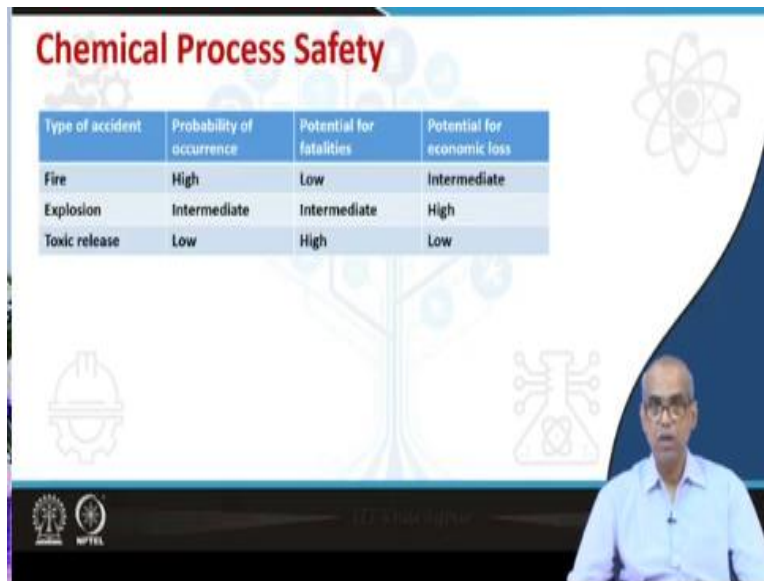


Plant Design and Economics
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Lecture No -54
Toxic Release, Hazard Identification and MSDS

Welcome to lecture 54 of plant design and economics. We have talked about the fires and explosions. Now, we will talk about toxic release which has the greatest potential for fatalities. We will also talk about very briefly Hazard identification as well as material safety data sheet or commonly known as MSDS.

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| 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 |

So we have been talking about these three different accidents in chemical process industries, fire explosions and toxic release. Toxic release has low probability of occurrence, also it has low potential for economic loss, but it has the highest potential for fatalities.

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Toxic Release Hazard

The hazard posed by toxic release depends on

- The chemical species
- On the conditions of exposure

The high disaster potential from toxic release arises in situations in which large numbers of people are briefly exposed to high concentrations of toxic material.

However, the long-term health risks associated with prolonged exposure at low concentrations over a working life also present serious hazards.

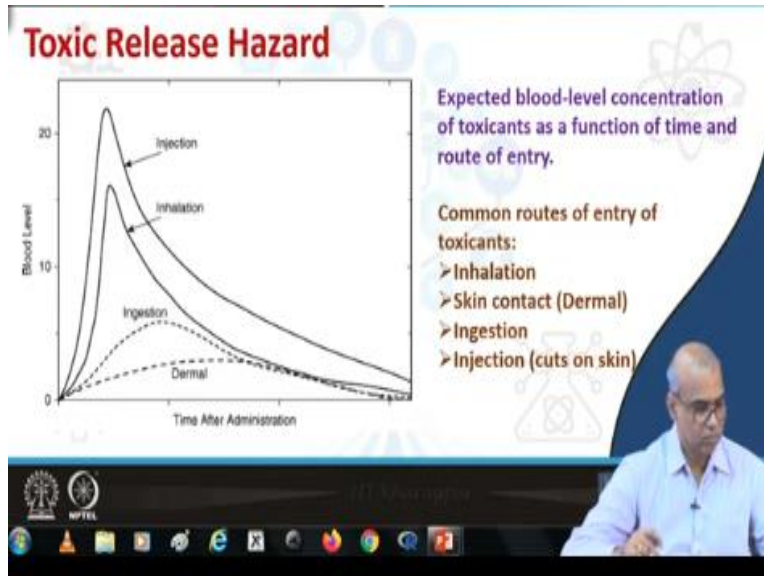
For a chemical to affect health, a substance must come into contact with an exposed body surface. The common three ways in which this happens are by inhalation, skin contact and ingestion.

Logos for IIT Bombay and MPTEL are visible in the bottom left corner of the slide.

