

## ACCIDENT SIMULATION AS A TOOL FOR ASSESSING AND CONTROLLING ENVIRONMENTAL RISKS IN CHEMICAL PROCESS INDUSTRIES: A CASE STUDY

Faisal I. Khan, J. Deepa Rani and S. A. Abbasi<sup>†</sup>

Risk Assessment Division, Centre for Pollution Control & Energy Technology,  
Pondicherry University, Pondicherry-605 014

(Received 18 January 1997 • accepted 26 December)

**Abstract** – Accidents involving toxic releases, explosions, and fires in chemical process industries take a heavy toll of property, human lives, and environment quality. If one could forecast the accidents likely to occur and the damage they were likely to cause, one could devise appropriate strategies to prevent the accidents and contain the damage that did occur. Using this concept, we have developed a computer-automated tool for accident simulation. In this paper the applicability of the concept and the tool is described on the basis of a case study of a typical petrochemical industry. The study reveals that out of eight credible accident scenarios, four would be 'stand-alone' events, whereas four others would also cause secondary or higher order accidents (*domino effects*). Of the accidents in the former category, the one as per scenario 8 is the worst as it would adversely impact (within the set limit of 50% probability of causing lethality) larger areas than the other three such accidents. Among the second category, scenario 1 would be the most undesirable because it would simultaneously cause heat radiation, shock waves, and missile effects over a larger area.

Key words: Risk Assessment, Industrial Hazard, Industrial Accidents, Petrochemical Industry

### INTRODUCTION

The history of the chemical process industry is replete with major accidents [Khan and Abbasi, 1994; Lees, 1980; Kletz, 1986; Khan and Abbasi, 1996]. Such accidents, information on a few of which is summarized in Table 1, have had catastrophic implications, causing massive losses of property, human lives, and environmental quality. The reverberations of the worst such disaster, which happened in Bhopal in 1984, are still being felt more than a decade later.

Increasing population and developmental needs keep putting ever-increasing pressure on the available land space. Even those industries which were earlier set up in remote areas away from human dwellings now find themselves being enveloped by residential colonies. The risk posed by industrial accidents is thus increasing even in situations where the quantities of the hazardous materials being handled, or the manner in which they are being handled, remains the same as before [Khan and Abbasi, 1996].

Unlike the normal release of gaseous, liquid or solid wastes from industrial processes which take place slowly and are controllable-accidental toxic releases, explosions, or fires occur all of a sudden leaving no chance for people to escape, let alone control the accident. Special techniques, tools and management strategies are therefore required to handle the hazards or accidents in chemical process industries.

The most feasible way to deal with such accidents is to

anticipate them and take all possible steps to prevent them. Even to devise any meaningful emergency preparedness plan one needs to forecast what can happen and then take all such steps to minimize the adverse impacts if an accident does occur [Khan and Abbasi, 1995; Greenberg and Grammer, 1991].

We have recently developed a computer-automated tool MAXCRED (MAXimum CREDible accident analysis) with which one can rapidly and quantitatively simulate accidents in any chemical process industry [Khan and Abbasi, 1996]. The tool enables forecasting of the type of accidents and the type and extent of damage such accidents would cause. Once this information is available by conducting simulations with the aid of MAXCRED, it becomes easy to devise the necessary accident prevention and damage control strategies on the basis of the characteristics of the industrial site.

In this paper we illustrate the applicability of this concept of accident simulation based risk assessment with the help of a case study of an industry which employs a number of hazardous chemicals: propylene, propylene oxide, ethylene, ethylene oxide, glycerin, chlorine, and propylene glycol.

### MAXCRED'S ESSENTIAL FEATURES

MAXCRED is a software package developed at the risk assessment division of the Centre for Pollution Control and Energy technology [Khan and Abbasi, 1996]. The package enables simulation of accidents and estimation of their damage potential. MAXCRED has been developed to provide a more versatile and accurate tool for rapid risk assessment than is possible with existing packages. This is illustrated in Table 2

<sup>†</sup>To whom all correspondence should be addressed.  
E-mail: cpet@vsnl.mdz.net.in

**Table 1. List of accidents occurred during handling of chemicals in chemical process industries**

S.No.	Year	Location	Chemical	Event	Deaths/Injuries
1	1917	Wyandotte, Mi	Chlorine	Toxic release (from storage tank)	1d
2	1926	St.Auban, France	Chlorine	Toxic release (from storage tank)	19d
3	1944	Cleveland, Ohio	Gasoline	Fire and Explosion	128d, 200-
4	1949	Perth N.J.	Hydrocarbon	Fire	4d
5	1952	Wilsum, Germany	Chlorine	Toxic release (from storage tank)	
6	1955	Whiting, ind	Naphtha	Explosion	2d, 30i
7	1956	New York, USA	Ethylene	Explosion (CVCE1)	2d, 10i
8	1958	Signal Hill, California	Oil Forth	Fire	2d
9	1959	Phillips burg N.J.	Lubricating & seal oil	Explosion (in compression)	6d, 6i
10	1960	Freeport	Allyl dichloride, propylene chloride	Explosion	6d, 14i
11	1962	Ras Tanura, Saudi Arabia	Propane	Fire	1d, 114i
12	1962	Cornwall, Ont	Chlorine	Toxic release (from rail tank car)	89i
13	1962	Doc Run, Kenya	Ethylene Oxide	Explosion (UVCE2)	1d, 9i
14	1963	Texas, USA	Polypropylene	Explosion (CVCE)	-
15	1964	Hebronville, Mass.	Polyvinyl chloride plant	Explosion	7d, 22i
16	1965	Louisville,	Monovinyl acetylene	Explosion	12d, 60i
17	1966	Feyzin, France	Propane	Fire & Explosion	18d, 81i
18	1966	Larose	NGL	Fire (on pipeline)	7d
19	1966	LaSalle, Quebec	Styrene	Explosion	11d, 10i
20	1966	W. Germany	Methane	Explosion	3d, 83i
21	1968	Paris, France	Petrochemical plants	Explosion	400 evacuated
22	1968	Pernis, Netherlands	Oil slopes	Explosion	9d, 85i
23	1968	Kennedale, Texas	Gasoline	Explosion (on road tankers)	28i
24	1969	Escom breras	Petroleum	Explosion	4d, 3i
25	1969	Long Beach California	Propylene	Explosion	1d, 83i
26	1969	Pnerts la Cruz	Light hydrocarbon	Explosion	5d
27	1969	Basel, Switzerland	Nitro liquid	Explosion	3d, 28i
28	1969	Teesside, UK	Cyclohexane	Fire	2d, 23i
29	1970	Philadelphia	Catalytic cracker	Fire	33i
30	1970	Port Hudson	Propane	Explosion (on pipeline)	25i
31	1970	Mont Bolivia, Texas	Butane	Explosion (on pipeline)	3i
32	1971	Houston, Texas	VCM	Explosion (BLEVE3)	1d, 50i
33	1971	Longview, Texas	Ethylene	Explosion	4d, 60i
34	1972	Hearne, Texas	Curde oil	Fire and Explosion	1d, 2i
35	1972	Lynchbriog	Propane	Fire and Explosion	1d, 2i
36	1972	Netherlands	Hydrogen	Explosion	4d, 4i
37	1972	New Jersey, Turnpike, New Jersey	Propane	Explosion (on road tanker)	2d
38	1972	Brazil	Butane	Explosion (UVCE)	37d, 53i
39	1972	West Virginia USA	Gas	Explosion	21d, 12i
40	1972	Billings	Butane	Explosion	4i
41	1973	St. Amandes-Eaux, France	Propane	Explosion (on road tanker)	5d, 40i
42	1973	Staten Island New York	Gasoline	Fire (in empty storage tank)	40d
43	1973	Port Chefstroom USA	NH <sub>3</sub>	Toxic release	18d, 34i
44	1973	Staten Island	LNG	Fire	40d, 34i
45	1974	Flixborough, UK	Cyclohexane	UVCE	28d, 134i
46	1974	Decatur, III	Propane	Explosion (on railway)	7d, 152i
47	1974	Rotterdam, Netherlands	Petrochemicals	Fire	110i
48	1974	India	Crude oil	Explosion	35i
49	1974	Beaumont, Tex	Isoprene	Explosion (UVCE)	2d, 10i
50	1974	Czechoslovakia	Ethylene	Explosion (UVCE)	14d, 79i
51	1974	Mississippi, USA	Butane	Explosion (UVCE)	24i
52	1975	Beck, Netherlands	Hydrocarbons	Explosion	1d
53	1975	Ilford, Esses	Hydrogen-Oxygen mixture	Explosion	1d
54	1975	Philadelphia USA	Crude oil vapor	Explosion	8d, 2i

