

CHEN 455
PROJECT REPORT

INHERENT SAFETY

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EXECUTIVE SUMMARY

TO BE SUBMITTED BY DIVYA

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1. INTRODUCTION

It is a known fact that prevention is always better than control but traditionally safety measures within the field of engineering is usually applied to control the hazards rather than reducing them. This approach based on controlling a hazard is often referred to as ‘extrinsic safety’ as opposed to the approach of reducing the presence of a hazard, which is called ‘inherent safety’¹⁵.

The concept of inherent safety comes from theories formulated by Trevor Kletz, in his article, entitled “What You Don’t Have, Can’t Leak. Years later in 1991, Mr. Kletz published a more updated version of his studies titled “Plant Design for Safety – A User-Friendly Approach”, which gave rise to the modern concepts of inherent safety. Inherently safer design has been advocated since the explosion at Flixborough in 1974, which raised a lot of question about safety in chemical plants.

As mentioned earlier an inherently safer design is one that avoids hazards instead of controlling them, particularly by removing or reducing the amount of hazardous material in the plant or the number of hazardous operations²¹. Hazards can be reduced or eliminated by changing the materials, chemistry, and process variables such that the reduced hazard is characteristic of the new conditions and such a process with reduced hazards is described as inherently safer. Inherent safety recognizes there is no chemical process that is without risk, but all chemical processes can be made safer by applying inherently safer concepts. Therefore in order to reduce the hazards we need to be able to understand the various concepts of inherent safety, more commonly called ‘inherently safer design strategies’²¹. The inherently safer design strategies have been grouped into four major strategies:

1. Intensification: Using smaller quantities of hazardous substances.
2. Substitution: Replacing a material or a process with a less hazardous one.
3. Simplification: Designing facilities which eliminate unnecessary complexity.
4. Attenuation: Facilities which minimize the impact of a hazardous release.

2. TRANSITION TOWARDS INHERENT SAFETY

In the past, the concept of extrinsic safety has been widely used, which focuses on how to control a hazard in the event of an accident. This practice mainly involves adding layers of protection around a hazardous system, hence when something happens the safety systems in place are expected contain the problem. But this is not always the case, because in the past we have seen safety systems failing at crucial times, like during the Bhopal Tragedy¹⁴. Even though this may seem like a good approach towards safer operations, it ignores the main cause of all safety practices that in place today, the hazards itself. Rather than focusing on ways to eliminate the problem, this approach just focuses on how to mitigate the consequences.

The transition from traditional practices to inherently safer practices has been a slow process. It was only after the Flixborough accident in 1974 and the Seveso disaster in 1976, due to which people began to re-consider the traditional approach to safety. People began to accept the concept of ‘inherent safety’ as proposed by Dr. Kletz in the 1970’s, and tried to incorporate some of his theories. The final step in the transition came in 1996 when the Eurpian Union passed the ‘Seveso II’ Directive. The ‘Seveso II’ Directive (96/82/EC) was aimed at the prevention of the major accident hazards involving dangerous substances, and the limitation of their consequences for man and the environment, with a view to ensuring high levels of protection throughout the

community in a consistent and effective manner. As a part of the prevention measures the directive clearly stated that “Hazards should be possibly avoided or reduced at source through the application of inherently safe practices”¹⁹.

Nowadays, the safety approach is based around inherent safety, using its concepts as the primary safety measures. The traditional approach is now applied as a secondary safety measure, to reinforce the overall safety of a process. This insures that if an inherently safer process goes out of hand, a secondary safety system is in place to control the consequences. Together inherent safety and extrinsic safety form what is known as a ‘Layer of Protection’ around a hazard, making sure nothing hopefully goes wrong. This relationship between the two is shown in the figure below:

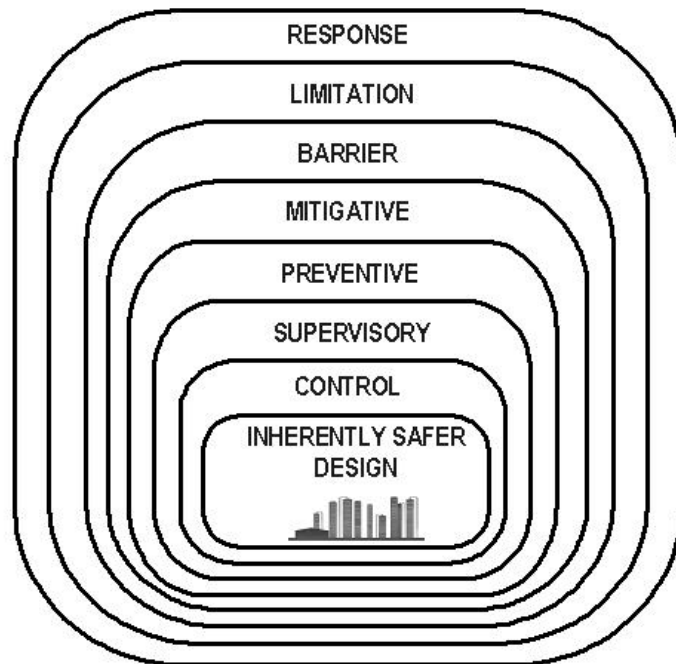


Fig. 1: Layers of Protection around a system

3. INHERENT SAFETY

An inherently safer process or chemical relies on various engineering principles like physics, chemistry and math, to prevent accidents from happening rather than focusing on control systems and measures to contain the accident. The major components of inherent safety that were outlined earlier will now be discussed in detail. Examples will be provided showing how these principles have been applied to various processes and chemicals today.

3.1 INTENSIFICATION

Intensification aims to eliminate or reduce the presence of hazardous inventories in plants. This reduction can be done on the inventory of different process units such as the storage tanks, reactors, distillation units and pipelines. Moreover, intensification is being applied more and more in the process industry because of its economic profitability; smaller plants require less capital to initiate, maintain, control and are safer. Inventory intensification will be discussed for two different process unit reactors and storage tanks.