The hazard posed by toxic release depends on the chemical species and also on the conditions of exposure. The high disaster potential from toxic release arises in situations in which large numbers of people are briefly exposed to high concentration of toxic material. However, the long term health risks associated with prolonged exposure even at low concentrations over a working life also present serious hazard. So we must consider both short term exposure as well as long term exposures.

Exposures to high toxic concentrations for short duration as well as long term exposure to low concentrations, so both present serious hazards. For a chemical to affect health or toxic material to affect our health condition, a substance must come in contact with an exposed body surface. And what are the roots through which such contact is possible? They happen by inhalation, skin contact and ingestion or swallowing through mouth.

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Now when toxic material gets into our body either through inhalation or skin contact, which is known as dermal or ingestion, that is through the mouth, the concentration of the toxic material in the blood will increase. And if we plot the concentration of the toxic material in the blood versus time after administration you will get typical curves like this. So this is for inhalation, this is for ingestion and this is for skin contact. Among these three, note that inhalation shows a quick peak.

Now, if a worker has say cuts on skin and then that cut portion is exposed to toxic material. So the effect will be something similar with injecting toxic material to the worker. And through injections you are sending this toxic material directly to the blood. So, obviously you will get a very high peak that means a large amount of toxic material in the blood very soon after the administration.

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Toxicants: Method of Control

| Entry route | Entry organ | Method for control |
|-------------------|------------------|--|
| Ingestion | Mouth or stomach | Enforcement of rules on eating, drinking, and smoking |
| Inhalation | Mouth or nose | Ventilation, respirators, hoods, and other personal protection equipment |
| Injection | Cuts in skin | Proper protective clothing |
| Dermal absorption | Skin | Proper protective clothing |

Now, these are some of the methods for controlling the entry of such toxic materials to various roots. When the entry root is ingestion, the entry organ is mouth or stomach and to avoid entry of toxic material at the workplace rules should be enforced on eating, drinking and smoking habits. When the entry root of toxic material is inhalation, the entry organ is mouth or nose and the method for control should be ventilation, respirators, hoods and use of other personal protection equipment.

If a worker has cuts in the skin, the entry root of the toxic material may be injection, so the worker must use proper protective clothing. Similarly, to avoid entry of toxic material through skin or dermal absorption, workers must be using proper protective clothing.

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Toxic Release Hazard

In preliminary process design, the primary consideration is contact with toxicants by inhalation.

This happens either through accidental release of toxic material to the atmosphere or the fugitive emissions caused by slow leakage from pipe flanges, valve glands, pump and compressor seals.

Care should be taken while filling a tank with a liquid. Tank filling causes emissions when the rise in liquid level causes vapour in the tank to be released to atmosphere.

The slide features a background with faint chemical symbols and icons of a tank and a valve. A speaker is visible in the bottom right corner. Logos for IIT Bombay and NPTEL are at the bottom left.

Well we have different routes of entry of toxic materials to the human body. In a preliminary process design, the primary consideration is given to the contact with toxicants by inhalation. Now this happens either through accidental release of toxic material to the atmosphere or the fugitive emissions caused by slow leakage from pipe flanges, valve glands, pumps and compressor seals.

So accidental release of toxic material to the atmosphere or fugitive emissions which is caused by slow leakage of toxic material from pipe flanges, valve glands, pumps or compressor seals. Such things if happens, then the toxic material can enter the workers body through inhalation. So during the preliminary process design, we must take this into consideration. Care should also be taken while filling a tank with a liquid. Tank filling causes emission when the rise in liquid level causes vapour in the tank to be released to the atmosphere.

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Brief Exposure: LC_{50} and LD_{50}

The acceptable limits for toxic exposure depend on whether the exposure is brief or prolonged. Lethal concentration (LC) for airborne materials and lethal dose (LD) for non-airborne materials are measured by tests on animals.

LC_{50} : This refers to the concentration of airborne toxicant (gaseous) that is lethal to 50% of the test group over a given exposure period, usually four hours.

LD_{50} : For non-airborne materials, lethal dose LD_{50} refers to the quantity of material administered, which results in death of 50% of the test group.