1. CVCE-Confined vapor cloud explosion

2. UVCE-Unconfined vapor cloud explosion

3. BLEVE-Boiling liquid expanding vapor explosion

Table 1. Continued

S.No.	Year	Location	Chemical	Event	Deaths/Injuries
55	1975	Antwerp Belgium	Ethylene	Explosion (UVCE)	
56	1976	Los Angeles, California	Gasoline	Explosion	6d, 45i
57	1976	Westoning, Beds	Petroleum	Explosion (on pipeline)	3i
58	1976	Chalmette, LA	Ethyl Benzene	Explosion	13d
59	1976	Seveso, Italy	Tera choloro di-benzo paradioxin	Toxic release	-
60	1977	Colombia	NH <sub>3</sub>	Toxic release	30d, 45i
61	1977	India	Hydrogen	Explosion	20i
62	1978	Waverly, Tenn.	Propane	Explosion (on railway)	12d, 50i
63	1979	Bantry Bay, Eise	Oil	Explosion (on oil tanker at terminal)	50d
64	1981	Montanos, Mexico	Chlorine	BLEVE	29d
65	1981	Foggia, Italy	Chlorine	Toxic release and dispersion	1d, 16i
66	1982	Spencer, USA	Steam	BLEVE	7d, 2i
67	1983	Houston, USA	Methyl bromide	BLEVE	2d
68	1984	Mexico city, Mexico	Propane	BLEVE and fire	500d
69	1984	Bhopal, India	Methyl-iso cynate	Toxic release	2500d, 1500i
70	1985	Gwalior, India	Chlorine	Toxic release and dispersion	125i
71	1986	Kennedy space centre, USA	Hydrogen	BLEVE	7d
72	1986	Karwar, India	Chlorine	Explosion and toxic release	2d, 35i
73	1987	Antwerp, Belgium	Ethylene oxide	UVCE	6d, 15i
74	1987	Pampa, Texas, USA	Acetic acid	UVCE	3d, 12i
75	1988	India	Naphta	Pool fire	25d, 23i
76	1988	Henderson, USA	Ammonium perchlorate	BLEVE	2d
77	1988	Louisiana, USA	Propane	UVCE	16d, 34i
78	1989	Karwar, India	HCl	Explosion	3d, 15i
79	1989	Antwerp, Belgium	Aldehyde	Explosion	32d
80	1989	USSR	Ammonia	Explosion and toxic release	7d, 34i
81	1989	Pasadena, USA	Ethylene	Explosion	23d, 45i
82	1990	Port de Leixoes, Portugal	Propylene oxide	Explosion	5d
83	1990	Thane, India	Hydrocarbon	Fire and explosion	35d, 12i
84	1991	Kerala, India	Chlorine	Toxic release and dispersion	125i
85	1990	Maharashtra, India	Petroleum products	Fire	2d, 50i
86	1993	Panipat, India	Ammonia	Explosion and toxic release	3d, 15i
87	1995	Gujrat, India	Natural gas	Fire	Factory damaged
88	1996	Mumbai, India	Hydrocarbon	Fire	Factory damaged

which presents the capabilities of MAXCRED and nine other software packages in the context of an inter-institutional study conducted by Contini et al. [1991] on the risk assessment of accidental release of ammonia. It may be seen that MAXCRED has significantly greater capabilities than other commercial packages. A total of seven different models are available in MAXCRED relevant to the study of the above-mentioned problem, whereas software such as WHAZAN and SAFTI has only five models. Moreover, only MAXCRED generates the scenario BLEVE, followed by toxic release, while others are unable to do so. A brief description of the contents and capabilities of MAXCRED is given below; further details have been reported elsewhere [Khan and Abbasi, 1996].

### 1. Software

Coding medium	: C++
Working environment	: MS DOS, WINDOWS
Main menus	: as in Fig. 1
Basic algorithm	: as in Fig. 2

MAXCRED [Khan and Abbasi, 1996] has four main modules (options): scenario generation, consequence analysis, file,

and graphics. In the scenario generation, module accident scenarios are generated for the unit under study. It is a very important input for the subsequent steps. The more realistic the accident scenario, the more accurate is the forecast of the type of accident, its consequences, and associated risks; consequently, the more appropriate and effective the strategies for crisis aversion and management. Each accident scenario is basically a combination of different likely accidental events that may occur in an industry. Such scenarios are generated based on the properties of chemicals handled by the industry, physical conditions under which reactions occur or reactants/products are stored, geometries and material strengths of vessel and conduits, in-built valves and safety arrangements etc. External factors such as site characteristics (topography, presence of trees, ponds, rivers in the vicinity, proximity to other industries or neighborhoods etc.) and meteorological conditions are also considered.

