

ENVIRONMENTAL IMPACT OF MAJOR CHEMICAL ACCIDENTS

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The direct and indirect effects of major chemical accidents are amongst the greatest concerns facing the industry, governments, environmentalists and the public in almost every country in the world today. With chemical industrial growth coming to be regarded as barometer of a country's development, and a 1000 or so new chemicals getting added to some 70,000 already in every day use around the world, there is genuine cause for concern in the matter of safety in the design, operation and handling of chemicals and chemical installations.

Major industrial disasters are occurring at more frequent intervals than the rate at which humanity and the environment can recover from one. Effects of chemical accidents on the environment range from a temporary change of manageable proportion through serious, acute, temporary actions of high magnitude to drastic, long term environmental impairment.

According to a 1974 UNIDO classification, a country qualified to be designated as industrialised when manufacturing industries account for more than 30% of Gross Domestic Product. Even at that time 38 countries of the Third World could be ranked as industrialised. As more and more nations expand their development activities, the chemical and allied industries naturally register rapid growth providing products for civilian and defense needs. A good number of the chemicals involved in such industries are hazardous and highly toxic to humans, animals and the environment.

Although the chemical industry has itself pioneered the invention of hazard assessment procedures and techniques and has been, in general, responding positively to demands for greater safety and controls, several recent disasters question the ability of even experienced industrial giants to face a crisis. The 'Schweizerhalle' fire caused the release of at least 30 metric tons of toxic chemicals including 150 kg of mercury into the Rhine river, in addition to roughly 10,000 m³ of the fire extinguishing water. Severe ecological damage occurred over a length of 250 km killing river fauna and flora and the company's safety systems could not contain the damage. A more recent case has raised serious doubts whether the much advertised ability of the petroleum industry to prevent and effectively clean up oil spills is more in theory than practice. The oil leak from VALDEZ and its disastrous consequences to Alaska's ecology and

environment has once again revived international debate on our ability to manage major emergencies and contain environmental upsets.

The paper will discuss four different chemical disasters as examples of varying degrees of environmental impact and highlight the following:

- Strategies for reducing threats from chemical accidents;
- Risk assessment and engineering for intrinsic safety;
- Role of information in the prevention of and response to future accidents;
- Analytical tools and techniques; and
- Areas for research and international cooperation.

INTRODUCTION

It is now well recognised that an important indicator of industrial development of a nation is the production and rate of growth of the chemical and allied products industry which caters to basic societal needs, industrial diversification, trade and national security. As more and more nations join the mainstream of this development innumerable new manufacturing units are getting established, often in locations unacceptable from public safety considerations. Chemicals are produced, stored and transported in large volumes. Chemical Abstracts lists over six million chemical species made in the laboratory. An estimated 70,000 different types of chemicals are now in use world over. World production of chemicals of all types is now several hundred million tonnes every year with demands continually increasing by 10 to 15 percent.

The manufacture of chemicals involves a complex set of unit operations and processes involving transfer of mass and heat in varying degrees and reaction conditions ranging from very low to very high temperatures and pressures requiring or releasing varying levels of energy. Chemical substances used in manufacturing operations tend to be reactive and it is this very property that forms the basis of chemical operations. A large number of them are also toxic and therefore potentially hazardous to human health and the environment. A major chemical accident can arise from uncontrolled developments in the course of an industrial or a rare natural activity involving one or more hazardous substances, with serious consequences to people and the environment. Typical examples of conditions which can cause major accidents are:

- (i) Thermal radiations exceeding 5 kw/m^2 intensity for several seconds;
- (ii) Release of a dangerous substance beyond the specified limits;
- (iii) Vapour or gas explosions with blast over-pressures exceeding 0.5 kg/cm^2 ; and
- (iv) Explosion of a reactive substance.

SCHWEIZERHALLE INCIDENT (Switzerland)

On 1 November 1986, in the centenary year of Sandoz, the chemical giant became the focus of international attention for having caused an ecological and environmental

catastrophe from its Schweizerhalle works in a suburb of Basle, Switzerland. At nineteen minutes past midnight on that morning, a fire originated in Warehouse 956 and spread with extreme rapidity releasing noxious smoke over Basle and the French countryside further down the Rhine river. No deaths were reported but the environmental damage the disaster caused was much more serious, and shattered public faith in an industry that contributes half of Basle's earnings and the image of Switzerland as a clean and environmentally model country.

Warehouse 956 was purposely built and approved for storage of agricultural chemicals with a flash point of over 21°C. Even four days before the accident it had been inspected and cleared for fire safety. The fire produced a heavy smoke of phosphoric esters and mercaptans. Ten fire brigades with 160 men could only manage to prevent it spreading to the neighbouring warehouses and manufacturing operations. The emergency task force of the city sounded the C- (chemical) alarm warning the communities in the area and the city of Basle to stay indoors and await the 'clear' signal which was given after seven hours. For the people a threat to their lives was eliminated but for the Rhine river and the countries along its course the consequences were beginning to unfold.

In chemical terms the river received in a matter of hours roughly 66,000 pounds of highly toxic chemicals, among which were the pesticides atrazine, disulfotam, fenitrothion and parathion, phosphoric acid esters and mercaptans used as intermediates in the pesticide synthesis and an estimated 150 kilograms of mercury in aqueous concentrates. Since the fire could not be fought with foam alone, large amounts of water were used and nearly 10,000 cubic metres of this effluent also drained into the Rhine river. Atrazine, one of the toxic chemicals involved in this disaster, has a high water solubility and limited tendency to absorption to soil, and is therefore capable of persisting in ground water and deep soil layers (Pocchiari *et al.*, 1987a).