NOTE: It is difficult to extrapolate tests on animals to human beings.



Now we will define two terms known as lethal concentration and lethal dose. These two terms are used when our workers are exposed for a brief period of time, so brief exposure. The acceptable limits of toxic exposure depends on whether the exposure is brief, that means taking place over a short period of time or the exposure is prolonged taking place over a long period of time. The lethal concentration is used for airborne material and the lethal dose is used for non airborne metric toxic material.

That means, how much toxic material is lethal for a living organism? So these lethal concentrations or lethal doses are measures of that. Now, such tests are conducted on animals and then extrapolated for human beings. So let us first define lethal concentration and this refers to concentration of airborne toxic material. If we are using toxic material that is airborne, the quantity that is lethal is determined by LC_{50} .

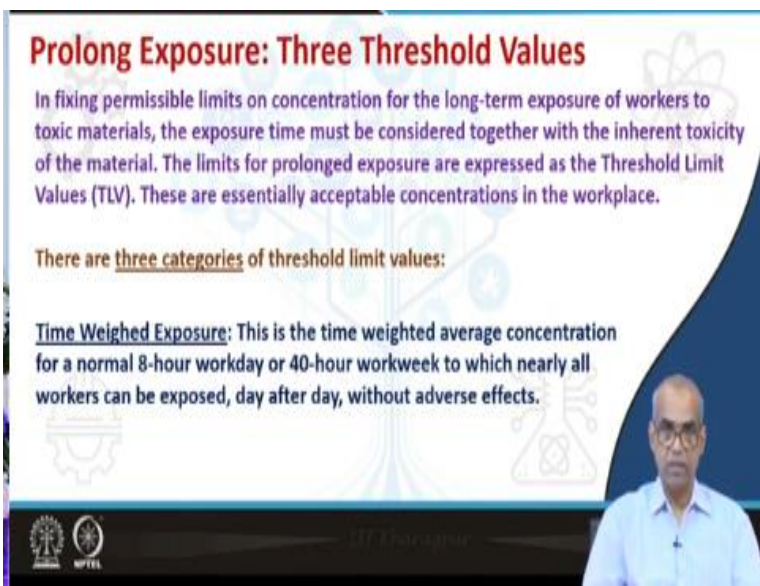
LC_{50} refers to the concentration of airborne toxicant, which is the gaseous toxicant that is lethal to 50% of the test group over a given exposure period. And this exposure period is short because you are talking about quantifying brief exposure and this is confusedly taken as 4 hours. So LC_{50} refers to the concentration of airborne gaseous toxicant that is lethal to 50% of the test group over a given exposure period, usually 4 hours.

So test groups constitute the candidates over which such tests are being conducted and as you

have discussed before the test is conducted on animals and extrapolated for human beings. For non airborne material, we use lethal dose, so LD50 will be used for non airborne material and LD50 refers to the quantity of material administered which results in death of 50% of the test group. So, both the definitions are very similar in fact same definitions, one is for airborne gaseous toxic material and the other one, which is lethal dose is for known airborne material.

So both represent a quantity which is lethal; that means we will kill 50% of the test group over a given exposure period. Note that it is difficult to extrapolate tests on animals to human beings but these numbers will give us an idea about their lethality on human beings.

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Prolong Exposure: Three Threshold Values

In fixing permissible limits on concentration for the long-term exposure of workers to toxic materials, the exposure time must be considered together with the inherent toxicity of the material. The limits for prolonged exposure are expressed as the Threshold Limit Values (TLV). These are essentially acceptable concentrations in the workplace.

There are three categories of threshold limit values:

Time Weighted Exposure: This is the time weighted average concentration for a normal 8-hour workday or 40-hour workweek to which nearly all workers can be exposed, day after day, without adverse effects.

The slide features a background with faint chemical and laboratory icons. A small inset image of a man in a light blue shirt is visible in the bottom right corner of the slide area. Logos for IIT Bombay and IIT Madras are at the bottom left.

Similar to brief exposure we can also quantify such exposures for prolonged periods and we use three different threshold values for prolonged exposure to toxic materials. So the way LC50 and LD50 represents the quantity that is lethal to 50% of the test group for a brief exposure, we have threshold values and we use three threshold values which basically gives us permissible limits on concentration of the toxic material to which workers can be exposed.