The consequence analysis module involves assessment of likely consequences if an accident scenario does materialize. The consequences are quantified in terms of damage radii (the radii of the area in which the damage would readily oc-

**Table 2. List of models available with different software for simulating release and dispersion of ammonia**

Software	Models available with the packages@	Models usable for the remarks study of catastrophic release of pressurized liquified gas@
CRUNCH	1. Gas outflow 2. Two-phase outflow 3. Evaporation but not time dependent 4. Light gas dispersion 5. Heavy gas dispersion	2,5
DEGADIS	1. Gas outflow 2. Two-phase outflow 3. Evaporation but not time dependent 4. Light gas dispersion 5. Heavy gas dispersion	2,5
DENZ	1. Gas outflow 2. Two-phase outflow 3. Evaporation but not time dependent 4. Light gas dispersion 5. Heavy gas dispersion	2,5
HEAVG-PLUME	1. Gas outflow 2. Two-phase outflow 3. Evaporation but not time dependent 4. Light gas dispersion 5. Heavy gas dispersion	2,5
DECRARA	1. Gas outflow 2. Two-phase outflow 3. Evaporation but not time dependent 4. Light gas dispersion 5. Heavy gas dispersion	2,5
WHAZAN	1. Liquid out flow 2. Gas outflow 3. Two-phase outflow 4. Evaporation time dependent 5. Heavy gas dispersion	3,4,5
SAFTEI	1. Liquid out flow 2. Gas outflow 3. Two-phase outflow 4. Evaporation time dependent 5. Heavy gas dispersion	3,4,5
RISKIT	1. Liquid outflow 2. Gas outflow 3. Two-phase outflow 4. Heavy gas dispersion	3,4
EFFECTS	1. Liquid outflow 2. Vapor outflow 3. Gas outflow 4. Two-phase outflow 5. Evaporation but not time dependent	4,5
MAXCRED	1. Explosive release 2. Liquid release is capable 3. Gaseous release of studying the possible 4. Two-phase release of NH <sub>3</sub> as BLEVE 5. Evaporation but not followed by evaporation time dependent and dense gas dispersion 6. Light gas dispersion 7. Heavy gas dispersion	1,5,7

@ As listed in Contini et al. [1991]

cur), damage to property (shattering of window panes, caving of buildings) and toxic effects (chronic/acute toxicity, mor-

tality). The assessment of consequence involves a wide variety of mathematical models. For example, source models are

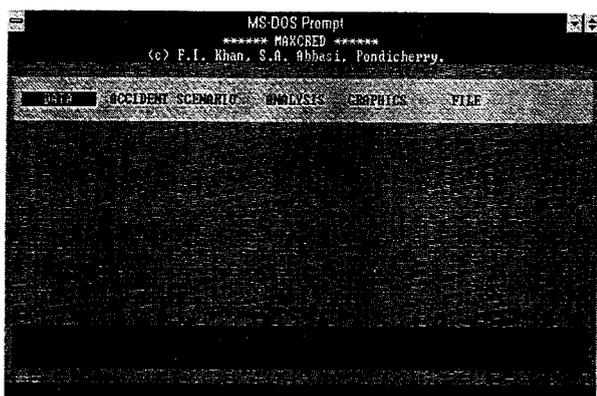


Fig. 1. Main submodules of MAXCRED.

used to predict the rate of release of hazardous material, the degree of flashing, and the rate of evaporation. Models for explosions and fires are used to predict the characteristics of explosions and fires. Impact intensity models are used to predict the damage zones due to fire, explosion and toxic load. Lastly, toxic gas models are used to predict human response to different levels of exposures to toxic chemicals. A list of empirical models included by us in MAXCRED for consequence estimation is given in Appendix A. Several different types of explosion and fire models such as confined vapor cloud explosion (CVCE), unconfined vapor cloud explosion (UVCE), boiling liquid vapor cloud explosion (BLEVE), pool fire, flash fire and fire ball are included. Likewise, models for liquid release and two-phase release have been incorporated. A special feature of MAXCRED is that it is able to handle dispersion of heavy (heavier-than-air) gases as well as light-as-air and lighter-than-air gases. A brief description of different types of accident events is presented in a subsequent section.

The graphics module enables visualization of risk contours in the context of the site of accidents. The option has two facilities: site drawing and contour drawing. The site drawing option enables the user to draw any industrial site layout by using freehand drawing or any already defined drawing tool. The contour drawing option has the facility for drawing various damage/risk contours over the accident site. The contours can be drawn in different shapes and sizes as per the requirement of the user.

The file module of MAXCRED mainly deals with the handling of different files such as data file, scenario file, output file and flow of information. This object works as an 'information manager'. It provides the necessary information to each module and submodule to carry out desired operations, and stores the results in different files. It also provides all commonly used file operations such as copying, deleting, consolidating and printing. All in all, MAXCRED, which is envisaged to be self-contained in the sense that it does not need other packages for data analysis or graphics support, is a versatile tool for risk assessment [Khan and Abbasi, 1996].

## 2. Hardware Requirement

System : PC/AT-386 or higher  
Minimum RAM needed : 2 MB

March, 1998

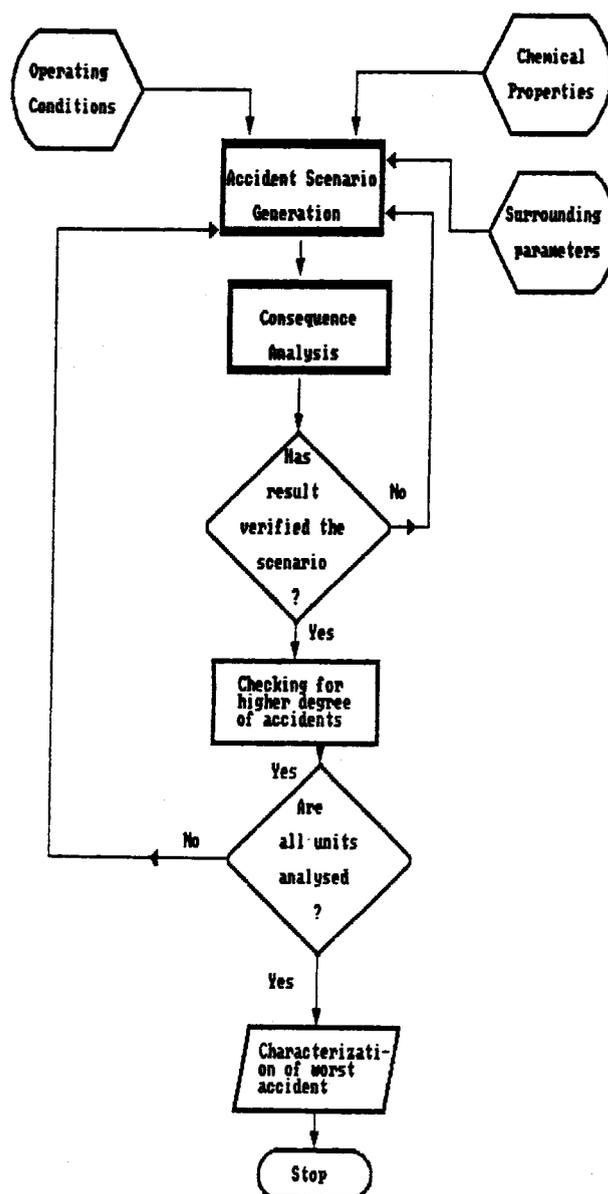


Fig. 2. The MAXCRED algorithm.