Most appalling was the action of several other major chemical companies along the Rhine who took advantage of the disaster and discharged a lot of their highly toxic wastes into the river contaminating the water further and complicating the efforts of Sandoz and the River authorities to repair the damage and restore life to the dead river. Companies reportedly (Layman, 1987) involved in compounding the tragedy were Ciba-Geigy (400L of atrazine, herbicide spill), BASF (1089 kg of 2, 4-D acid, ethylene glycol), Lonza (2.7 t of PVC), Bayer (methyl alcohol) and Hoechst (chlorinated hydrocarbons).

By the Company's own admission the consequences of "Schweizerhalle" were more ecological and psychological than on human health.

Human health

Complaints such as headache, nausea burning sensation in the eyes and respiratory discomforts were reported (Salzmann, 1987). No long term health hazard is expected although this would need to be confirmed by monitoring those who were exposed to the effects of the toxic fumes.

Ecological damage

Severe ecological damage was observed over a length of 250 km of the Rhine with the fish population, especially eels, completely wiped out. EAWAG (Swiss Federal Institute for Water Resources and Water Pollution Control) had been involved in the assessment of effects and the study reported that while the river's bacteriological regenerative capacity was not affected, the invertebrate microorganisms would be restored gradually allowing conditions for restocking with fish.

However, the psychological damage created by this disaster would take a very long time to heal especially in the other countries down course.

Schweizerhalle works subsequently implemented several measures such as cutting down insecticide production by 60%, a one-third cut in stocking of agrochemicals, discontinuation of phosgene storage and phosgene-based manufactures, along with a review of the entire manufacturing programme involving hazardous chemicals and intermediates. In retrospect it would appear that the disaster could have been avoided, had these measures been taken in the normal course of review.

BHOPAL INCIDENT (India)

"Worker panic in the plant, a sleeping community outside as the gas begins to spread. Bodies roused, coughing, crying out, eyes burning and watering. Thousands running, staggering through the dusty streets and alleys, many clutching their babies, not knowing where to run to escape.

Unconsciousness, injury and death by the thousands. Pandemonium in the hospitals. By day break, the scene of silence around those left behind; fathers, mothers, children, cows, bulls, goats, dogs, all in final repose. A peace in its eeriness never more heart wrenching. The bodies disposed of by cremation and mass burials."

The above is the chilling description by Lepkowski (1985) of the early hours of 3 December 1984, the day of the worst industrial disaster in the history of the world chemical industry. The leakage of poisonous methyl isocyanate (MIC) gas from the chemical plant of Union Carbide at Bhopal left in its wake over 2,500 dead and over one hundred thousand injured, with irreparable damage to a high percentage of them. The calamity rocked the consciousness of the chemical industry and sowed the seeds for a continuing vastness to the subject of industrial safety.

Union Carbide was producing carbaryl (Sevin) and other pesticide formulations in a large manufacturing facility in Bhopal in Central India (Fig. 1). For the synthesis of carbaryl the company employed the route (Fig. 2) involving the key intermediate MIC, one of the most poisonous and reactive chemicals known. For three years, before starting actual production at the Bhopal plant in 1980, MIC was imported in stainless steel drums from Union Carbide's MIC plant in USA. Local production of MIC in Bhopal involved production of carbon monoxide and phosgene and the process as well as basic engineering designs were provided by the parent company as for the synthesis of Sevin itself.