In fixing permissible limits on concentration for the long term exposure of workers to toxic materials, the exposure time must be considered together with the inherent toxicity of the material. The limits for prolonged exposure are expressed as the Threshold Limit Values and these are basically acceptable concentrations of the toxic materials in the workplace. Typically,

these values are expressed in terms of ppm, parts per million. There are three categories of threshold limit values.

So all basically represent the permissible limits on the concentration of the toxic material to which the (())(16:20)) can be exposed for long term. Time weighted exposure; so one of the three threshold limit values or TLV is time weighted exposure. This is the time weighted average concentration for a normal 8 hour workday, that means 8 into 5 Monday to Friday, say 5 days a week, 40 hour workweek to which nearly all workers can be exposed day after day without any adverse effect.

So time awaited exposure is the time weighted average concentration of the toxic material for a normal 8 hour workday or 40 hour workweek to which nearly all workers can be exposed, day after day, without adverse effect.

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Prolong Exposure: Three Threshold Values

Short-Term Exposure: This is the maximum concentration to which workers can be exposed for a period of up to 15 min continuously without suffering from (1) intolerable irritation, (2) chronic of irreversible tissue change or (3) narcosis (state of drowsiness, unconsciousness) of sufficient degree to increase accident proneness, impair self-rescue or materially reduce efficiency, provided that no more than four excursions per day are permitted, with at least 60 min between exposure periods, and provided the daily time weighted value is not exceeded.

Ceiling Exposure: This is the concentration that should not be exceeded, even instantaneously.

The slide features a blue and white color scheme with faint background icons of a gear, a flask, and a person. A small inset video of a man in a light blue shirt is visible in the bottom right corner. Logos for IIT Bombay and NPTEL are at the bottom left.

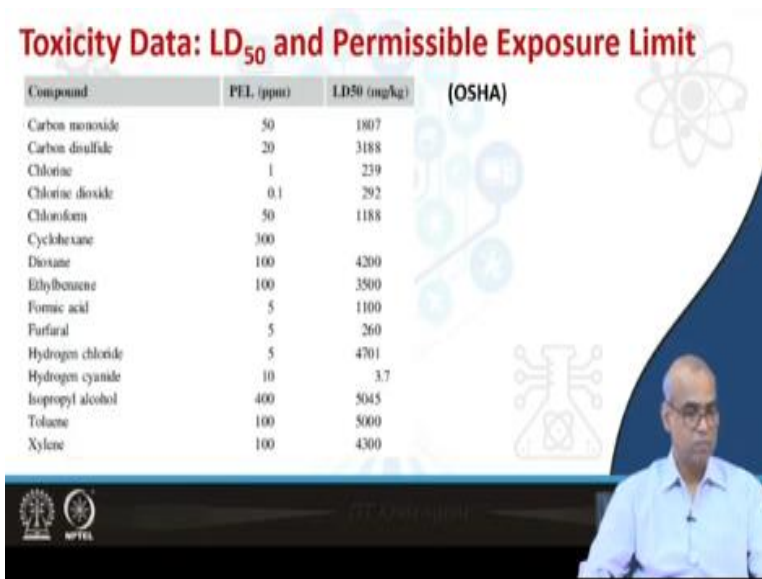
The second threshold values short term exposure. This is the maximum concentration to which workers can be exposed for a period of up to 15 minutes continuously without suffering from certain adverse effects such as; intolerable irritation, chronic irreversible tissue change or narcosis. Narcosis means a state of drowsiness or unconsciousness upon taking a drug. So this gives you short term exposure.

The maximum concentration of the toxic material to which workers can be exposed for a period of 15 minutes continuously without suffering from certain effects which are intolerable irritation, chronic irreversible tissue change or state of drowsiness or unconsciousness, which is called narcosis. Finally ceiling exposure. This is the concentration that should not be exceeded even if the workers are exposed for a very very brief period of time instantaneously. So, these are three different types of threshold values.