Minimum ROM needed : 8 MB

## 3. Operating Time

The entire accident simulation exercise beginning from keying in the input data to obtaining easy-to-use tabulated/graphic print-outs is approximately 30 minutes.

## CASE STUDY

Ras-Petro is a petrochemical industry situated some 30 km from Pune, off the Bombay-Pune highway. Many medium scale industries are located within an area of ~15 km<sup>2</sup> around Ras-Petro. The site also includes several densely populated villages (Fig. 3). The industry is engaged in the manufacturing of a wide variety of chemicals, e.g. propylene glycol, polyol, low density poly ethylene (LDPE), high density poly ethylene (HDPE) and polyvinyl chloride. To produce these products, the industry processes a number of chemicals at extreme

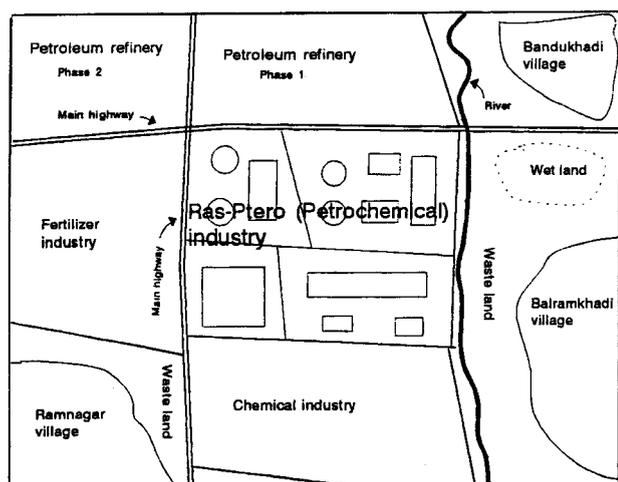


Fig. 3. Layout of the study area showing location of industry and their surroundings.

conditions of temperature and pressure. The industry also stores various hazardous chemicals (raw materials, intermediates) in bulk quantities. The present study analyzes the hazards associated with the storage of various chemicals (Table 3) in the industry using MAXCRED. A typical input data sheet of MAXCRED is presented in Table 4.

#### 1. Most Credible Accident Scenarios

We have developed eight scenarios of 'credible' accidents, i.e. accidents likely to occur given the history of failures in chemical process industries. 'Credible' accidents are those which have a high likelihood of occurrence as contrasted to freak accidents such as the mid-air collision of two airplanes, or a car accident involving a bird-hit [Pitersen, 1990; Kayes, 1985; Khan and Abbasi, 1996].

##### 1-1. Pool Fire

Continuous release of flammable liquid results in a pool fire. The characteristics of such a fire depend mainly on the duration of release, saturation pressure, and flammable properties of materials.

##### 1-2. Flash Fire

A flash fire occurs mainly due to the instantaneous release of material having a boiling point lower than atmospheric temperature. It does not explode when the material release rate and flame speed are not high enough. However, it spreads quickly throughout the flammable zone of the vapor cloud.

##### 1-3. Fire Ball

Instantaneous ignition of flammable vapor cloud would lead to the formation of a fireball. The radius of the fireball, its radiation heat intensity, and temperature in the fireball depend upon the dimension of the flammable cloud as well as the mass of the vapor released in the cloud. A very high temperature of 500 to 1,500 K is developed in the confines of a fireball. It is potentially the most disastrous of industrial fires that may be caused by highly flammable gases stored or processed under pressure.

The damage associated with such fires may be assessed on the basis of the dose of heat radiation received from them in a given time interval.

##### 1-4. Boiling Liquid Expanding Vapor Cloud Explosion (BLEVE)

Table 3. Quantities, and storing conditions of the chemicals handled in the Petrochemical industry

Chemical	Property
Chemical name	Propylene
Storage capacity	Two bullets of 1003 m
Storage characteristics	
a. Storage temp.	Ambient
b. Pressure	Saturated
Chemical name	Propylene oxide
Storage capacity	2 Bullets of 160 m <sup>3</sup> each.
Storage characteristics	
a. Storage temp.	10 °C
b. Pressure	2.5 Kg/Cm <sup>2</sup> g
Chemical name	Ethylene oxide
Storage capacity	One bullet of 30 m <sup>3</sup>
Storage characteristics	
a. Storage temp.	0-10 °C
b. Pressure	3.5 kg/Cm <sup>2</sup> g
Chemical name	Glycerine
Storage capacity	One tank of 18 m <sup>3</sup> capacity
Storage characteristics	
a. Storage temp.	100 °C
b. Pressure	6" WG
Chemical name	Mono-propylene glycol
Storage capacity	2 storages of 225 m <sup>3</sup> each
Storage characteristics	
a. Storage temp.	Ambient
b. Pressure	6" WG
Chemical name	Polyol
Storage capacity	7 tanks of 18 m <sup>3</sup> capacity each
Storage characteristics	
a. Storage temp.	50° to 100 °C (depending on grade)
b. Pressure	6" WG
Chemical name	Chlorine
Storage capacity	Two bullets of 100 m each
Storage characteristics	
a. Storage temp.	Ambient
b. Pressure	Saturated
Chemical name	Ethylene
Storage capacity	Two bullets of 100 m each
Storage characteristics	
a. Storage temp.	Ambient
b. Pressure	Saturated
Chemical name	Di-chloro propane
Storage capacity	Two tanks of 80 m <sup>3</sup> each
Storage characteristics	
a. Storage temp.	Ambient
b. Pressure	6" WG

BLEVE is a phenomenon which results from sudden release of gas or liquid stored at temperatures above their boiling points. At the vent or release point, a sudden decrease in pressure results in explosive vaporization of the stored material leading to a blast effect. The magnitude of BLEVE mainly depends on the material capacity and its rate of release.

##### 1-5. Unconfined Vapor Cloud Explosion (UVCE)

UVCE generally occurs when sufficient amount of flammable material (gas or liquid having high vapor pressure) gets released and mixes with air to form a flammable cloud such

**Table 4. Typical input data set to be keyed by the user to process any accident scenario using MAXCRED**

Parameters	Values
Mass released (kg):	6.130000e+04
Working pressure (kPa):	1.425000e+03
Operating temperature (C):	2.500000e+01
Density of air (kg/cu.m):	1.210000e+00
Boiling point (C):	-4.800000e+01
Specific heat of gas (KJ/kg/C):	2.014000e+00
Density of liquid (kg/cu.m):	6.130000e+02
Heat of combustion (KJ/kg):	4.480000e+04
Heat of vaporization (KJ/kg):	2.140000e+02
Mass of fragment generated (kg):	4.000000e+00
Atmospheric pressure (kPa):	1.011500e+02
Ambient temperature (C):	2.500000e+01
Density of gas (kg/cu.m):	2.300000e+00
Wind velocity (m/s):	3.500000e+00
Higher explosion limit (wt%):	1.100000e-01
Lower explosion limit (wt%):	2.400000e-02
Distance of study (m):	1.000000e+02

that the average concentration of the material in the cloud is higher than the lower limit of explosion. The resulting explosion has high potential for damage as it occurs in an open space covering large areas. The intensity of the explosion mainly depends on the quantity of material released and the strength of the ignition source.