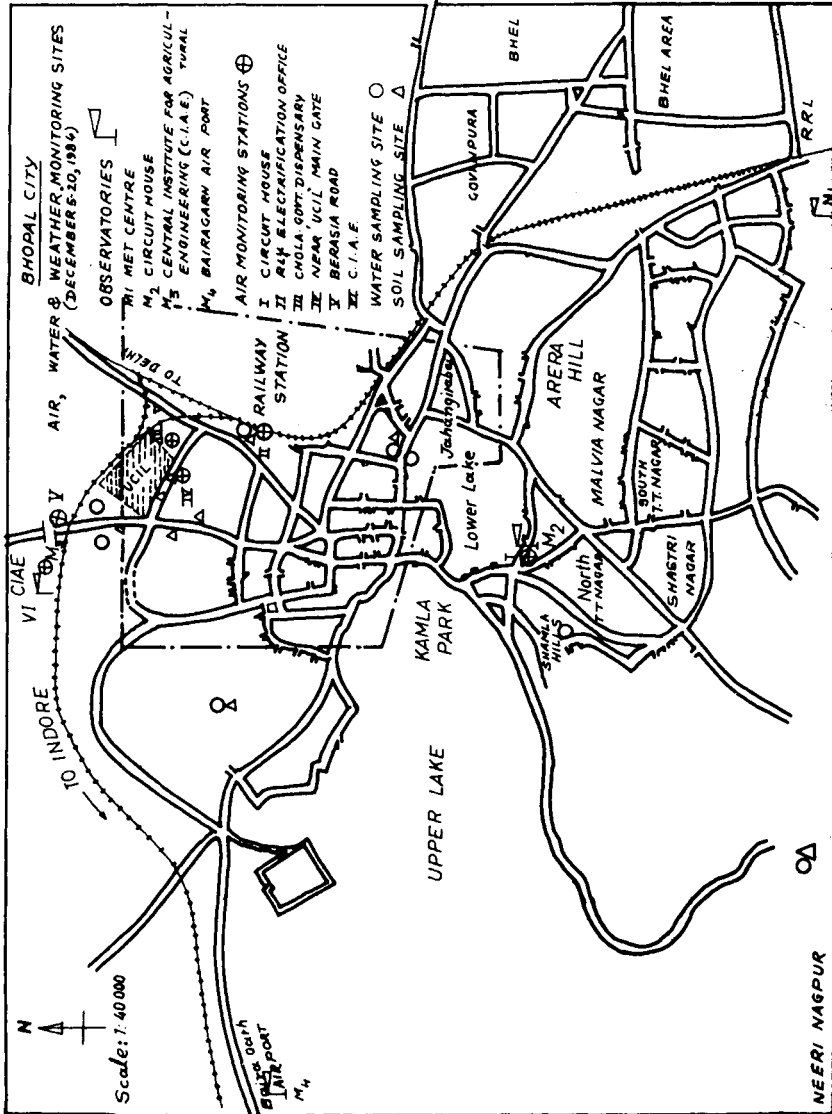


Fig. 1. Bhopal city map.

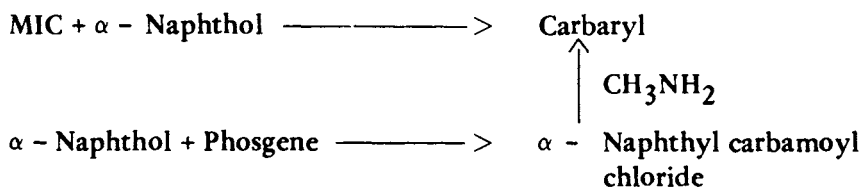


Fig 2. Carbaryl synthesis with and without MIC.

The chemical reactions involved in the synthesis of MIC are shown in Fig. 3. Phosgene and MMA were reacted in vapour phase to give MCC which upon quenching in chloroform and subsequent pyrolysis decomposed to give MIC and HCl. The pyrolyser condenser fed the MIC Refining Still (MRS) and the MIC, freed from chloroform, was led directly into the storage system which consisted of three horizontal, mounted 15,000 gallon (57 m³) tanks designated E 610, E 611 and E 619 (Fig. 4). Normally two of the three tanks were used to store, under high priority nitrogen pressure, product of acceptable quality while the third was used to store off-specification MIC which was then reprocessed. The two tanks together would hold 90 t of MIC, a 30 days inventory for Sevin production. All three tanks were interconnected by a maze of pipelines and common headers linking the Process Vent Header (PVH), Safety Relief Valves (SRV), and Relief Valve Vent Header (RVVH) and Vent Gas Scrubber (VGS). The VGS was meant to neutralise toxic gases from the MIC production plant and from the storage system, by scrubbing them with counter current flow of 10% caustic solution, the strength of which was maintained by pumping in a 20% make up solution. Finally, a flare tower was responsible for burning vent gases, coming from VGS, MIC storage tanks, as well as from the production range.

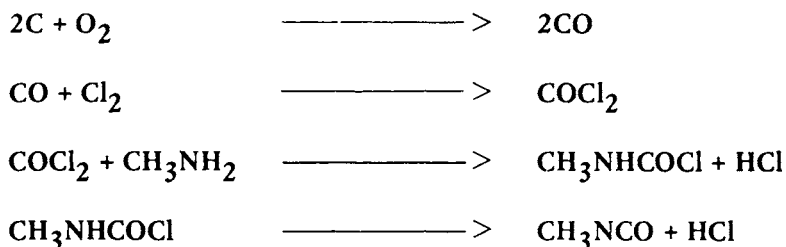


Fig 3. MIC Synthesis.

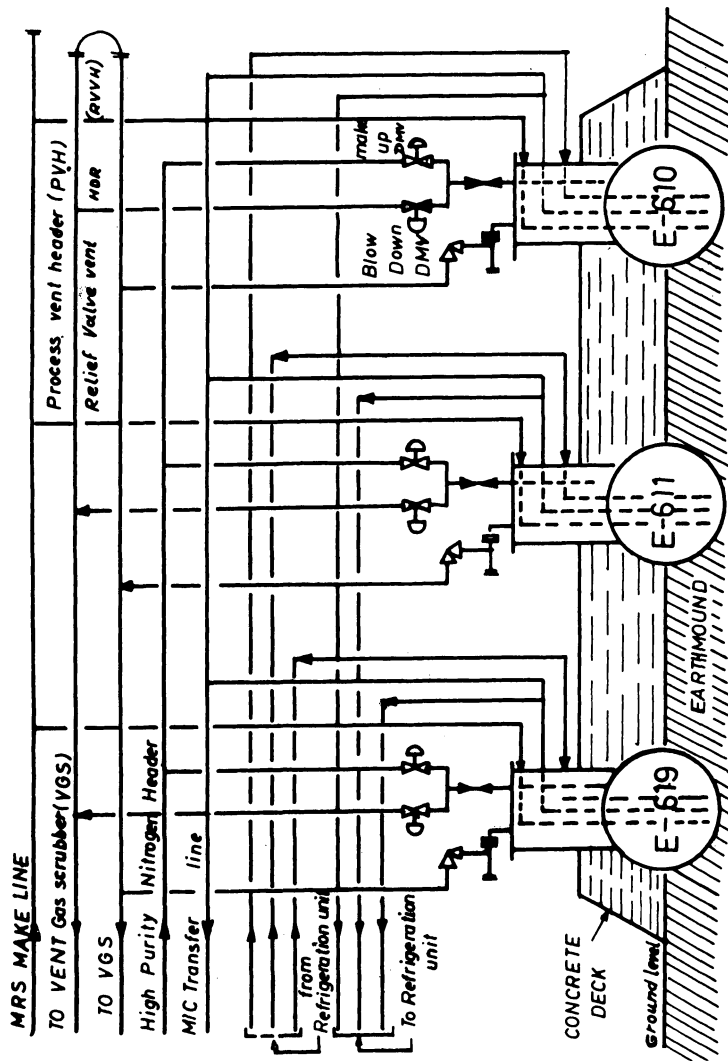


Fig. 4. Schematic layout of common headers of MIC storage tanks.

