TCDD from entering the food chain, and by 1978 over 80,000 animals had been slaughtered.



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Now the safety measures because this is again the lack negligence from the company official point of view because, because it was a two-step process, first step is usually carried out at distributed temperature and there was a necessity to lower down the temperature by the addition of water and it was neglected by the plant official that is called of the human error and it was neglected, once it was neglected the temperature remained at 150, 60 degree Celsius and due to the thermal runaway reaction the temperature rose of up to 300 degrees Celsius and all the safety devices failed at that particular point because the reactor was not designed to handle such type of scenario.


So all TCDD, which is in very low quantity in the discharge but obviously because it is extremely dangerous to human kind, it released into atmosphere, so the safety measures and the clean-up and restoration, the safety measures taken by the company and the authorities were badly coordinated, in the previous module we have discussed about the responsibility of the occupier, as well as the responsibility of the authorities, so at least a week passed before it was publicly stated that a dioxin pollution occurred and another week passed before the evacuation began.

Now within a day total 3,300 animals were found dead, mostly poultry and rabbits, emergency slaughtering started to prevent a TCDD from entering to the food chain of human being and in 1978 over 80,000 animals had been slaughtered, so you can imagine that it took around two years to completely restore and clean-up the things based on this particular discharge.

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The Judiciary Case

- In **1980** the **Director** of Production at ICMESSA was **shot** by a member of a terrorist organization.
- A few months later a **compensation agreement** was signed by representatives of the Region, President of the Italian Republic and Givaudan/ICMESSA. The total amount of the agreement was about **20 billion lire**.
- The **technical director of ICMESSA**, was sentenced to five years imprisonment in the first degree trial, then had his sentence reduced to two years and was **paroled on appeal**.




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Then a lot of judiciary cases were filed, in 1980, the director of the production of the company was shot by a member of terrorist organization because it was outcome of that particular incident. A few months later the compensation agreement was signed by the representatives of region, the president of the Italian Republic and the company officials, the total amount of the agreement was about 20 billion lire. The technical director of the company was sentenced to five years imprisonment in the first degree trial and then had his sentence reduced to two years and was paroled on appeal.

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Bhopal Gas Tragedy





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Bhopal Gas Tragedy

Occurrence: 3rd December 1984.
Place of occurrence: Bhopal, Madhya Pradesh, India.
Company: Union Carbide Corporation.
Chemical: Methyl Isocyanate (27-30 tons)




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Bhopal Gas Tragedy

- Half a million people were exposed to the gas
- 25000 have died to date as a result of their exposure.
- More than 120,000 people still suffer from ailments caused by the accident and the subsequent pollution at the plant site.
- These ailments include blindness, extreme difficulty in breathing, and gynecological disorders.
- The site has never been properly cleaned up and it continues to poison the residents of Bhopal.



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Now the third major accident is Bhopal gas tragedy, you can see the severity of that particular accident, this was occurred on 3 December night 1984 and the company who owned that particular plant was Union Carbide Corporation and the chemical, which was released was Methyl Isocyanate and it was released in the quantity of say 20 to 30 tons, now the severity you can see in this particular slide, that a half a million people were exposed to the gas, 25,000 have died to date as a result of this particular exposure, this is an approximate figure, more than 120,000 people still suffer from different type of ailments caused by the accident and the subsequent pollution at the plant site and this may be attributed to the gene change over because MIC is again more prone towards changing the genes.



This ailments includes the blindness, extreme difficulty in breathing and different type of gynaecological disorders, now this site has never been properly cleaned up and it continues to poison the residents nearby, we will discuss this particular, this Bhopal gas tragedy in details with attribution to accidental analyses.

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Union Carbide Corporation


- Started in 1969 in Bhopal
- Phosgene, Monomethylamine, Methyl Isocyanate (MIC) and the pesticide Carbaryl, also known as Sevin.
- Taken over by DOW Chemicals in 2001.
- DOW refused Union Carbide's Liabilities in Bhopal, India.