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Toxicity Data: LD₅₀ and Permissible Exposure Limit

| Compound | PEL (ppm) | LD ₅₀ (mg/kg) | (OSHA) |
|-------------------|-----------|--------------------------|--------|
| Carbon monoxide | 50 | 1807 | |
| Carbon disulfide | 20 | 3188 | |
| Chlorine | 1 | 239 | |
| Chlorine dioxide | 0.1 | 292 | |
| Chloroform | 50 | 1188 | |
| Cyclohexane | 300 | | |
| Dioxane | 100 | 4300 | |
| Ethylbenzene | 100 | 3500 | |
| Formic acid | 5 | 1100 | |
| Furfural | 5 | 260 | |
| Hydrogen chloride | 5 | 4701 | |
| Hydrogen cyanide | 10 | 3.7 | |
| Isopropyl alcohol | 400 | 5045 | |
| Toluene | 100 | 5000 | |
| Xylene | 100 | 4300 | |



So here some LD50 values and the permissible exposure limit PEL expressed in ppm for various compounds. Note that hydrogen cyanide is also reported here which has LD50 values of only 3.7 mg per kg. So the OSHA, Occupational safety health administration has released a very long list which reports the LD50 values as well as PEL or permissible exposure limit for a wide range of compounds that is common that we use in chemical process industries and these toxicity data are very important and safety measures should be taken accordingly.

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Toxic Release: Prevention

When synthesizing a flow-sheet, it is obviously best to try and avoid, where possible, the use of toxic materials altogether.

However, this is often just not possible. In this case, the designer should take particular care to avoid processing and storing toxic liquids under pressure at temperatures above their atmospheric boiling points.

As with flammable materials, if a leak occurs, whether large or small, the mass flow-rate through a hole of a given size is far greater for a liquid than for a gas. Release of a flashing liquid will result in higher levels of exposure than the release of a sub-cooled liquid or a gas.



Now, let us see how we prevent toxic release. When synthesizing a flow sheet, it is obviously best to try and avoid as far as possible, the use of toxic materials all together. However, this may not be possible all the time. So in that case, the designer should take particular care to avoid processing and storing toxic liquids under pressures at temperatures above the atmospheric boiling points.

As with flammable materials, if a leak occurs, whether large or small, the mass flow rate through a hole of a given size is far greater for a liquid than for a gas. Release of a flashing liquid will result in higher level of exposure then the release of a sub-cooled liquid or a gas.

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Toxic Release: Prevention

Low-level toxic emissions are most often fugitive in nature. Fugitive emissions are accidental emissions of vapours or gases from pressurised apparatus, either due to faulty equipment, leakage or other unforeseen mishaps. The best way to avoid fugitive emissions is by using leak-tight equipment (e.g. changing from packing to mechanical seals or even using sealless pumps, etc.).

If this is not possible, then regular maintenance checks can reduce fugitive emissions. If all else fails, the equipment can be enclosed and ventilated. The air would then be treated before finally passing to atmosphere.

To reduce emissions from tank filling, the vapour space must be prevented from breathing to the atmosphere. This can be achieved through vapour treatment, use of floating roofs or use of membranes in the tank roof.



Low level toxic emissions are most often fugitive in nature. Fugitive emissions are accidental emissions of vapors or gases from pressurised apparatus, either due to faulty equipment, leakage or other unforeseen mishaps. The best way to avoid such fugitive emissions is by using leak type equipment. For example, we change from packing to mechanical seals or even we can use sealless pumps so that the leakage is completely avoided.

If this is not possible, then regular maintenance checks should be in place and regular maintenance checks can reduce fugitive emissions. If all else fails, the equipment can be enclosed and ventilated, but before ventilation the air should be treated. To reduce emissions from tank filling, the vapour space must be prevented from breathing into the atmosphere. This can be achieved through vapour treatment, use of floating roofs or use of membranes in the tank roof.