The explosive power of a UVCE can be expressed in terms of blast wave characteristics (overpressure, overpressure-impulse, reflected pressure, duration of shock wave, etc.). The peak overpressure is a very important parameter; its magnitude depends on the speed of flame propagation. Any obstruction in flame propagation enhances the blast effect.

#### 1-6. Confined Vapor Cloud Explosion (CVCE)

CVCE, as the name suggests, is a vapor explosion occurring in one or another type of confinement. Explosions in vessels and pipes are examples of CVCE. Excessive generation of high pressure in the confinement leads to this type of explosion. It also has high potential for causing damage as it may generate fragments (missiles) propelled at high velocities which can cause newer accidents. The energy delivered to the fragments by the blast wave causes the fragments to become air-borne and to act as missiles. The missiles are characterized by velocity, weight and penetration strength. However, the cumulative effect of CVCE depends upon the mass of material involved in the explosion and the explosion pressure.

##### (1) Ethylene storage: scenario 1

An excessive pressure development in ethylene vessel leads to CVCE. The cloud generated by CVCE on ignition produces a fireball.

##### (2) Propylene oxide storage: scenario 2

An instantaneous release of propylene oxide under high pressure (comparatively lower than the one that caused CVCE), leads to BLEVE and, as the chemical is highly flammable, the released cloud on meeting an ignition source turns into a fireball.

##### (3) Propylene storage: scenario 3

Propylene is a highly flammable chemical having a low autoignition temperature. A high pressure build-up either due to autoignition or sudden boil-up of liquid in the vessel results in a CVCE. The released unburned cloud of chemical on ignition becomes a fireball.

##### (4) Propylene dichloride storage: scenario 4

An instantaneous release of propylene dichloride either through a vent valve or through any other accidental opening causes the flammable vapor cloud formation which on ignition leads to a flash fire.

##### (5) Ethylene oxide storage: scenario 5

An excessive pressure development in the storage vessel of ethylene oxide (under high pressure and temperature) leads to CVCE. The vapor cloud generated by CVCE gets ignited and turns into a fireball.

##### (6) Propylene glycol storage: scenario 6

Propylene glycol is a flammable chemical stored in liquefied state at moderate conditions of temperature and pressure. The release of the chemical on meeting an ignition source turns into a pool fire.

##### (7) Glycerin storage: scenario 7

The accident scenario for glycerin is visualized as continuous release of glycerin, which on ignition leads to pool fire.

##### (8) Chlorine storage: scenario 8

Chlorine is a non-flammable toxic gas, which is stored under high pressure in a liquefied state. A sudden release of pressure causes a rupture in the tank and generates a BLEVE followed by dispersion of toxic gas.

These scenarios have been processed for damage estimation through MAXCRED. A brief note on the damage-effect cal-

**Table 5. The output of MAXCRED for ethylene storage vessel (scenario 1)**

MAXCRED	
F. I. Khan & S. A. Abbasi, Pondicherry-605 014	
Parameters	Values
Results of MAXCRED simulation for scenario -CVCE	
accident followed by fire ball	
Distance from accident epicenter	(m) : 200
<u>Explosion : CVCE</u>	
Total energy released	(kJ) : 7.2e+11
Peak overpressure	(kPa) : 600.0
Variation of overpressure in air	(kPa/s) : 598.8
Shock velocity of air	(m/s) : 740.0
Duration of shock wave	(ms) : 2916
<u>Missile characteristics</u>	
Initial velocity	(m/s) : 787.5
Kinetic energy of fragment	(kJ) : 1.25e+09
Fragment velocity at study point	(m/s) : 501.2
Penetration ability at study point (based on empirical models)	
Concrete structure	(m) : .217
Brick structure	(m) : .248
Steel structure	(m) : .085
<u>Fire ball</u>	
Radius of fire ball	(m) : 306.4
Duration of fire ball	(s) : 125.2
Energy released by fire ball	(kJ) : 2.5e+09
Radiation heat flux	(kJ/sq.m) : 2435.3

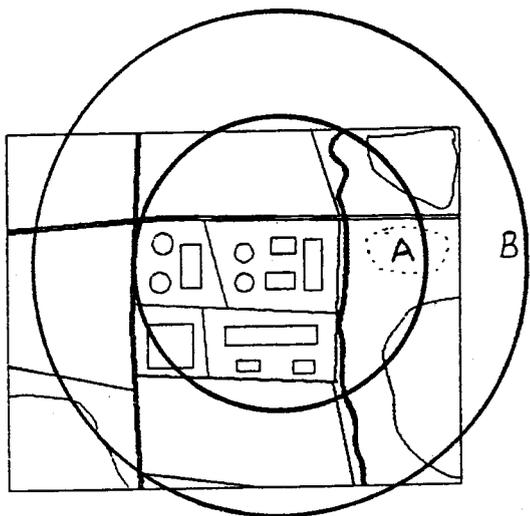


Fig. 4. Risk contours for scenario 1 indicating the impact area with 50 % probability of damage/lethality due to heat load (A) and shock wave (B).

ulation models used for the detailed study is presented below.

## 2. Hazard and Risk Quantification

The confined vapor cloud explosion in an ethylene tank as per scenario 1 would generate severe shock waves and missiles effects (Table 5). The damage potential due to these shock waves and the missiles is observed over a wide area. The released ethylene from the vessel would form a vapor-air mixture which on ignition would form a fireball. A lethal heat load would be observed over an area of ~200 m radius due to the fireball.

To estimate the risk factors (over the impact area), the probability of occurrence of each scenario (accidental events) has been adopted from literature [Contini et al., 1991; Lees, 1980; Reliability Directorate, 1992; European Community, 1992]. Fig. 4 presents the risk contours of different effects over the site of the accident as per scenario 1. Risk contours for a shock wave with 50 % probability of causing fatality is observed over an area of ~1,100 m radius. The risk contour for heat radiation effects with 50 % probability of lethality is observed over an area of ~700 m radius.

The output of MAXCRED for *scenario 2* is presented in Table 6. This scenario (BLEVE followed by a fireball) would cause extensive damage. The risk contours are shown in Fig. 5. It is clear from the figure that a damage-causing shock wave would occur over an area of ~700 m radius while heat radiation effects of 50 % lethality would occur over an area of ~450 m radius.