1. REACTORS

There are two main reasons for having large inventories in reactors- the slow rate and/or the low conversion of the reaction. Slow reactions will take a large amount of time to yield the desired product, but increasing the inventory will yield more products within the same amount of time. As for low conversion, most of the output is recycled back to the reactor leading to the presence of a high inventory in the system¹.

For some reactions, the low conversion and slow rate are not intrinsic to the reaction but

result from bad design choices, for example poor mixing or operating the process at pressure and temperature conditions that will slow the reaction. These can be resolved through better understanding of the process and accordingly designing the unit to give a higher yield. This should be done in the initial design stages because once the process is set up not a lot of changes, in most cases, could be done. But to keep the process safe, more add-ons are going to be needed to control the system, a high hazardous inventory which leads to more redundant safety system.

Nitroglycerin production

Nitroglycerin, an explosive liquid, is obtained by mixing glycerin with concentrated nitric and sulfuric acid. The reaction is very exothermic and necessitates constant cooling to prevent the heating of the explosive Nitroglycerin. The reaction has been conducted “traditionally in large stirred pot reactor batchwise containing about one tone of material”¹. The low reaction conversion necessitates the presence of a large inventory which constitutes a dangerous hazard. This requires a good amount of add-ons such as cooling system, relief valves, temperature and pressure controllers¹.

Engineers working on the Nitroglycerin production found out that the slow rate of the reaction is not caused by the intrinsic kinetics of the reaction but rather by the poor stirred mixing that is happening in the batch reactor, which is an example of poor design.

Following a better understanding of the nature of the reaction and the process, a well mixed continuous reactor was proposed instead. This new reactor needs around 1 Kg of inventory compared to the tone required for the batch process¹. This inherently safer practice reduced the hazard present on-site and reduced the need for many process add-

ons. Continuous reactors, in general, are now being suggested in guidelines as safer reactors compared to the batch reactor³.

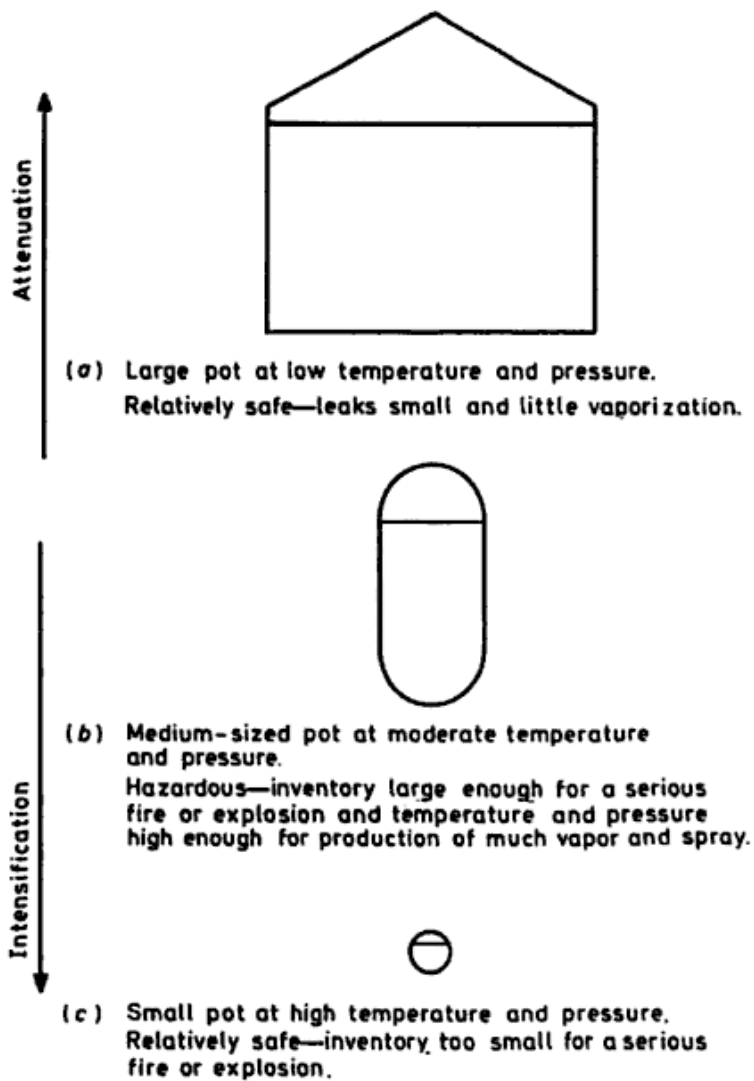


Fig. 2: The effect of varying conditions in liquid phase reactor

2. STORAGE TANKS

Storage tank inventories constitute the greatest hazard for explosions in plants because they contain the largest amount of inventory present in plants. These tanks could store reactants, intermediate products or any other sort of material needed in the process.

An example of a storage tank inventory reduction was done by a US company that was storing 120,000 ton of Methyl IsoCyanate, the fluid that leaked during the Bhopal incident. This was done by processing MIC at a larger rate and storing the less hazardous final product instead MIC; by this new engineering design the plant became inherently safer¹.

For this case, the solution was straightforward and required a better engineering design but in many other instances the solution might lay in better inventory management such as decreasing the time needed for the inventory shipment arrival in order to maintain the required production while having less storage tank inventory².

3.2 SIMPLIFICATION

While plants in the chemical industry will always contain certain complexities that are intrinsic to the system; simplification aims to eliminate or reduce unnecessary complexities. Simpler plants have less equipment that could develop faults such as leakage and fewer opportunities for error such as human errors or control instrumentation error^{1,9}. Simplification can be summarized

in the words of the founder of inherent safety” equipment you don’t install cannot develop faults or be operated at the wrong time or in the wrong way”

Stronger equipments instead of relief systems

In order to minimize the effect of failures in equipments, relief valves are used¹⁰. Generally, the substances being handled are not discharged to the atmosphere because of environmental, safety and health concerns, but rather to a proper disposal system such as a flare system for flammable gas or scrubber system for solids. Relief systems are expensive, quite complex and will need to be continually maintained; moreover these systems are prone to error, which is the case of every system, the problem is that since these equipments are only used in emergency situation, the errors might be hidden and failure could occur in an emergency situation. A simpler solution that is cheaper and less prone to errors would be to use strong equipments that can contain the maximum or minimum pressure conditions within the system^{1,11,12}. For example¹, when pressure drop exists between vessels that are in series, as shown in the figure bellow, then if a failure happens, the valves will fail open resulting in a high upstream pressure in the downstream vessels.