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Toxic Release: Prevention and Mitigation

| Major area | Examples |
|--------------------|---|
| Inherent safety | Inventory reduction: Less chemicals inventoried or less in process vessels Chemical substitution: Substitute a less hazardous chemical for one more hazardous Process attenuation: Use lower temperatures and pressures |
| Engineering design | Plant physical integrity: Use better seals or materials of construction Process integrity: Ensure proper operating conditions and material purity Process design features for emergency control: Emergency relief systems Spill containment: Dikes and spill vessels |
| Management | Operating policies and procedures Training for vapor release prevention and control Audits and inspections Equipment testing Maintenance program Management of modifications and changes to prevent new hazards Security |

The slide also features a logo of a stylized atom on the right side and a small inset video of a man in a light blue shirt in the bottom right corner. At the bottom of the slide, there is a Windows taskbar with various application icons.

So here certain prevention and mitigation measures for release of toxic materials. We should reduce our inventory, so let us chemicals should be stored, we should use less hazardous chemicals, that means design processes such that we can avoid use of more hazardous material. So if it is possible, we should substitute less hazardous chemicals for one more hazardous chemical. During the design state we should come up with processes such that we do not have to use extreme temperatures, extreme high temperatures we should not use.

Management has a major role to play, there should be training for vapour release prevention and control, audits and inspections should be held, regular equipment tests should be done, maintenance programs should be followed religiously.

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The slide is titled "Toxic Release: Prevention and Mitigation" in red text. It features a list of measures categorized into three groups: "Early vapor detection and warning", "Countermeasures", and "Emergency response". The "Countermeasures" list includes "Deliberate ignition of explosive cloud". The "Emergency response" list includes "On-site emergency plans, procedures, training, and drills". The slide also contains a logo of a stylized atom in the top right, a logo of a tree and a globe in the bottom left, and a small inset video of a man in a light blue shirt speaking in the bottom right corner.

| Category | Measures |
|-----------------------------------|--|
| Early vapor detection and warning | Detection by sensors Detection by personnel |
| Countermeasures | Water sprays Water curtains Steam curtains Air curtains Deliberate ignition of explosive cloud Dilution Foams |
| Emergency response | On-site communications Emergency shutdown equipment and procedures Site evacuation Safe havens Personal protective equipment Medical treatment On-site emergency plans, procedures, training, and drills |

Early vapour detection and warning should be in place. There should be water sprays, water curtains, steam curtains and air curtains, there should be emergency response. If anything happens, emergency shutdown equipment and procedures should be in place, sight evacuation strategies should be in place, there should be arrangement for immediate medical treatment, management should arrange for one side emergency plans, training and reels regularly.

All workers should use personal protective equipment. So, such steps should be followed which will prevent and mitigate the toxic release to a large extent.

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Hazard Identification

From the beginning of a process design the hazards need to be identified, such that where possible the design eliminates or mitigates the hazard when making basic design decisions. Plant layout and location of facility can also be decided accordingly.

1. Inventories of hazardous material
2. High pressure
3. Vacuum pressure
4. High temperature
5. Sub-ambient temperature
6. Utility failure
7. Runaway reactions
8. Unreliability
9. Maintenance hazards
10. Lifting hazards
11. Transportation
12. Access and evacuation hazards
13. Access for emergency vehicles
14. Location of occupied building
15. Wind direction
16. Natural and environmental hazards



Now will briefly talk about hazard identification. From the beginning of a process design the hazards are to be identified. And we need to identify hazards such that wherever possible the design can eliminate or mitigate the hazard while taking basic design decisions. This should also apply to plant layout design as well as deciding on the location of the facility. So, these are the list of hazard identification, inventories of hazardous material, high pressure, vacuum pressure, high temperature, sub ambient temperature, utility failure, runaway reactions.