MIC (bp 30°C) itself is a highly toxic, volatile and inflammable chemical, always to be stored and handled in stainless steel 304 and 316 equipment since metallic impurities such as iron, aluminium, zinc, galvanised iron, copper or their alloys would cause violently explosive polymerisation. Purified MIC will react with itself under the influence of a catalyst (e.g. strong bases, certain metallic chlorides) to form a cyclic trimer or a high molecular weight polymer. Highly purified MIC spontaneously polymerises exothermically. With these sensitive properties MIC qualifies as an explosive besides being a highly toxic chemical.

The event

MIC produced between 7 and 22 October was stored in E 610 mixed with old material (6.4 t) already contained in it. After a transfer of 23 t to E 611, further production was fed into E 610 which at the time of the runaway reaction contained approximately 42 t of MIC. About the same quantity was present in E 611 as well.

As per operating practice MIC in the storage tank was normally maintained under nitrogen pressure of 1 kg/cm²g. On 22 October E 610 registered an abnormal drop in pressure to 0.25 kg/cm²g and continued so. When Sevin production was commenced MIC was drawn from E 611 but it developed a pressurisation problem on 30 November. Attempts to pressurise E 610—to draw out MIC—did not succeed. Meantime an alternative system for pressurising E 611 succeeded and MIC was drawn from this tank—a further attempt once on 1 December on E 610 proved negative.

Rapid developments occurred from 2330 hours on 2 December. MIC leakage was noticed in the MIC production area near the VGS, along with dirty water. At 0015 hours the Control Room operator observed E 610's pressure shooting up and in the range of 25-30 psig which rose to over 55 psig by 0030 hrs, along with a loud hissing noise. Efforts to start VGS failed, and the flare was not on.

The gases surged past and into the atmosphere, got condensed with cold air and aided by atmospheric inversion settled down slowly on the ground starting the tragedy.

Scientific investigations on the causes of the catastrophe have now established that the factors which led to the toxic gas leakage and its heavy toll existed in the unique properties of MIC's high reactivity, volatility and inhalation toxicity. It was foolish to store this chemical in large quantities for indefinitely long periods with no arrangement to check its quality or condition. Serious defects in design, in choice of materials of construction, in instrumentation and warning systems coupled with inadequate controls on stored MIC and underdesigned refrigeration and scrubber systems all provided a combination of conditions for such a tragedy to happen (Varadarajan, 1985).

Assessing the effects of MIC leakage in the aquatic environment involved examination of end-products of degradation of MIC in water and fish in the Upper and Lower Lakes of Bhopal. While the far-away Upper Lake recovered from MIC effects except for excessive amounts of free ammonia, the Lower Lake, nearer to the factory, was completely eutrophicated and remained dead for all practical purposes even after 140 days (of the disaster).

Air, soil and water were monitored and the environment at Bhopal was cleared as safe on the evening of 5 December.

SEVESO INCIDENT (Italy)

2, 3, 7, 8 - Tetrachlorodibenzo-p-dioxin, also called Dioxin or TCDD is 70,000 times as deadly as cyanide, and has the nickname 'Super poison'. It is invariably a contaminant in trichlorophenol (TCP) which is a key intermediate in the preparation of 2, 4, 5 - trichlorophenoxyacetic acid (2, 4, 5-T) a defoliant ill-reputed as Agent Orange. TCP itself is produced by reaction of 1, 2, 4, 5-tetrachlorobenzene (TCB) with caustic alkali.

The company involved was Givaudan belonging to the Swiss chemical giant—Hoffmann la Roche. On Friday, 9 July 1976 operators charged the reaction kettle with 2 tonnes of TCB, 27 sacks of NaOH flakes, xylene and glycol. The initiated reaction was interrupted and the plant shutdown for the weekend.

Almost 24 hours later, at 12.37 pm on Saturday, the reactor exploded rupturing the safety disk of the kettle and toxic contents spilled into the air—valve commanded a pipe located over the roof—carrying an estimated 2 kg of the deadly dioxin. Consequences, observed and feared, caused schools to be closed, whole areas were evacuated. The medical and environmental emergencies led to the opening of a