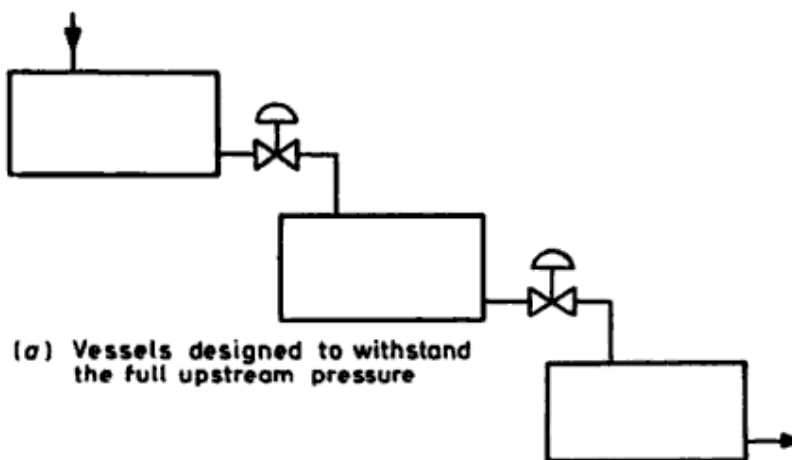


Fig. 3: Vessels in series

In order to prevent the downstream vessels from being exposed to this excess pressure, relief valves are used to discharge the fluid from the system¹⁰. The simpler solution would be to construct the vessels from a strong material that could withhold the maximum excess pressure; then the relief system won't be needed anymore and the possibility of error is eliminated.

3.3 SUBSTITUTION

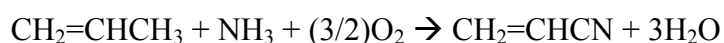
It is the concept of inherent safety that involves replacement of a substance or a process which reduces or eliminates the hazards associated with it. For example, It could involve replacing a chemical with a less hazardous substance or replacing a process route with one which has a fewer number of associated hazards. Over the years with the development of new technology and processes, older and more hazardous processes or chemicals have been abandoned in favor of newer and safer approaches. In order to properly explain the concept, here are a few examples showing how processes have become safer by substituting dangerous substances and processes with something inherently safer. Listed below are a few areas in the chemical industry where the principle of substitution has been employed:

1. **REACTION CHEMISTRY:** A lot of chemical engineering processes involve numerous complex reactions which make use of highly toxic chemicals. Thus with the use of less hazardous materials and chemical reactions with safer chemicals offers the great potential for improving inherent safety in the chemical industry. Here are some examples:

- a. Acetonitrile manufacture: Back in the day, acetonitrile was manufactured using acetylene and hydrogen cyanide.



As we all know cyanide is as a highly toxic compound because it halts respiratory functions of the body cause by the cyanide ion. In order to reduce the risks involved, an alternative route is being used to manufacture acetonitrile using an ammoxidation process involving propylene and ammonia²¹. Here is the related reaction:



- b. Bhopal Disaster: The bhopal disaster was the worst ever chemical disaster in the world. It resulted from the release of a very toxic gas Methyl-Iso-Cyanate (MIC), which is a reaction intermediate in the formation of Carbaryl. Here is the associated reaction, where methylamine (1) reacts with phosgene (2) to form methyl isocyanate (MIC) (3). MIC then reacts with 1-naphthol (4) to give Carbaryl (5):

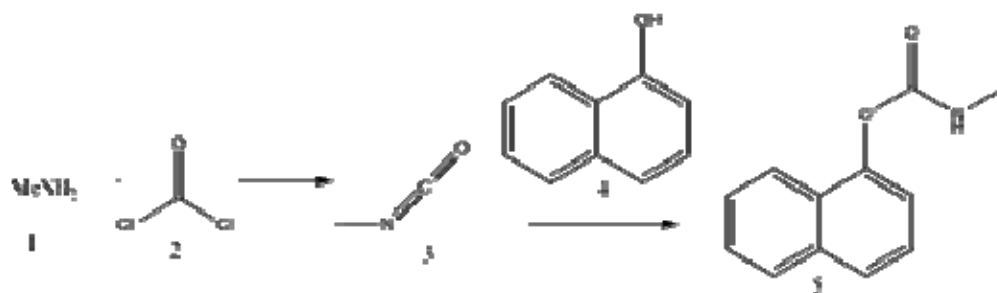


Fig. 4: Reaction mechanism to form Carbaryl using MIC as an intermediate

Due to what happened in Bhopal, the reaction to form Carbaryl has now been replaced with a new safer reaction involving less toxic components²¹. The new reaction involves reacting 1-naphthol (1) with phosgene (2) in NaOH to create chloroformate (3), which then reacts further with methylamine to give the desired product Carbaryl (4). The reaction is shown below:

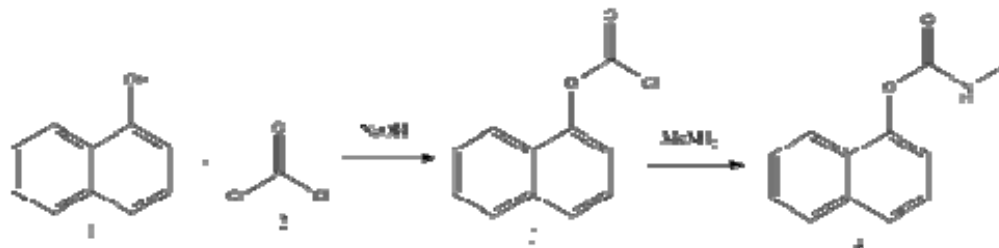


Fig. 5: Alternate reaction mechanism to form Carbaryl

2. **SOLVENTS:** Replacement of volatile organic solvents with less hazardous organic materials has helped reduce the risk of harm and consequently helped improve the inherent safety of many processing operations. Here are a few examples:
- Paints:** Use of water based paints rather than solvent based paints increases the safety of the paint. Earlier harmful solvents such as petroleum distillates, esters and glycol ethers. Since solvents mainly evaporate or disintegrate upon application, we humans can come in contact with them which can be harmful to us.
 - Paint Strippers:** Paint strippers are solvent mixtures designed to remove paint and other finishes, and also to clean the underlying surface. The principal active ingredient is usually dichloromethane, but it also contains other hydrocarbons

such as N-Methyl pyrrolidone, dibasic ethers, and organic esters. But these components can be hazardous to humans, for example Dichloromethane is a toxic chemical due to its high volatility which makes it an acute inhalation hazard. Dichloromethane is also metabolized by the body to form carbon monoxide which can lead to carbon monoxide poisoning. Due to the toxic nature of paint removers alternatives such as Heat Guns have been developed which are basically devices that emit a stream of hot air used to dry and strip paint, apply heat shrink tubing, apply shrink film, and dry out damp wood etc.

- c. Fiber-Glass Boats: Dibasic Esters (DBE) a solvent manufactured by DuPont has replaced acetone as a cleaning agent in the manufacture of fiber-glass boats. During the manufacture of these boats workers have to clean the equipment to avoid resin formation on them. Hence, acetone was used for the cleaning process but soon health concerns were raised due to worker over-exposure to acetone. Also the acetone that evaporated from the manufacturing facilities raised the VOC emissions¹⁸. VOC's are precursors of photochemical (Tropospheric) ozone creation that leads in turn to smog and related detrimental effects on health and the environment.
- d. ChloroFluoroCarbons(CFC's): CFC's were developed in the early 1900's under the brand name 'Freon' which was used primarily as a refrigerants, but was also used in fire-fighting and as propellants. Over the years the use of CFC's increased, and was used in the form of blowing agents, propellants in medicinal

applications, and degreasing solvents. Around 1970, scientists Sherry Rowland and Mario Molina found out about the harmful effects of CFC's, and how it was a major cause in the depletion of the ozone layer. CFC's have a characteristic low reactivity which is essential to hazardous nature. CFCs' lack of reactivity gives them a lifespan that can exceed 100 years, which enables them to diffuse completely into the upper stratosphere leading to ozone depletion. In order to combat the rise of CFC levels globally alternatives such as HydroChloroFluoroCarbons (HCFC's) which are less dangerous to the ozone but not completely safe. Nowadays, HydroFluoroCarbons (HFCs) are being developed, which will replace HCFCs with essentially no ozone destruction.²²

3.4 ATTEENUATION

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4. CASE STUDIES

Now that the concept of inherent safety as well as its underlying principles has been discussed, we will now look at some of the biggest engineering disasters through the years, to see how they could have been prevented by applying the concept of inherent safety.

4.1 BHOPAL DISASTER

Twenty years ago 250,000 people were exposed to toxic chemicals during a catastrophic gas leak from a pesticide plant in Bhopal, India. The gas in question here is Methyl-Iso-Cyanate (MIC) which is very toxic in nature. More than 5000 people died within days. A further 15,000 died in the following years. Around 100,000 people are suffering chronic and debilitating illnesses for which treatment is largely ineffective (8).

On the night of December 23, 1984, a dangerous chemical reaction occurred in the Union Carbide factory when a large amount of water got into the MIC storage tank # 610. This release was due to a runaway exothermic reaction involving MIC and water, which led to a major increase in the temperature inside the tank to over 200°C (400°F). This forced the emergency venting of pressure from the MIC holding tank, releasing a large volume of toxic gases. The reaction was sped up by the presence of iron from corroding non-stainless steel pipelines. A large amount, about 40 tons of Methyl-Iso-Cyanate (MIC), poured out of the tank for nearly two hours and escaped into the air, spreading within eight kilometers downwind, over the city of nearly a million people.

Sources say that there were a lot of reasons because of which the incident occurred, but nobody knows for sure what exactly happened. One of the biggest questions raised against Union Carbide was regarding the safety systems in place, in case a disaster such as this was to occur.

After detailed investigations it was found that the ‘six’ safety protocols in place were all non-functional at the time of the accident (1). Below is a list of the six safety systems that failed:

1. Flare Tower: It was disconnected
2. Vent Gas Scrubber: It was out of caustic soda and was inadequate for unsafe volume of gas
3. Water Curtain: Not functional because it was designed with inadequate height
4. Pressure Valve: was found to be leaking
5. Run Off Tank: Already contained MIC
6. Mandatory Refrigeration for MIC Unit: Shut down for 3 months to save money

There were also reports that a ‘jumper line’ was recently installed as a cheap solution to a maintenance problem. This line connected a relief valve header to a pressure vent header and enabled water from a routine washing operation to pass between the two, on through a pressure valve, and into MIC storage tank 610 (1).

Looking back at the disaster, it is not difficult to say that making the process inherently safer would have caused this disaster to never happen. Even though a lot of processes have associated safety systems present, it is always a possibility that the safety system is under maintenance or non-functional. Hence the better way to combat such loopholes in safety systems is to make the process inherently safer. Union Carbide could have prevented this disaster if they had applied some of the recommendation that will be discussed now.

As mentioned earlier inherent safety is an approach to accident prevention by minimizing, substituting, moderating and simplifying a hazard. To begin with, we can to start by looking for alternatives to the biggest contributor to the accident, Methyl-Iso-Cyanate (MIC). MIC is a

highly toxic chemical that was an intermediate in the production of Carbaryl. If the concept of substitution was applied here, Union Carbide could have used alternative chemicals or even an alternative reaction to manufacture Carbaryl. This would have made the process inherently safer because hazards levels would be lower as compared to before. Another application of the substitution principle involves knowledge about the exothermic nature of the reaction between MIC and water. Since, it was known that MIC and water reacted violently to form a toxic gas, Union Carbide should have used substances other than water for cleaning purposes, as well for safety systems such as water curtains.