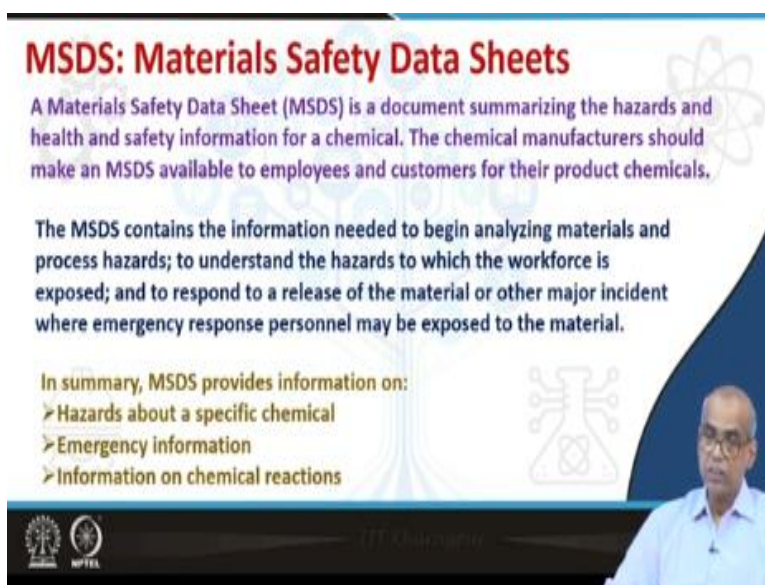
Unreliability, maintenance hazards, lifting hazards, transportation, access and evacuation hazards, access for emergency vehicles, location of occupied buildings, wind direction, natural and environmental hazards. So many hazards are related to inventories of hazardous materials and extreme operating conditions. So these must be identified and taken care of during the design stage. Among these, let us talk about the runaway reactions. Let us consider an exothermic reaction.

So, to control the temperature inside the reactor, there will be a cooling jacket around the reactor, so cooling water will be flowing through the jacket and there will be a control system which will sense the temperature of the reactor and accordingly change the coolant conditions, the flow rate of the coolant and will control the temperature of the reactor. Imagine the coolant fails, meaning let us say, the pump suddenly stopped working, the cooling system fails. What will happen? The temperature will start increasing.

Now, you know that the heat of reactions and the temperature relationships are exponentially in nature. So the rate of heat generation relations with the temperature will also be exponential in nature whereas the rate of cooling follows a linear relationship. So, when the cooling is inappropriate at neighbors temperature of the reactor exceeds, then it will start increasing very rapidly and when the temperature starts increasing rapidly, a large amount of the reactant can be vaporized and over pressurization of the reactor can take place.

There are reactions that will lead to over pressurization of the reactor leading to a very serious safety concern. So during the design stage, the designer must consider such utility failures and the runaway reaction issues.

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MSDS: Materials Safety Data Sheets

A Materials Safety Data Sheet (MSDS) is a document summarizing the hazards and health and safety information for a chemical. The chemical manufacturers should make an MSDS available to employees and customers for their product chemicals.

The MSDS contains the information needed to begin analyzing materials and process hazards; to understand the hazards to which the workforce is exposed; and to respond to a release of the material or other major incident where emergency response personnel may be exposed to the material.

In summary, MSDS provides information on:

- Hazards about a specific chemical
- Emergency information
- Information on chemical reactions

The slide features a presenter in the bottom right corner and includes logos for IIT Bombay and NPTEL at the bottom left.

Finally, we will talk about material safety and data sheets. This is commonly known as MSDS. A material safety data sheet or MSDS is the document summarizing the hazards and health and safety information for a chemical. The chemical manufacturers should make an MSDS available to employees and customers for all the chemicals they produce are all the chemicals they sell. In fact, it is mandatory in several countries for the manufacturers of chemicals to make the MSDS available to all employees as well as customers for their product.

The MSDS contains the information needed to begin analyzing materials and process hazards; to

understand the hazards to which the workforce is exposed and to respond to a release of the material or other major incident where emergency response personnel may be exposed to the material. MSDS is basically a very important piece of document and wherever we work with chemicals, we first look at the MSDS for the chemical.

Whether you are working in industry with chemicals or whether we are working at our lab, let us say your research lab or the lab you are doing experiments may be the lab for your course work and if you are using chemicals, we should first read the MSDS. MSDS for chemicals can be easily downloaded from the net and I suggest that whenever you work with chemicals and if you please read MSDS. MSDS is an important document to summarize the hazards and the health and the safety information for that particular chemical.

In summary, MSDS provides information on hazards about a specific chemical, information on chemical reactions as well as emergency information. With this we stop our discussion.