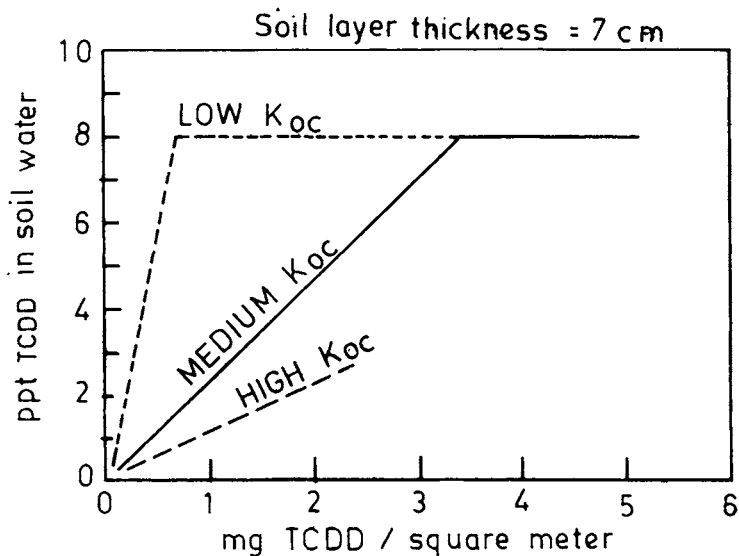


Fig. 5. TCDD saturation trend in soil.

Special Office at Seveso (SOS) in June 1977 with authority from over 11 towns with an aggregate population of 2,20,000.

Reclamation work alone lasted up to 1982 and involved scraping or washing buildings with solvents, removal of contaminated top soil to a depth of 20 cm or elimination of objects that could not be treated (Strigini, 1983). Some 8,200 m³ of vegetation was removed. The contaminated materials thus removed had to be isolated and for this purpose two basins with a combined capacity of 2,30,000 m³ were constructed near the site. TCDD represents a class of organic compounds with a strong tendency to be absorbed into soil as was the case after the Seveso release. Figure 5 shows that TCDD vertical distribution scarcely changed after an initial permeation—a relatively stable and long term contamination scenario (Pocchiari, 1987b). The prevention of initial permeation therefore becomes a matter for immediate attention in any rehabilitation and reclamation activity arising out of accidentally released chemicals. In the Seveso case the problem was further compounded by lack of information on its physico-chemical fate in nature. Dioxin's well documented data on carcinogenicity and embryo toxicity was equally threatening.

Immediate effects of the toxic release were:

- (i) Animal deaths (over 100,000);
- (ii) Chloracne—a persistent and disfiguring skin disease, with loss of muscular strength and psychological disturbances especially in children;
- (iii) Spontaneous abortion in pregnant women; and
- (iv) Contamination of over 1,800 ha of soil and vegetation.

Of greater concern were the 'unknown dimensions' such as:

- (v) Determining who had been or had not been exposed to dioxin;
- (vi) Mapping contamination areas accurately;
- (vii) Area reliability before resuming agricultural activities;
- (viii) Epidemiology of dioxin (carcinogenicity, embryotoxicity);
- (ix) Risk of cancer and genetic defects which takes years to manifest; and
- (x) Disposal of toxic waste.

Apart from individual out-of-country settlements, worker compensation and payments to affected farms, the towns affected by the accident demanded and got compensation all totalling over \$100 million.

The disposal of the piled up toxic waste created another story. The 41 containers filled with an estimated 150 g of dioxin were quietly buried by a contract company in the background of a French village for nearly 8 months until it was traced and exposed. The Swiss firm took charge and destroyed the dioxin by high temperature incineration (Strigini, 1983).

The Seveso disaster is attributable to bad process practice and negligence, particularly since there had been four previous instances of TCP runaway reaction in USA (1949), West Germany (1953), Holland (1963) and UK (1968) affecting between 50 and 200 workers in each case.

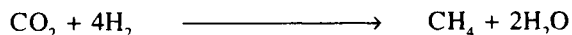
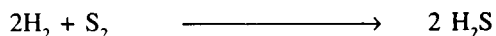
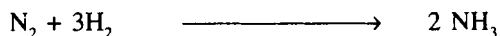
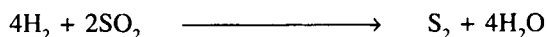
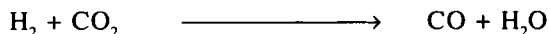
LAKE NYOS INCIDENT (Cameroon)

Lake Nyos is situated in a valley in the North-West Province of Cameroon, an area with a history of extensive volcanic activity in the geologically recent past. The lake has a surface area of 1.48 km and is probably only a little over 200 m deep suggesting that it was possibly formed by the eruption of a volcano.

On 21 August 1986, late in the evening a large volume of toxic gas erupted from beneath and within the lake and the aerosol mix of this toxic cloud descended on the valleys to the north of the Lake leaving a trail of 1,700 dead people, young and old and over 4,000 dead and dying livestock.

While international relief efforts were quickly mounted to help the survivors and monitor environmental clean-up this disaster prompted several scientific investigations to understand the phenomenon and its suddenness. These studies and the scientific conferences which discussed the geological, geochemical, physical-chemical and toxicological dimensions of the disaster have produced voluminous data from which the following conclusions are summarised:

- (i) The Lake lost 200,000 t of water or an equivalent volume, based on an observed recharge rate of 50,000 t of water per day. The Lake got saturated with CO₂ of volcanic origin just days prior to the event, and on the fateful day a pulse of volcanic gas—mostly CO₂ but also H₂S—caused the CO₂-charged bottom waters to surge up which, upon reaching the surface, transformed into a fine aerosol and sent a wall of water crashing across the lake, and down the valleys. About 6,000 t of gas equivalent to 3 million m³ at atmospheric temperatures and pressures must have been released (Freeth and Kay, 1987);
- (ii) In physico-chemical terms the following reaction equilibria would appear to account for the principal gases observed in a volcanic environment (Hassan El-Etr, 1987);