Another big problem with the accident was the presence of tanks on-site containing large amounts of toxic MIC. This is a recipe for disaster because in the event of an incident a huge amount of toxic chemical would be exposed to the environment around. Hence, an alternative approach would be to implement the concept of minimization, which would require a reduction in the amount of unwanted MIC being stored on-site. If only a small amount of the hazard is present, the consequences would also be reduced greatly.

Applying the concept of moderation to the scenario at hand, Union carbide should have built the factor far away from an urban city. This would have led to fewer fatalities once the toxic gas began to spread. By constructing the factor right next to a big city, Union Carbide put the lives of nearly a million people in jeopardy. Another application of the moderation concept would have been to install dikes or bunds of some form to make sure a toxic gas release didn't get released into the surrounding atmosphere.

Lastly, by employing the idea of simplification, Union carbide should have designed a reactor which could sustain the maximum pressure or temperature during a runaway reaction. This

would eliminate the need for multiple safety systems that need maintenance round-the-clock. Summing things up, no matter how many secondary safety measures or safety systems are present during an accident such as this, the best and most successful risk mitigation process would be to make the process and its auxiliary components inherently safer, thereby removing any chance of such a disaster of from happening.

4.2 FLIXBOROUGH DISASTER

The Flixborough disaster, UK's largest explosion in the chemical industry, happened on June 1974 in a plant that produced nylon for Nypro. This accident resulted in 28 fatalities and the almost complete destruction of the plant. The incident occurred in the liquid-phase cyclohexane oxidation unit of the plant where cyclohexane at 150°C and a pressure of 9 bar was being oxidized. This process took place in 6 chain reactors R1 to R6, converting cyclohexane into the KA mixture of cyclohexanone and cyclohexanol^{4,5}. Two month earlier, a 20 in pipe was introduced into this process to bypass the leaking reactor 5, to form a bridge connecting reactor 4 to reactor 6⁶.

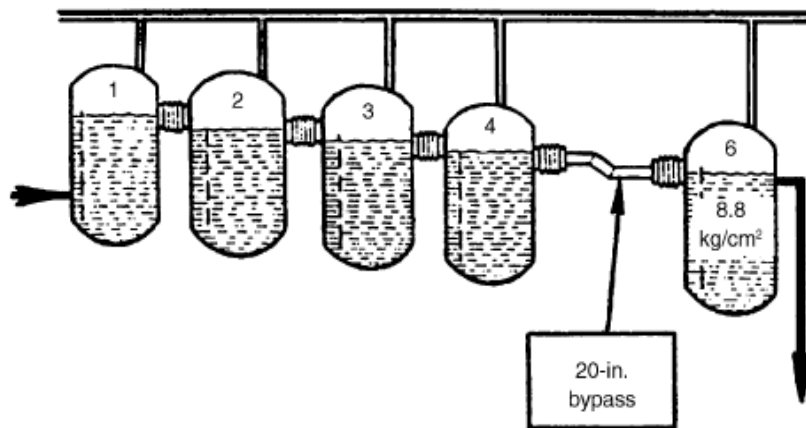


Fig. 6: The reactors and the 20-in bypass

Following the investigation, there was a consensus that this new bypass line had ruptured, which led to leakage of 50 tons of cyclohexane in a short period of time, almost a minute⁴. The cyclohexane vaporized to produce a vapor cloud which ignited and led to the disastrous explosion. A disagreement occurred over the root cause of the rupture, but there were three main hypothesis⁷:

- Rupture of the bridging assembly because of internal pressure
- A leak from a bellow at reactor 4 or reactor 6, followed by a minor explosion that led to the rupture of the bridging assembly
- Rupture of an 8 inch distillation pipeline that led to a minor explosion, which ruptured the bridging assembly.

The poor design of the 20 in bypass and the failure to comply with both safety norms and design requirements have been much discussed. Hence, most of the official recommendations focused on these operational issues. Although, specific standards and procedures should always be practiced on any plant, these were peripheral issues in the Flixborough incident when compared to the instantaneous leak of 50 tons of cyclohexane, which tremendously magnified the extent of the explosion. In fact, Trevor Kletz has posed several questions⁴ to understand why such a large amount of cyclohexane leaked, and it was found that the large leak was primarily caused by the usage of large pipes which were necessary for the 400 ton inventory. If the incident is approached from an inherently safer perspective, the root cause that magnified the extent of the explosion is definitely the presence of a large inventory of cyclohexane, and the improvements should have been focused on reducing total amount of the hazard.

How could the risk have been reduced in the event of a leakage, if the concepts of inherent safety were used? The reason for the large inventory was the low conversion in the formation of the KA mixture; the amount of air, the oxidizing agent, could not be increased to better the yield because oxygen would have reached the Limiting Oxygen Concentration which could cause a deflagration^{4,8}. The inherently safer approach should combine process engineers and safety specialist at the design stage to produce the required product with less inventory⁸.

The usage of pure oxygen instead of air increases the yield which leads to a reduction of the inventory of cyclohexane, but the problem with the usage of pure oxygen is that it increases the possibility of deflagration because the system will be operating close to Limiting Oxygen Concentration. Recent development in this field have shown that if water was added to the system with pure oxygen, water could “replace the nitrogen as the inert component and moderate the flammability of the cyclohexane/oxygen mixture”⁶. In fact, water would decrease the temperature of the cyclohexane-water mixture and an increase in the vapor pressure compared to pure cyclohexane. In addition, the usage of oxygen as the oxidizing agent will give twice more product and reduced the inventories⁸. In the event of a leakage, vapor cloud formation will still form but the cyclohexane amount leaked will be less because of the high yield, the amount of cyclohexane that will vaporize is less as well because of the decrease of the system temperature and the formation of water vapor will reduce the vapor cloud concentration moving the system further from the flammability limits⁶.