As per *scenario 3*, CVCE would generate shock waves as well as missiles. In addition there would be secondary impact of the released material getting ignited and forming a fireball, thereby generating additional heat load. The output of MAXCRED for this scenario is presented in Table 7. *Scenario 4* for the release of the propylene dichloride reveals the likely buildup of comparatively negligible overpressure (Table 8). Yet the lethal heat load impact would go up to and beyond a radius of ~200 m. Figs. 6 and 7 present the risk contours for different adverse impacts of *scenarios 3* and 4. It

Table 6. MAXCRED output for an accident scenario in propylene oxide storage vessel (scenario 2)

MAXCRED	
F. I. Khan & S. A. Abbasi, Pondicherry- 605 014	
Parameters	Values
Results of MAXCRED simulation for accident scenario-CVCE followed by fire ball	
Distance from accident epicenter	(m): 200
Explosion : BLEVE	
Energy released during explosion	(kJ): 2.4e+08
Peak over pressure	(kPa): 238.4
Variation of over pressure in air	(kPa/s): 135.5
Shock velocity of air	(m/s): 434.9
Duration of shock wave	(ms): 1345
Missile characteristics	
Initial velocity of fragment	(m/s): 338.7
Kinetic energy of fragment	(kJ): 3.5e+06
Fragment velocity at study point	(m/s): 207.3
Penetration ability at study point (based on empirical equations)	
Concrete structure	(m): 0.071
Brick structure	(m): 0.113
Steel structure	(m): 0.007
Fire : Fire ball	
Radius of the fire ball	(m): 154.178947
Duration of the fire ball	(s): 85.134566
Energy released by fire ball	(kJ): 7.6e+07
Radiation heat flux	(kJ/sq.m): 172.8

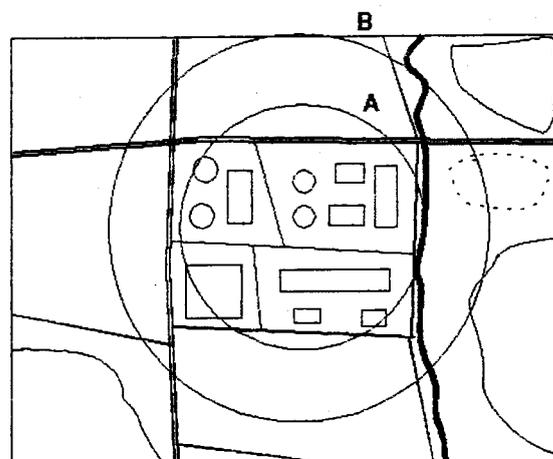


Fig. 5. Risk contours for scenario 2 indicating the impact area with 50 % probability of damage/lethality due to heat load (A) and shock wave (B).

is revealed by Fig. 6 that risk contours for damage-causing shock waves cover an area of ~600 m radius, while the risk contours for heat load effects extend up to an area of ~400 m radius. Thus an area of ~400 m radius is under great threat due to various damaging effects (shock waves, and heat load). The risk contours for *scenario 4* due to heat load would, however, be limited to ~300 m radius.

Table 9 presents the summary of calculations (output of MAXCRED) for *scenario 5*. The missiles generated by CVCE may hit nearby targets and can lead to secondary explosions or toxic releases. The vapor cloud generated by CVCE on ig-

**Table 7. The output of MAXCRED for propylene storage vessel (scenario 3)**

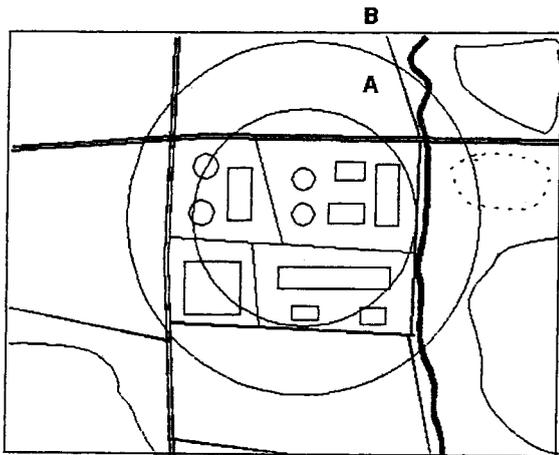
MAXCRED  
F. I. Khan & S. A. Abbasi, Pondicherry- 605 014

Parameters	Values
<b>Results of MAXCRED simulation for accident scenario-CVCE followed by fire ball</b>	
Distance from accident epicenter	(m) : 200
<b>Explosion : CVCE</b>	
Energy released during explosion	(kJ) : 1.01e+11
Peak overpressure	(kPa) : 273.6
Variation of overpressure in air	(kPa/s) : 271.4
Shock velocity of air	(m/s) : 555.0
Duration of shock wave	(s) : 2141
<b>Missile characteristics</b>	
Initial velocity of fragment	(m/s) : 586.9
Kinetic energy of fragment	(kJ) : 3.8e+07
Fragment velocity at study point	(m/s) : 334.5
Penetration ability at study point (based on the empirical equations)	
Concrete structure	(m) : 0.105
Brick structure	(m) : 0.182
Steel structure	(m) : 0.012
<b>Fire : Fire ball</b>	
Radius of fire ball	(m) : 278.4
Duration of fire ball	(s) : 141.8
Energy released by fire ball	(kJ) : 1.2e+09
Radiation heat flux	(kJ/sq.m) : 1190.5

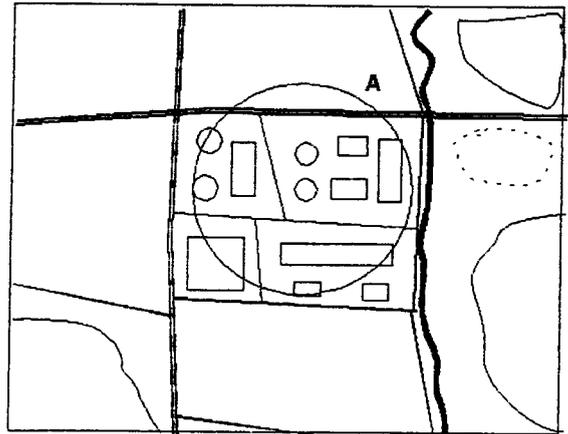
**Table 8. MAXCRED output for an accident in propylene dichloride storage vessel (scenario 4)**

MAXCRED  
F. I. Khan & S. A. Abbasi, Pondicherry-605 014

Parameters	Values
<b>Results of MAXCRED simulation for accident scenario-flash fire</b>	
Distance from accident epicenter	(m) : 200
<b>Fire : Flash fire</b>	
Volume of vapor cloud	(cub.m) : 11629.2
Duration of fire	(sec) : 3876.3
Radiation heat flux	(kJ/sq.m) : 141.9



**Fig. 6. Risk contours for scenario 3 indication the impact area with 50 % probability of damage/lethality due to heat load (A) and shock wave (B).**



**Fig. 7. Risk contours for scenario 4 indicating the impact area with 50 % probability of damage/lethality due to heat load (A).**

