TECHNIQUES FOR THE IDENTIFICATION AND ASSESSMENT OF MAJOR ACCIDENT HAZARDS

K. R. Davies*

The CIMAH regulations require a written report to demonstrate the safety of major hazard plants. Techniques such as check lists, safety audits, reviews against codes of practice and hazard and operability studies can be used to produce a qualitative hazard assessment. Where the hazards posed are severe then a quantitative assessment may be demanded. Under these circumstances reliability tools including fault tree analysis, Markov analysis, FMECA and simulation are likely to be useful. The paper gives examples of each of these techniques related to a small plant which is one section of a major hazard unit. It is concluded that the techniques can be extremely valuable provided the limitations posed by data availability can be overcome.

INTRODUCTION

The CIMAH regulations require certain manufacturers to prepare a written report to show that their 'activity' is being carried out safely. The regulations also require a description of the hazards which can arise during the 'activity' together with a statement of the controls exercised in preventing the hazards being realised or limiting their consequences.

The regulations apply to both existing and new plants involving chemicals in the listings appended to the regulations. For many existing plants, the preparation of a 'safety case', as the written report has been termed, may be a simple qualitative exercise. This qualitative approach is likely to be acceptable for plants handling chemicals at the lower end of the spectrum of those deemed major hazards, particularly if processing is at ambient temperature and pressure.

For more complex units operating with higher risk chemicals it is envisaged, although not stated in the regulations, that a degree of quantification may be required. This quantified approach is also likely to be necessary for any new plant, particularly on a 'green field' site, or where risks are to be significantly intensified. The end result of the safety case must be a review of the risks to the general public and the environment from the activity, against criteria of acceptable risk. This allows decisions to be made as to whether the plant requires any improvements to reduce risk levels.

^{*} The Associated Octel Company Limited.

The assessment of the risk posed by a piece of plant rests largely on the quantification of the reliability of the equipment and its operators. The earliest impetus in quantification of reliability came from the field of air travel (Ref. 1). The 1950's saw the spread of reliability techniques into the nuclear and defence fields. The 1960's saw the considerable effort expended in space in ensuring the reliability of the Mercury and Gemini programmes, while in the early 1970's the extensive risk study by the US Atomic Energy Commission into Reactor safety "Wash 1400" (Ref. 2) was a landmark in reliability assessment development. From the late 1960's the process industry in the UK has been using reliability techniques to review the hazards posed by its plants (Ref. 3).

This paper therefore does not present new techniques but looks afresh at the application of these well-tried techniques to a major hazard plant and in particular the special problems involved in their use on a process plant.

In order to illustrate the use of the techniques an example plant has been used. It is a small chlorine recovery unit operating within a mercury cell facility.

THE EXAMPLE PLANT

The chlorine recovery plant is an auxiliary to the chlorine liquefaction units and operates to separate gaseous impurities from chlorine gas to give improved liquefaction efficiency.

The tail gases vented from liquefaction together with gases from stock tanks and rail tank vents are first compressed to 100 psig. The gases at this stage contain 20-50% v/v chlorine. The compressed gas is then cooled and subsequently refrigerated. This causes partial condensation of chlorine if the inlet concentration is high and at the outlet from the condenser the gas concentration is reduced to approximately 25% v/v.

The chilled gases then pass up an absorption column where the chlorine is virtually completely absorbed in chilled carbon tetrachloride. The absorber is packed with 2" pall rings and runs at 90 psig under a pressure control valve on the vent line.

Chlorine is stripped from the carbon tetrachloride in a second column and carbon tetrachloride is then recycled to the absorber after being rechilled.

CHEMICAL HAZARD IDENTIFICATION

The first stage in any hazard study is a review of the materials involved. If the study is to relate to the CIMAH regulations then the plant inventory needs to be compared with the chemicals listed in the regulations. If the chemicals are listed then is the plant inventory above the critical inventory? Table 1 shows a listing of some of the materials that will be found on a typical mercury cell plant.