4.3 SEVESO ACCIDENT

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5. CONCLUSION

The overall safety of a process relies on various layers of protection. The first and most important part of this safety blanket is inherent safety. Inherent safety can greatly help reduce the risks associated with a certain hazard because it deals with reducing the hazard itself, rather than controlling the consequences resulting from the hazard.

In today's world where technology has led to more complex and dangerous process, it is of utmost importance that we incorporate the concept of inherent safety into our designs. In order to apply these concepts, one has to understand the underlying principles of inherent safety namely: Intensification, Minimization, Substitution and Attenuation.

By successfully understanding and applying the principles of inherent safety, we can reduce the occurrences of huge chemical disasters such as Bhopal, Flixborough and Seveso, that greatly impacted the way we perceive safety today. We also need to look back at those disasters, and learn from our mistakes, because there a lot to learn from what happened in the past.

6. REFERENCES

1. Kletz T. Process Plants: A handbook for Inherently Safer Design. Philadelphia: Taylor & Francis; 1998.
2. Scheffler N E. Inherently Safer Latex Plants. The Dow Chemical Co.
3. Hendershot D C. Conflicts and Decisions in the Search for Inherently Safer Process Options. Process Safety. January 1995; 14:1
4. Kletz T A. Accident investigation: Keep asking “why?”. Journal of Hazardous Materials, 2006; 130:69-75
5. Kletz T A. The flixborough cyclohexane disaster. Loss Prevention: A CEP Technical Manual, 1975; 9:106-113
6. Venart J E S. Flixborough: A final footnote. Journal of Loss Prevention in the Process Industries, 2007; 20: 621–643
7. Venart J E S. FLIXBOROUGH: THE EXPLOSION AND ITS AFTERMATH. Process Safety and Environmental Protection, 82; B2: 105–127
8. Chen J-R. An inherently safer process of cyclohexane oxidation using pure oxygen - An example of how better process safety leads to better productivity. Process Safety Process, March 2004; 23:1
9. AnnaMari Heikkilä. Inherent safety in process plant design: An index-based approach. VTT Publications: 1999.
10. Relief devices. American Chemistry website .2002. Available at: <http://www.liu.edu/CWIS/cwp/library/workshop/citama.htm>. Accessed November 15, 2009
11. Hendershot D C. Designing Safety into a Chemical Process. Rohm and Haas Company; 1999
12. Available at <http://home.att.net/~d.c.hendershot/papers/pdfs/asiapacrc.pdf>. Accessed November 16, 2009
13. Hendershot D C, Post R L. Inherent Safety and Reliability in Plant Design. Rohm and Haas Company; July 31, 2000. Available at: <http://home.att.net/~d.c.hendershot/papers/pdfs/mkoc2000.pdf>. Accessed November 16, 2009

14. Students for Bhopal. International Campaign for Justice for Bhopal (ICJB), 2009.
Available at: www.bhopal.net. Accessed October 27, 2009.
15. Hendershot D C, Post R L. Inherent safety and reliability in plant design. 2000.
16. Gentile M. Development of a hierarchical fuzzy model for the evaluation of inherent safety. 2004.
17. Howat C S. Introduction to inherently safer processes. 2002
18. Hoffman D J. Solvent substitution to reduce air emissions for FRP industry. 1998
19. Wettig J. Seveso II- Background, contents and requirements. Available at:
<http://www.ess.co.at/HITERM/REGULATIONS/regulations.html>. Accessed November 2, 2009.
20. Browning, Jackson, Gottschalk et al. Union Carbide: Disaster at Bhopal. Crisis Response. 1993
21. Kletz T, Bollinger, R E, Hendershot, Lutz W K. Inherently Safer Chemical Processes, A Life Cycle Approach. 1996.
22. EPA. Ozone Layer depletion. Available at: <http://www.epa.gov/ozone/defns.html>. Accessed on October 28, 2009.

AGGIE HONOR CODE

“An Aggie does not lie, cheat or steal, or tolerate those who do.”

WAJIH IDRIS (TEAM LEADER)	
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1. Attenuation

The use of hazardous materials in their least hazardous forms, or implementing processing options that involve less severe processing conditions is called attenuation or moderation techniques¹. Hence in the case of chlorine and ammonia, they are stored as refrigerated liquids at atmospheric pressure rather than at high pressure, at ambient temperature. The lower pressure results in lower leak rates and the lower temperature lowers the vaporization rate¹.

Changing designs or process conditions, rather than adding on protective equipment that may fail, limits the possible effect of the hazard. For example, it is better to prevent overheating by using a fluid at a lower temperature rather than use a hotter fluid and relying on a control system². Therefore application of attenuation strategy can significantly lower overall process safety risk.

Moderation of process variables, like pressure, velocity or temperature, can also be considered as a minimization strategy. Although one is not minimizing a quantity to reduce a hazard but instead, one is primarily minimizing a process quality to do so. Hence attenuation is effectively a procedure that minimizes process variables in order to attain an inherently safer system.

Furthermore, if all accidents can be expressed as having three components: initiation, propagation and termination, the inherent safety strategy used affects specific components². Generally, whenever the process is made inherently safer by means of impacting the initiator, it is a form of hazard minimization, substitution, or moderation of process quality². However, when the impact of an inherent safety strategy lessens the accident effect by affecting either the propagation of the hazard, or the consequences experienced at termination, it is an example of the attenuation strategy².

The attenuation strategy can be applied to many real life situations, some of which are listed below. Unlike liquefied gases, for which pressure and temperature are the major process condition that are

moderated to make them safe, the following example cases delve into other possible process variables which might make the process inherently safer.