**Table 9. MAXCRED output for an accident in ethylene oxide storage vessel (scenario 5)**

MAXCRED  
F. I. Khan & S. A. Abbasi, Pondicherry-605 014

Parameters	Values
<b>Results of MAXCRED simulation for accident scenario-CVCE followed by fire ball</b>	
Distance from accident epicenter	(m) : 200
<b>Explosion : CVCE</b>	
Total energy released	(kJ) : 3.87e+11
Peak over pressure	(kPa) : 446.6
Variation of over pressure in air	(kPa/s) : 443.5
Shock velocity of air	(m/s) : 695.1
Duration of shock wave	(ms) : 2450
<b>Missile characteristics</b>	
Initial velocity	(m/s) : 647.4
Kinetic energy of fragment	(kJ) : 4.0e+08
Fragment velocity at study point	(m/s) : 415.4
Penetration ability at study point (based on empirical equations)	
Concrete structure	(kJ) : 0.137
Brick structure	(m) : 0.203
Steel structure	(m) : 0.043
<b>Fire : Fire ball</b>	
Radius of the fire ball	(m) : 289.4
Duration of the fire ball	(s) : 133.5
Energy released by fire ball	(kJ) : 1.35e+09
Radiation heat flux	(kJ/sq.m) : 1211.4

nitration may cause a fireball and hence severe heat radiation effects. The shock wave generated due to CVCE would be highly injurious and could also cause second order accidents by seriously damaging other vessels. It has been estimated that shock waves with 50 % probability of causing injury would be observed over an area of ~500 m radius. The heat radiation effect with 50 % probability of lethality would encompass an area of ~300 m radius and missile effects with 50 % chances of damage would reach across an area of ~750 m radius. The risk contours for various events are plotted in Fig. 8. Damage causing shock waves at 50 % probability would

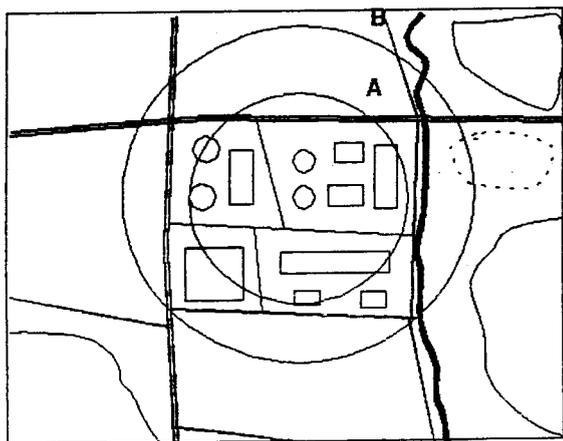


Fig. 8. Risk contours for scenario 5 indicating the impact area with 50 % probability of damage/lethality due to heat load (A) and shock wave (B).

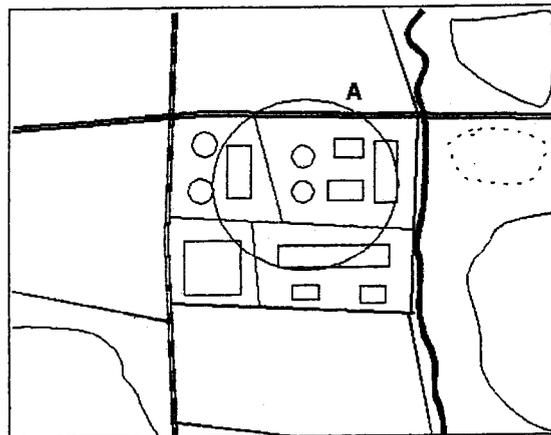


Fig. 9. Risk contours for scenario 6 indicating the impact area with 50 % probability of damage/lethality due to heat load (A).

Table 10. MAXCRED output for an accident in propylene glycol storage vessel (scenario 6)

MAXCRED

F. I. Khan & S. A. Abbasi, Pondicherry-605 014

Parameters	Values
Results of MAXCRED simulation for accident scenario-pool fire	
Distance from accident epicenter	(m): 200
Fire : Pool fire	
Instantaneous model	
Radius of the pool fire	(m): 5.0
Burning area	(sq.m): 78.5
Burning rate	(kg/s): 38.4
Heat flux	(kJ/sq.m): 1160.1

extend up to ~500 m, whereas the contour for heat load is limited to ~300 m.

A study of the consequences of *scenario 6* for the release of propylene glycol (pool fire) reveals that the likely damage due to this event in terms of shock waves, missiles, and heat load would be less intense than forecasted by *scenarios 1-5*. However, the MAXCRED output (Table 10) reveals that even at a distance of ~200 m from the accident epicenter, the intensity of the heat load would be severe enough to cause lethal damage. The risk contours for this *scenario* are presented in Fig. 9. The risk contours for 50 % damage causing



Fig. 10. Risk contours for scenario 7 indicating the impact area with 50 % probability of damage/lethality due to heat load (A).

heat load would cover an area of ~200 m radius.

The output of MAXCRED for *scenario 7* is presented in Table 11. Compared to any other accident scenario, the propensity of this to cause damage likely is less. The risk contour for 50 % probability of damage extends to only ~150 m (Fig. 10).

The accident scenario generated for the chlorine storage vessel is a sudden explosive release of chlorine as BLEVE followed by dispersion (*scenario 8*). The output of MAXCRED for this scenario is presented in Table 12. Lethal overpressure (shock waves) as well as lethal toxic effects would occur over an area of ~200 m radius. The risk contours for toxic load having potential to cause 50 % fatality would envelope a waste area of ~3,000 m radius (Fig. 11), while the risk contour for lethal damage causing shock waves would reach up to ~200 m.

Table 11. MAXCRED output for an accident in glycerin storage vessel (scenario 7)

MAXCRED

F. I. Khan & S. A. Abbasi, Pondicherry-605 014

Parameters	Values
Results of MAXCRED simulation for accident scenario -pool fire	
Distance from accident epicenter	(m): 200
Fire : Pool fire	
Continuous Model	
Burning area	(sq.m): 223540.7
Burning rate	(kg/s): 150484.8
Heat flux	(kJ/sq.m): 897.8

## SUMMARY AND CONCLUSIONS

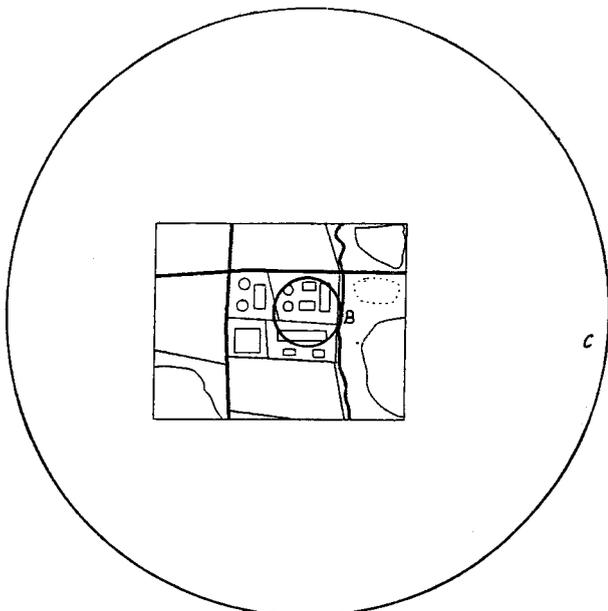
This paper presents a detailed risk analysis of storage units of a typical petrochemical industry conducted using the