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25,000 KILLED
120,000 SEVERELY AFFECTED

**...And you thought only weapons
could cause Mass Destruction**



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Now Union Carbide Corporation they started their activity in Bhopal in 1969 and the material they use the Phosgene, Monomethylamine, Methyl Isocyanate and Pesticide Carbonyl and they use to produce the pesticide name as, commercial name as Sevin, it was taken over by the DOW chemicals in 2001, unfortunate part is that DOW refuse to take the Union Carbides liability in Bhopal, now see almost 25,000 killed and is still 1.2 lakhs severely affected. Still, they are suffering and we thought that only weapons could cause the Mass destruction, this is Mass destruction.

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Jaipur Terminal Fire, India **29th October 2009**



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Jaipur Terminal Fire

- In addition the plot accommodated the facilities for pipeline division which operated the cross country pipeline, viz. the Koyali Sanganer product pipeline feeding this terminal.
- The marketing terminal occupied 105 acres and the pipeline division facilities were located in 15 acres in the north east corner of the facility.



The Jaipur terminal fire, it happened on 29th of October 2009, IOCL, they are having this Jaipur terminal and in addition to this, the plot accommodated the facility for pipeline division, which operate the cross-country because it was on the pipeline grid, the Koyali Sanganer product pipeline feeding that particular terminal, they are having the marketing terminal occupied 105 acres land and a pipeline division facilities were located in 15 acre in the North East corner of the facility.

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Losses

- About 60,000 KL of petroleum products stored in the Terminal at the time of the accident and the installation was totally destroyed.
- Buildings in the immediate neighborhood were heavily damaged and minor damages and window panes breakages occurring upto ~ 2 Km from the site.
- The total loss estimated on account of the fire and explosion as reported by IOC in the Press, which includes the loss for finished products, stores, fixed assets and compensation for third party losses, amount to **approx. Rs. 280 crores.**
- Eleven people lost their lives in the accident
 - ✓ Six from IOC and five outsiders, and several others were injured



Now there was a certain release of petrol and diesel from this particular facility and a vapour cloud was formed and somehow this vapour cloud was got ignited and initiation took place, now because of the combustion of this petroleum product a lot of heat being liberated and because of this, because of delta H, enthalpy content of those petroleum product, now

because of the net release of energy on other tanks they got heated up and vapour clouds tends to form.

Now because of this vapour cloud the propagation took place because through conduction, through auto ignition or through radiation these remaining tanks they got ignited and propagation took place and plant officials were not in a position to control this things, so termination could not be possible at a moment and they followed the let it go policy, so they waited for a long period to consume all the petroleum product within the plant by the fire.

So, about 60,000 kilo litre of petroleum product stored in that particular terminal at the time of accident and the installation was totally destroyed, building in the immediate neighbourhood were heavily damaged and minor damages and window panes breakages occurring up to 2 kilometre from the site, you can see the gravity because the formation of vapours due to the attributed, due to the heat.


So the total loss estimated on account of fire and explosion as reported by Indian oil Corporation, in press, which includes the loss of finished product, stores, fixed assets and compensation for third-party losses, amounted about rupees 280 crores, 11 people within the site lost their lives in the accident, six from IOC, five they were outside and several others were injured, so this is the true example of initiation, propagation and termination and termination usual control measures they did not work, they were not in a position to control that particular fire because of the generation of lot of heat.



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Overall Lessons Learnt

Based on the Jaipur incident a few lessons learnt are highlighted:

- Facilities and installations with inherently high hazards should incorporate redundancy in safety systems and ensure their upkeep at all times.
- Management should ensure that reliable systems are in place to give timely feedback on the current practices and state of readiness in different facilities.
- Management must ensure that identified actions are being carried out.
- A high priority on safety from the senior and top management groups will send the right signals down the line to ensure safety and production.



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So overall lesson learned based on Jaipur incident the a few lessons are learnt they are highlighted like facilities and installations with the inherently high hazards should incorporate redundancy in safety systems and ensure their upkeeps at all times, management should ensure that reliable systems are in place to give timely feedback on the current practices and state of readiness in different facilities, management must ensure that identified actions are being carried out, a high priority on safety from the senior and top management groups will send the right signals down the line to ensure the safety and production.

Now in this particular module we have studied about the safety, different accidents, we have studied about what are the major things in the safety things like fire, toxic release and explosions etc, in the subsequent modules we will discuss all this things in detail. Thank you.