1.1. Case of a BLEVE fireball

The case of a fireball that results from a BLEVE (Boiling Liquid Expanding Vapor Explosion) of a tank truck containing large quantities flammable liquid will be analyzed to deduce the impact on a recipient. Exposure duration for the recipient is either the fireball duration or the escape time, assuming the recipient is able to escape from harm's way². The extent of injury, the recipient will endure, is mainly dependent on the exposure duration and the level of personal protection the recipient was wearing². From the definition of attenuation strategy it can be implied that anything done to impact the transport of radiation from the fireball to the recipient, or to impact the duration of exposure, or to impact the absorption of radiation that reaches him would be an example this strategy. Therefore the distance between the potential origin of the fireball and a receptor is a process condition that if moderated will make the system inherently safer². Maximizing this distance limits the effects of a fireball on a receptor.

1.2. Dilution of hazardous material

Inherent safety can be established by diluting a hazardous material with a less hazardous material. If the diluted material is spilled, the partial pressure of the hazardous material will be lower than for the pure material³. This implies that the concentration of vapor at the spill will be reduced and consequently reducing the downwind concentration in air³.

In the case of a flammable material, dilution with a non-flammable material such as water may significantly reduce the fire hazard³. In some cases, pure materials such as hydrogen chloride or ammonia may require pressurized storage, while relatively concentrated aqueous solutions can be stored at atmospheric pressure³. Although many applications require the use of a pure material, many do not. Therefore such applications, for example neutralization with ammonia or hydrochloric acid, aqueous materials could be considered³.

Moreover stability of some solid materials can also be enhanced by dilution with an inert material. The dynamite is an example of an inherently safer design as the unstable nitroglycerine is absorbed onto an inert carrier³.

1.3. Case of a Dust Explosion

The impact of an accident can also be moderated by altering the physical characteristics of a material. In the case of dust explosions the hazard of a combustible dust is a function of its particle size³. Increasing the particle size, by handling these materials as granule or pellets, will make the process inherently safer³.

Some reactive or toxic materials can be immobilized by attaching them to a solid substrate³. This will make the toxic particles less likely to come into contact with people, as it will be heavier and will settle. For example, acid or basic functionality can be provided as a solid ion exchange resin or a membrane³. Metal catalysts are often bonded to an inert carrier³.

2. Seveso accident

2.1 Introduction

On Saturday, 9th of July 1976, a bursting disc ruptured on a chemical reactor at the works of the Icmesa Chemical Company at Meda near Seveso, a town of about 17,000 inhabitants some 15 miles from Milan⁴. The disk rupture resulted in a release of a white vapor cloud that dispersed and settled. Among

the substances deposited was a very small amount of TCDD, 2,3,7,8-Tetrachlorodibenzo-p-dioxin, one of the most toxic chemicals known⁴. After the release of toxic TCDD, there followed a period of confusion as the company was inexperienced and ill equipped to deal with such an accident. Over the next few days, animals died and people fell ill in the contaminated area⁴. Only a partial evacuation was later carried out. In the immediate aftermath there were no deaths directly attributable to the release, but a number of pregnant women who had been exposed had abortions⁴.

The process which gave rise to the accident was the production of 2,4,5-trichlorophenol (TCP) in a batch reactor⁴. TCP is used for herbicides and antiseptic and the company required it for making the bacteriostatic agent, hexachlorophene⁴. It manufactured its own because the herbicide grades contained impurities unacceptable in this application. The formation of TCP involved two stages of reaction as illustrated in Figure 1.

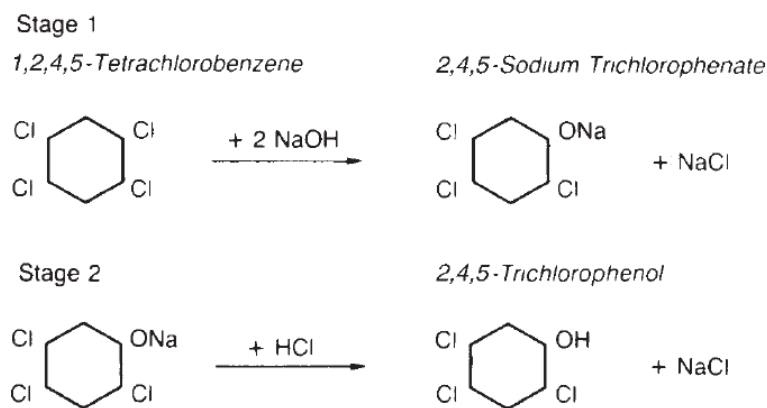


Figure 1: The reaction for the production of TCP⁴

Stage 1 of the reaction was performed at 170 to 180°C with ethylene glycol as solvent and on completion of this stage, some 50% of the ethylene glycol would be distilled off and the temperature of the reaction mixture lowered to 50 to 60°C by the addition of water⁴. In this reaction the formation of

small quantities of TCDD as a by-product was unavoidable. The chemical structure of TCDD is illustrated in figure 2.

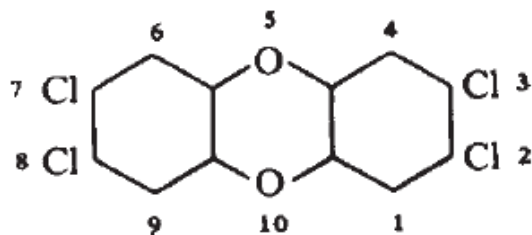


Figure 2: The chemical structure of TCDD⁴

At a reaction temperature below 153°C, the formation of TCDD is zero, and is less than 1ppm when the temperature is 180°C⁴. However the concentration increases a thousand folds with prolonged heating in the temperature range 230 to 260°C to about 1600 ppm⁴.

2.2 Properties of TCDD

TCDD is one of the most toxic substances known. The lowest LD50 quoted is for guinea pigs and is 0.6 mg/kg, which is a dose of 0.6×10^{-9} per unit of body weight⁴. TCDD can be taken into the body by ingestion, inhalation or skin contact. A leading symptom of TCDD poisoning is chloracne, which is an acne-like skin effect caused by chemicals⁴. A mild case of chloracne usually clears within a year, but a severe case can last many years. Other effects of TCDD include skin burns and rashes and damage to liver, kidney and urinary systems and to the nervous system⁴. It also interferes with metabolic activity and is known to have carcinogenic and mutagenic properties. TCDD is a stable solid which is almost insoluble in water and resistant to destruction by incineration except at very high temperatures⁴. This makes TCDD extremely difficult to dispose.