Table 1

Chlorine Hydrogen Sodium Hydroxide Sodium Chloride Mercury Brine Additives Sodium Hypochlorite Carbon Tetrachloride Water

Nitrogen Trichloride Chlorine Hydrate

Having listed the chemicals and their inventories the next step is to establish their properties. This seems at first thought a simple statement, but, the task of determining all the relevant properties is extremely complex and time consuming and for an uncommon material can be extremely expensive. If a critical property is not determined or is incorrectly determined then any subsequent study may be worthless. Properties required include, physical, chemical, corrosion, thermodynamic, toxicological and combustion.

Table 2 contains a listing of some of the properties required for chlorine.

	Tak	ole 2
Chlori	ne	Properties

Molecular Weight	= 70.91
Boiling Point @ 1 atm	= 239.1° K
Freezing Point	= 172° K
Critical Temp.	= 417° K
Critical Press.	= 7710.83 kPa
Specific Gravity	= 1.424 @ 15°C (liquid)
Surface Tension	= 26.55 dynes/cm @ - 35.3°C
Ratio of Specific heats	= 1.327
Latent Heat of Vaporisatio	m = 287.75 kJ/kg

Chlorine: Long term exposure limit (8 hrs TWA) = 1 ppm Short term exposure limited (10 min TWA) = 3 ppm IDLH limit (NIOSH) = 25 ppm

Ref. 5, 6, 7.

Chlorine is a good example of a common material, the properties of which are relatively well known, but which has pitfalls which can catch all but the most cautious, for example the corrosion properties of chlorine.

From Table 3 the corrosive nature of chlorine can be seen to vary considerably with its moisture content. Special care is therefore clearly needed in specifying the material of construction for a chlorine unit and also in ensuring that the operating conditions remain unchanged during the operating life.

In the example plant the material of construction is mild steel and there are driers installed in the inlet gas lines. Operating instructions include statements on drying procedures for sections of plant before they are returned to duty.

Table 3 Corrosion Properties

Titanium

			Conc	Temp	Reaction
Chlorine o	gas	(wet)	>0.7% water >0.95% water >1.5% water	Room 140°C 200°C	No Reaction No Reaction No Reaction
Chlorine o	gas	(Dry)	<0.005% Water	Room	Ignition
Steel					
Chlorine o	gas	dry wet		Room 30°C-80°0	No Reaction C Some Reaction

Liquid Chlorine dry Room No Reaction

(Ref. 4)

Not only do the primary materials require consideration but also possible secondary materials in this case listed in Table 1 column 3. Special care needs to be taken to ensure that nitrogen trichloride, which is capable of spontaneous detonation, is not allowed to concentrate in any part of the liquid chlorine system. All of these properties need to be recorded and easily recoverable to use in producing a safety case. Where gaps exist in the knowledge then laboratory work will be required. Only when the properties are properly determined and recorded can the next stage be approached, that of process hazard identification. An unknown hazard cannot be identified!!!

PROCESS HAZARD IDENTIFICATION

A number of techniques exist for identifying hazards. These include: Hazard and Operability Studies, Safety Audit, Check Lists, Review against Codes of Practice.

These techniques are very dependent on the people who use them. The hazard which is not identified cannot be protected against. HAZOP is very much a team affair. A group is gathered together to represent the most useful disciplines for the plant under consideration and under the leadership of a neutral chairman they are led through the P & I diagrams by a questioning technique looking for deviations from the normal which may cause problems. (Ref 8). This approach is normally applied to new plants but can be used on those existing equally well.

Safety Audit is again a team approach. Usually an agreed number of specific areas of the plant are examined by a team looking in great detail. This approach can only be used on existing plants but is particularly useful from the operations view point. (Ref 9).