Since these involve the breaking down and re-arrangement of gas molecules, some or all of them may be slow, even at the high volcanic environment temperatures such that equilibrium is not always reached;

- (iii) The dead suffered burns indicating sulphuric acid presence. Death in most cases must have resulted from asphyxia (Tanya *et al.*, 1987);
- (iv) All species of living things which came into contact with the gases succumbed. No reptiles, birds, arthropods or flies were visible even one week after the disaster (Tanya *et al.*, 1987);
- (v) Apart from trees and vegetation uprooted and thrown by the powerful surge of water, pastures did not suffer any lasting damage. There was no significant chemical damage to the vegetation (Freeth and Kay, 1987; Tanya *et al.*, 1987);
- (vi) The seismicity of the region is on the increase with forebodings of more events in the area. The gas emanations are also indicative of future volcanic activity (Hassan El-Etr, 1987); and
- (vii) Hazard evaluation and mitigation should receive high priority (Oskarson, 1987).

ACCIDENT RECORD OF THE CHEMICAL INDUSTRY

Table 1 is a partial listing of major chemical accidents around the world during the period of 1974-1988. An analysis highlights the following general causes or causative factors:

- (i) Runaway reactions, explosions or fire in the plant;
- (ii) Design faults leading to accidental mixing of chemicals;
- (iii) Storage of unacceptably large quantities of hazardous and vulnerable chemicals;
- (iv) Accidents during transportation by rail, road or sea;
- (v) Inventory control failure;
- (vi) Improper waste disposal practices; and
- (vii) Human failure.

Specifically, major accident contributing factors are equipment or process-related. In an analysis (Sastri, 1987) of 110 losses, of over US \$ one quarter million each in chemical plants in the USA during 1974, 75 and 76 accidents were caused by equipment design (41%), chemical operator error (31%), maintenance (12%), process design (10%), and material hazard (6%). An analysis of 463 accidents in petroleum

refineries and petrochemical complexes in Japan revealed three main causes: (i) equipment construction or engineering; (ii) management; and (iii) operator-related (Nishikawa, 1983). In the UK chemical industry 2100 accidents during a three year period 1982-85 analysed as: (i) process-related (65%) and maintenance-related (30%); (ii) over 50% of the cases involved release of harmful substances; and (iii) over 25% of the accidents occurred while maintenance work was being carried out. It was possible to assign full or partial responsibility to the site management for 75% of the cases (Robinson, 1987).

Strategies for reducing threats from chemical accidents

In industry, resources both financial and technical, are never enough to totally remove all hazards. A practical way is to be devised to minimise the hazards on a cost effective basis. Hazard analysis is a practical loss prevention tool that can be tailored to the specific need of an industrial management to restrict its preventive costs only to those hazards whose severity and probability of occurrence are high enough to warrant expenditure. To achieve this objective, an industrial manager has to evolve meaningful quantitative data from the accepted norms and with his own engineering judgement.

Conventional approaches to hazard assessment were based on empirical codes and standards and were primarily intended to check for errors and omissions in design. No attempts were made to examine a chemical project as a dynamic running unit or to involve and integrate the skills of multidisciplinary teams. These are inadequate for the new process technologies and their complexities (Raghavan and Thyagarajan, 1988).

Modern Hazard Assessment techniques involve identification and analysis. Six principal methods available today are:

- (i) Failure Mode and Effect Analysis (FMEA);
- (ii) Hazard Analysis (HAZAN);
- (iii) Hazard and Operability Study (HAZOP);
- (iv) Fault Tree Analysis (FTA);
- (v) Consequential Analysis (CA); and
- (vi) Risk Rating (RR).

The modern philosophy is to make Hazard Analysis a continuous process throughout the life of a chemical process facility. The optimum times to conduct such studies are: (i) conceptual design phase; (ii) design freeze stage; (iii) prestart up period; and (iv) normal and modified operations. The usefulness of hazard analysis in each phase differs in its quality. During the conceptual design phase, the analysis will assist in the site selection and plant layout. Many potential hazards due to fire,

explosion and toxicity can be spotted and significant changes made at minimal cost. Hazard analysis during design freeze phase is extremely useful in making risk assessment of a new facility. Changes in the plant can still be made rather easily since most equipments, though already specified, will not have been ordered. Hazard analysis during prestart up phase should be a final check rather than an initial assessment. Of main concern would be the status of the recommended changes from the previous hazards/risks are unearthed during this phase, it is unlikely that they can be eliminated without significant cost or start up delays.

The later the hazard analysis is done, the more difficult it is to incorporate safety revisions without significant cost or time delays.

Failure mode and effect analysis

FMEA technique can be conveniently employed to a specific equipment or a particularly hazardous portion of a large process. The primary objective is to evaluate the frequency and the consequences of component failure on the process (US Dept of Navy, 1977). No attempt is, however, made to examine the component failures due to errors/deviations in operating procedures or those made by operators. This method becomes cumbersome when applied to a complex chemical process. Its utility is therefore limited.

Hazard analysis

HAZAN provides a systematic approach for the identification of risks. It may be undertaken at the preliminary stage for determining a plant location, basic design principles and process parameters to establish adequacy of basic safety of design, operation and environmental control. The major subcomponents of the study are:

- (i) Identification of flow path of all the fluids/solids in the process;
- (ii) Identification of likely sources of leakage;
- (iii) Size and duration of hazardous gas releases;
- (iv) Determination of sources of ignition; and
- (v) Collection of site specific data.