2.3 The accident

The release was the result of a runaway reaction in reactor causing the rupture of the bursting disk and the subsequent release of a vapor cloud. The schematic of the process plant is shown in the following figure 3. The release of the vapor cloud was from the rupture disk as can be seen from the diagram below.

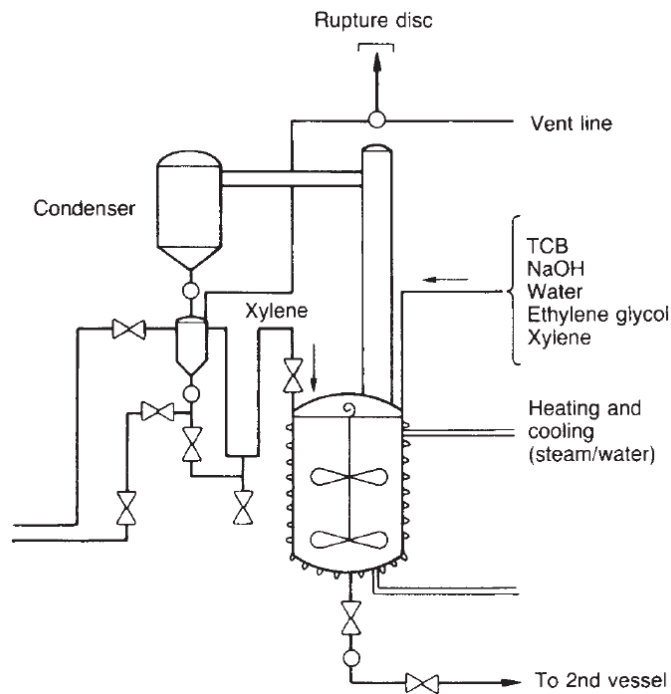


Figure 3: The reaction system at Seveso plant⁴.

The events prior to the accident involved the interruption of the production cycle, and allowing it to overheat over a prolonged period. The stages 1 and 2 of the reaction were switched and the only 15% of the ethylene glycol was removed prior to the occurrence of the incident⁴. The method of distillation was not accurately followed. This resulted in higher concentration of TCDD production. Furthermore, the set pressure on the bursting disk was high, which allowed the vapor cloud to have higher temperature and pressure⁴. This in turn permitted higher concentrations of TCDD to be discharged. And lastly, there was

no system installed for the collection or destruction of the vented material and therefore allowing a higher degree of contamination⁴.

2.4 Inherent Safety Strategies

The toxicity of TCDD is closer to that of a chemical warfare agent than to that of the typical toxic substance which the chemical industry is used to handling. Yet it was handled very poorly. In the following section the accident will be analyzed with respect to inherent safety strategies and how the failure to implement them resulted in the disaster.

2.41. Minimize

The process involved the production of TCDD as a by-product. TCDD's production could have been minimized by reducing the quantity of reactants being processed⁵. The reactor was charged with over 7000kgs of reactant and as a result of the runaway reaction caused a rather large vapor cloud.

2.42. Substitute

It was known that above 230°C such a mixture, like used in the Seveso plant, will undergo an exothermic decomposition reaction. Accidents had been known to occur involving a runaway reaction above this temperature. If the reaction was substituted with a less toxic process this disaster could have been prevented and the system to produce TCP would have been inherently safer.

2.43. Attenuation

The setting of the bursting disc was 3.5 bar. The function of this device was to guard against overpressure from the compressed air, which was used to transfer materials to the reactor⁴. On investigating the incident, it was found that if the set pressure had been lower, venting would have occurred at a lower, and less hazardous, temperature. And this would have resulted in lower TCDD discharge.

Furthermore, as the reaction was known to lead to a runaway reaction above a specified temperature, moderating the temperature and pressure values with more care could have prevented the discharge⁵. There were no automated controls and hence moderation of process variables could not be carried out efficiently.

2.44. Simplify

Proof has been provided of the inadequacy of the measuring equipment and also the absence of any automatic control system⁴. This complicates the system to a great extent. Moreover, operating procedures were not clearly mentioned or adhered to which was one of the major reasons of the failure. Also the original process required the charge to be acidified before distillation but the company reversed these two steps and thereby increasing the complexity of the system.

2.5. Outcome of the accident

“The impact of the Seveso disaster in Continental Europe has in some ways exceeded that of Flixborough and has led to much greater awareness of process industry hazards on the part of the public and demands for more effective controls.”⁴ As a direct result of the Seveso disaster, the European Commission passed a Directive on ‘Major Accident Hazards of 1982’. This Directive was initially often referred to as the ‘Seveso Directive’⁴. Later in 1996, the European Union passed the ‘Seveso II Directive’, to control major accident hazards involving hazardous substances⁴.

References

1. Sam Mannan. Challenges in Implementing Inherent Safety Principles in New and Existing Chemical Processes. 2002. Available at: http://psc.che.tamu.edu/wp-content/uploads/whitepaper_inherentsafety1.pdf. Accessed on November 5, 2009.

2. David G.Clark. Applying the ‘Limitation of effects’ inherently safer processing strategy when siting and designing facilities. *Process Safety Progress*. 2007; 27:121-130
3. Sam Mannan. Inherent Safety Design. In: *Lee’s Loss Prevention in Process Industries, Hazard Identification, Assessment and Control*. Third ed. Butterworth-Heinemann: 2005; 2: 2422-2439.
4. Sam Mannan. Appendix 3: Seveso. In: *Lee’s Loss Prevention in Process Industries, Hazard Identification, Assessment and Control*. Third ed. Butterworth-Heinemann: 2005; 3: 2674-2683.
5. Attiq G, Paul A et al. An Inherent Safety Based Incident Investigation Methodology. *Loss Prevention Symposium, AIChE 2004*. Available at: http://chemicalengineering.dal.ca/Files/InherentSafety_Westray.ppt. Accessed on: November 8, 2009.