**Table 12. The output of MAXCRED for chlorine storage vessel (scenario 8)**

## MAXCRED

F. I. Khan &amp; S. A. Abbasi, Pondicherry-605 014

Parameters	Values
Results of MAXCRED simulation for accident scenario	
-BLEVE followed by toxic dispersion	
Distance from accident epicenter	(m): 200
<u>Explosion : BLEVE</u>	
Total energy released	(kJ): 7.54e+06
Peak overpressure	(kPa): 137.3
Variation of overpressure in air	(kPa/s): 76.1
Shock velocity of air	(m/s): 338.1
Duration of shock wave	(ms): 975
<u>Missile characteristics</u>	
Initial velocity	(m/s): 225.4
Kinetic energy of fragment	(kJ): 2.2e+06
Fragment velocity at study point	(m/s): 85.9
Penetration ability at study point (based on empirical equations)	
Concrete structure	(m): 0.002
Brick structure	(m): 0.004
Steel structure	(m): 0.000
<u>Toxic release &amp; dispersion</u>	
Heavy gas dispersion characteristics	
<u>Box instantaneous: model</u>	
Concentration at distance 200	(kg/cu.m): 1.726654e-06
Concentration at cloud axis	(kg/cu.m): 1.461167e-02
Value of source height	(m): 8.0
<u>Puff characteristics:</u>	
Puff concentration at centre of cloud	(kg/cu.m): 8.169945e-04
Concentration at cloud edges	(kg/cu.m): 8.139317e-04
Distance along downwind	(m): 200.0
Dosage at study point	(kg/cu.m): 0.0536

**Fig. 11. Risk contours for scenario 8 indicating the impact area with 50 % probability of damage/lethality due to heat load (B) and toxic load (C).**

software MAXCRED. A total of eight different accident scenarios have been generated. These accident scenarios have been processed for detailed consequence analysis (hazard and risk quantification). The study reveals that *scenario 8* represents the worst possible disaster. It has the largest area-of-lethal-impact (lethal toxic concentration observed over ~3,000 m radius). If one takes into consideration the likelihood of a chain-of-accidents occurring (*domino effect*), then *scenario 1* would come out as worst, because more intense damaging effects *per unit* area due to simultaneous impacts of radiation, shock waves, and missile effects would eventually occur. As several other industries or units dealing with hazardous chemicals (flammable and toxic materials) are situated within striking distance of the impact area of this scenario, there will be secondary accidents which in turn may precipitate tertiary and higher order accidents. In summary, *scenario 8* is the worst as far as the largeness of its impact area is concerned, whereas *scenario 1* is the worst in terms of its potentiality for causing cascading (*domino*) effects.

**Appendix-A****Probit models in-built in MAXCRED for damage radii calculations**

Explosions, fires and toxic dispersions eventually cause damage in four ways. The potential of these effects can be expressed in terms of probit functions [Khan and Abbasi, 1996; Contini et al., 1991; European Community, 1992], which relate percentage of the people affected in a bounded region due to a particular different event by a normal distribution function.

**1) Heat radiation effect**

The probit function for 100 % lethality for heat radiation is given as:

$$Pr = -36.38 + 2.56 \ln [t \cdot q^{4/3}]$$

The probit function for 2nd degree of burn

$$Pr = -43.14 + 3.0188 \ln [t \cdot q^{4/3}]$$

The probit function for 1st degree of burn

$$Pr = -39.83 + 3.0186 \ln [t \cdot q^{4/3}]$$

where  $q$  is defined as thermal load ( $\text{kW/m}^2$ );  $t$  is time of exposure (s); and  $Pr$  is probit value.

**2) Toxic effect**

Lethality of a toxic load is expressed in terms of probit function as

$$Pr = a + b \ln (C^n \cdot t)$$

where  $a$ ,  $b$ ,  $n$  are constants;  $C$  is concentration in ppm, and  $t$  is time of exposure (s). The values of the contents for different gases are available in literature [Pitersen, 1990; Contini et al., 1991].

**3) Pressure and shock wave effect**

The probit equation for likelihood of death due to shock wave (lung rupture) is given by

$$Pr = -77.1 + 6.91 \ln P^o$$

For injury, the equation is

$$Pr = -15.6 + 1.93 \ln P^o$$

where  $P^o$  is peak overpressure ( $\text{N/m}^2$ )

**4) Missile effect**

The probit function for fatality in human beings or damage to vessels is expressed as:

$$Pr = -17.56 + 5.30 \ln S$$

where, S is the kinetic energy of the missile (J)

The probit function that relates fatality in human beings or damage to vessel due to missile velocity is expressed as:

$$Pr = -13.19 + 10.54 \ln V$$

where, V is fragment velocity (m/s).

#### ACKNOWLEDGEMENT

Authors thank All India Council for Technical Education (AICTE), New Delhi, for instituting Computer-Aided Environmental Management Unit which helped this study.

#### REFERENCES

- Contini, S., Amendola, A. and Ziomas, I., "Benchmark Exercise on Major Hazard Analysis", Joint Research Centre, ISPRA (1991).
- European Community, "Council Direction on the Major Accident Hazardous of Certain Industrial Activities", Report No. 82/50/501 EEC, London (1992).
- Greenberg, H. R. and Crammer, J. J., "Risk Assessment and Management for Chemical Process Industries", Van Nostrand Reinhold, New York (1991).
- Kayes, P. J., "World Bank Manual of Industrial Hazard Assessment Techniques", (Technica Ltd., London) (1985).
- Khan, F. I. and Abbasi, S. A., "Accident Simulation in Chemical Process Industries using Software MAXCRED", *Indian Journal of Chemical Technology*, 3, 338 (1996).
- Khan, F. I. and Abbasi, S. A., "Anatomy of Industrial Accidents", Report No. CPCE/R&D 1/94, Pondicherry University, Pondicherry (1994).
- Khan, F. I. and Abbasi, S. A., "MAXCRED- A Software Package for Quantitative Risk Analysis", Report No. CPCE/R&D 5/94, Pondicherry University, Pondicherry (1996); Environmental software (in press).
- Khan, F. I. and Abbasi, S. A., "Major Accident Case Studies in Chemical Process Industries", *Chemical Engineering World*, September (1996).
- Khan, F. I. and Abbasi, S. A., "Risk Analysis: An Optimum Scheme for Hazard Identification and Assessment", Proceeding of XIXth National System Conference, Coimbatore (1995).
- Kletz, T. A., "What Went Wrong", Gulf Publication, London, (1986).
- Lees, F. P., "Loss Prevention in the Process Industries", Butterworths, London, 1 (1980).
- Lees, F. P., "Loss Prevention in the Process Industries: Failure and Event Data", Butterworths, London, 2 (1980).
- Pitersen, C. M., "Consequences of Accidental Release of Hazardous Material", *Journal of Loss Prevention Process Industries*, 3, 136 (1990).
- Reliability Directorate, "Failure Frequency of Hardware Components", Report No. 87-2981R.27/NVE, Reliability Directorate (1992).