Based on the HAZAN study and the identification of major hazards associated with the various engineering systems, a HAZOP study can be carried out.

Hazard and operability study

HAZOP studies are undertaken at an advanced stage of project implementation when the design criteria for a chemical plant are well established. The studies are applicable to both new and operational plants and are based on the concept of a

systematic and comprehensive sectionwise examination of an installation on the basis of piping and instrumentation diagrams (Lawley, 1974). A HAZOP study supplemented by site inspection exercises enables all potentially dangerous situations likely to result from the unexpected interaction of seemingly safe components or methods of operations under exceptional conditions, to be anticipated and recognised.

The principal subcomponent activities of a HAZOP study are:

- (i) Division of the chemical process unit into sections identification of critical process equipments from hazard considerations;
- (ii) Likely process parameter deviations in critical process equipments;
- (iii) The likely causes for the deviations;
- (iv) Implications of the causes on the individual equipments;
- (v) Assessment of the capabilities of control instruments/indicators/alarms;
- (vi) Search for off-site hazard potential;
- (vii) Preliminary classification of identified hazards;
- (viii) Reclassification after technical discussions/relevant data acquisition/process analysis;
- (ix) Attempts for narrowing down the hazardous events; and
- (x) Quantification of the risks through FT/consequence analysis.

HAZOP which involves several subcomponent activities is to be carried out by multidisciplinary teams of experienced technical personnel possessing detailed knowledge of both the design and operations of chemical process plant. The study team should include experts from production, technical and engineering services, process control and instrumentation, research and development and safety departments. The team should be able to gather reliable data on failure rates of process equipments. The most appropriate time to commence a HAZOP study is at the design freeze stage when the design is firmed up and detailed engineering is in progress.

Fault tree analysis

The Fault Tree approach to system safety is an excellent tool for identifying and correcting system defects, and can be very effectively utilised in conjunction with a HAZOP study (Lee, *et al.*, 1985). The method is based on the promise that a loss incident or an accident has one or more causes/events/conditions which are deviations from the normal or planned state of the system. If only one such event or condition is sufficient to cause an accident, then the probability of its occurrence is equal to the probability of this cause event. If two or more independent events are required, then by the multiplication law, the probability of an accident is equal

to the product of the probability of these events. Because probabilities are expressed as fractions (10^{-1} - 10^{-7} per hour), the requirement for each additional cause event reduces the probability of an accident by several orders of magnitude. This principle is exploited in FTA to provide interlocks to prevent catastrophic reaction incidents.

Data reliability plays a crucial role in FTA of chemical process industries (Powers and Tompkins, 1974). Constructing fault tree is an instructive procedure requiring system and environment dependent data. Table 1 show typical failure data useful for process industries. It should be supplemented to system dependent data applicable to a particular plant and its environment. Human failure rates deserve special attention since human beings are less reliable by at least three orders of magnitude at repetitive and programmable tasks.

Table 1: Major Chemical Accidents during 1974-88

Year	Place	Nature of accident	Consequences	
			Death	Injuries
1974	Decatur, USA	Propane explosion	7	152
1974	Flixborough, UK	Explosion in caprolactum plant	28	89
1975	Beek, Netherlands	Propylene explosion	14	107
1976	Seveso, Italy	Runaway reaction, dioxin/TCDD emission	—	193
1977	Cartagenia, Columbia	Ammonia release	30	25
1978	Chicago, USA	Hydrogen sulphide release	8	29
1978	Santa Cruz, Mexico	Methane fire	52	—
1978	Xilatopec, Mexico	Gas explosion in transit	100	150
1978	Los Alfaques	Propylene transport accident	216	200
1979	Three Mile Island, USA	Nuclear reactor accident; 200,000 evacuated	—	—
1979	Novosibirsk, USSR	Chemical plant accident	300	—
1980	Sommerville, USA	PCl ₃ accident during rail transportation	—	300
1981	Tacoa, Venezuela	Oil explosion	145	—
1982	Taff, USA	Acrolein explosion; 17,000 evacuated	—	—
1984	Sao Paulo, Brazil	Petrol pipeline explosion	508	—
1984	Ixhuatepec, Mexico	LPG tank explosion	452	4,248
1984	Bhopal, India	Runaway reaction of stored MIC in pesticide plant	2,500	'000s
1986	Chernobyl, USSR	Nuclear reactor accident, 90,000 evacuated, transboundary fall-out in Europe	325	300
1986	Devnya, Bulgaria	Fire in a chemical complex	17	19
1986	Schweizerhalle, Switzerland	Fire-related spill of toxic chemicals. Rhine river pollution and ecological damage	—	—
1988	North Sea, UK	Piper Alpha oil rig explosion	166	—

Consequence analysis

For each credible event in a chemical processes system, consequence analysis can be made. It is based on specially evolved consequence modelling techniques. From such an analysis, the most hazardous events can be identified and safety measures suggested (van Deelan, 1987).

Risk rating techniques

These techniques rank the hazards of various plant units at the early stages of project design. These rankings can be used to layout a plant logically, determine spacing distances between various plant units and buildings, specify ventilation requirements and suggest fire fighting and other safety requirements in different sections of a plant. The initial calculations are made with no credit given for safety features. The approach to RR techniques is flexible and can easily be modified to suit specific problems or local requirements. They are normally offered as suitable starting points in safety analysis.

Hazard analysis for siting industries

Traditionally, the location and siting of chemical plants are determined by economic, market, labour, transportation, water, energy and associated factors. For installations that process hazardous, flammable and toxic materials, hazard analysis is a convenient tool in ensuring the safety of employees and the neighbouring community by providing adequate spacing within and between hazardous plants and the neighbouring community. These analysis may also stimulate designers to reduce inventories of hazardous materials, pipeline sizes and failure probabilities. Applying hazard analysis in the early planning stage of a chemical plant may provide a useful quantitative assessment of alternative layouts for hazardous plants. The technique can readily be computerized allowing easy checks and layout modifications and spacing provisions throughout the evolution of the project.

CONCLUSIONS

The paper has attempted to present two relevant dimensions to the Symposium theme: (i) the environmental effects of major chemical accidents; and (ii) possible ways of preventing the accidents. Given that modern society's needs are propelling fast technological developments, human and environmental consequences are to be anticipated. Technological disasters are becoming a source of major concern to all countries, developed or developing. As research in chemical and material synthesis finds advantages in exploring extremely high temperatures and extremely high pressures (Pimental Report, 1985) our goal must be to continually upgrade intrinsic safety in industrial innovation and reduce the probability of accidents and their subsequent impacts to the maximum extent possible.

Chemical safety has also assumed global dimensions calling for international cooperation in the transfer of hazardous chemical technologies. A systematic and comprehensive effort should be mounted to analyse previous chemical accidents and widely disseminate the information in the industry. For example there were four accidents in the process industries similar to the one which occurred in the Seveso plant.

There is also need for increased attention to analytical procedures and properties of chemicals. In Bhopal the threat of a second toxic release was looming large until correct analytical procedures were developed to establish the quality of MIC in the second tank for safe processing. In this experience the importance of correct analytical methods and its availability in a time of crisis was acutely felt.

Finally, there is need to promote research on chemical safety on a continuing basis, and to encourage radically fresh thinking in the planning and siting of chemical industries.

These and other initiatives may substantially contribute to reducing threats from chemical accidents for human lives and the environment.

REFERENCES

- Freeth, S.J. and Kay, R.L.F. (1987). The Lake Nyos gas disaster, *Nature*, **325**, 104-5.
- Hassan El-Etr, A. (1987). Physical-chemical processes of natural gas explosions. Paper presented at the International Conference on Causes of Lake Nyos Disaster in Cameroon, 6-22 March, Cameroon.
- Layman, P.L. (1987). Rhine spills force. rethinking of potential for chemical pollution, *C & E News*, 23 Feb, 7-11.
- Lawley, H.G. (1974). Operability studies and hazard analysis. Loss Prevention Series. Vol. 8, *AIChEJ*, New York.
- Lee, W.S., Gosh, D.L., Tillman, F.A. and Lee, C.H. (1985). *IEEE Trans on Reliability*, **34** (3), 194-197.
- Lepkowski, W. (1985). Bhopal, *C & E News*, 2 December, 7-18.
- Nishikawa, K. (1983). Accident prevention in the Japanese chemical industry, *Industry and Environment*, **6** (3), 9-13.
- Oskarson, N. (1987). Carbon Dioxide bursts of Lake Nyos modelled as periodic supersaturation in a counter-current reactor: Implications of chemical monitoring and future prevention, Paper presented at International Conference on Causes of Lake Nyos Disaster in Cameroon.
- Pocchiari, F., Silano, V. and Zapponi, V.A. (1987a). Immobilisation and Reclamation After Chemical Accidents. Proc World Conference on Chemical Accidents, Rome, July. CEP Consultants, UK. p 19.
- Idem, (1987b): Ibid, p 22.
- Powers, G.J. and Tompkins, F.C. (1974). Fault tree syntheses for chemical processes, *AIChEJ*, p 376.

- Raghavan, K.V. and Thyagarajan, G. (1988). Hazard and risk analysis. in 40 Years of Research — A CSIR Overview, Series II. CSIR, New Delhi, pp 53-67.
- Robinson, B.J. (1987). A Three Year Survey of Accident and Dangerous Occurrences in the UK Chemical Industry, Proc World Conference on Chemical Accidents, Rome, July. CEP Consultants, UK, pp 33-36.
- Salzmann, J.J. (1987). Proc. World Conference on Chemical Accidents, Rome, July, CEP Consultants, UK, 137.
- Sastri, D.S. (1987). Salus populi suprema Lex, Paper presented at the Indo-Dutch Seminar on Safety and Risk Analysis, Bombay, 20-30 April, pp 22-24.
- Strigini, P. (1983). The Italian chemical industry and the case of Seveso. in *Industry and Environment*, (a UNEP Publication) 6 (4), 16-21.
- Tanya, V.N, Saliki, J.T., Bamo, E.T. and Salah, J.N.S. (1987). The Effects of Lake Nyos Disaster on Animals and Pasture — A Report from Institute of Animal Research, Yaounda, Cameroon.
- The Pimental Report (1985). Opportunities in Chemistry. The Pimental Report. National Academy Press, Washington DC, pp 298-301.
- US Dept of Navy, (1977). Procedures for Performing a Failure Modes and Effect Analysis, Report MIL-STD-1629A, Washington DC.
- Van Deelan, C.L. (1987). Paper presented at the Indo-Dutch Seminar on Safety and Risk Analysis, Bombay, 28-30 April.
- Varadarajan, S. *et al.* (1985). Report on Scientific Studies on the Factors Related to Bhopal Toxic Gas Leakage. CSIR, India, 81.