Check lists can be used either individually or by a team. They can only be as good as the person who draws up the original check list, although it has to be said that many very good check lists are now available and they can be of a great deal of help to the less experienced person. (Ref 10). Codes of practice can also be particularly useful. Many industries now produce specific codes of practice to cover particular operations. There are also HSE guidance notes and codes and British Standards. (Ref. 11, 12, 13, 14). If one examines ones plant in relation to these codes and finds compatibility then this may be sufficient answer to HSE that the plant is constructed and designed in accordance with current codes of practice and that it includes the most up-to-date protective systems. If the plant does not meet the codes then discrepancies will indicate specific areas where improvement may be required.

When this step of process hazard identification is completed then the first part of the questions posed by the regulation can be answered i.e. a description of the hazards.

In order to answer the second part of the questions relating to hazard control and consequence limitation then a more detailed study of the hazards is required and it is at this point that reliability tools come into use. The most commonly used reliability tools are fault tree analysis, Markov analysis, and failure mode and effect analysis.

RELIABILITY ASSESSMENT TECHNIQUES

Fault Tree Analysis or Event Tree Analysis

Fault tree analysis was developed in the early 1960's to assist in the reliability study of the Minuteman Launch Programme.

A fault tree is simply a logical approach allowing the possible routes by which a hazard can occur to be studied. It may be used as a quantitative tool to predict a frequency for an event but may also be used as a qualitative tool, assisting the analyst to a detailed examination of the system. The basic structure of a fault tree is shown in fig. 1. [An event tree is very similar to a fault tree in construction except that construction is started from the basic event at the bottom and is built up to an end incident.] The problem is always that of complexity. Even a very simple plant, when analysed using fault tree analysis, will produce a system with many events and gates.

As an example of the use of the technique qualitatively, a very much simplified fault tree is shown for our example plant, in figure 2. The end event studied is a fire in the absorber column. This is clearly of concern since it can lead on to a major fire and potentially a chlorine release.

One specific path through the tree shows that a fire can be the result of a chlorine/steel reaction in the presence of moisture. This reaction can be initiated at 100°C in the presence of water and temperatures of 100°C are attainable within the column.

The fault tree was based on an actual incident on the plant and was used to improve the system and prevent a recurrence;remedial actions can easily be resolved from the fault tree. The water cooled heat exchanger was replaced by an air cooled exchanger and the carbon tetrachloride was monitored on a more frequent basis for water content.

Quantification of fault trees is achieved by assigning failure data or probability to each event on the tree. These data are then summed using

Boolean algebra to reach a probability that the top event can occur. Fault trees are particularly difficult to quantify for a chemical plant in that the data are difficult to obtain. If the fault tree for our example plant is to be examined quantitatively we find that this particular type of unit is not common so generic data for such a unit are almost impossible to obtain. Clearly, however, it is possible to examine the effects of the improvements that can be made if some tentative estimates of failures are considered. Figure 3 shows the effects before and after improvements based on best estimates.

It must be realised that fault trees are not a panacea for all ills. They are only as good as the analyst and even more important when treated quantitatively they are only as good as the data.

For a fault tree of any size computer assistance is invaluable since it can resolve the minimal number of cut sets (set of primary faults needed to reach the top event). It can also be particularly useful for sensitivity analysis where there is doubt about the data used in any particular part of the tree.

Attempts are being made to produce computer programmes which will generate fault trees automatically based on P & I diagrams (Ref. 15, 16 and 17).

Markov Analysis

A fault tree normally assumes that basic events are independent. The only exceptions to this are the case of common cause failures and standby redundant systems. These cases have to be carefully handled. Markov analysis can be used to provide a system unavailability for substitution into the tree quantification.

Taken at its simplest level the Markov diagram for a single component is shown in Fig. 4.

The figure shows the graphical representation of the equipment which has a failure rate of and a maintenance rate of u.

The probability that the equipment is in the working condition at time t + dt can be expressed mathematically as:-

 $Pw (t + dt) = Pw(t) - \lambda dt Pw(t) + \mu dt P_F(t)$ $\frac{d Pw}{dt} = -\lambda Pw + \mu P_F$

which on integration gives:

$$Pw = \frac{1}{\lambda + \mu} (\mu + \lambda e^{-(\lambda + \mu)t})$$

If this is applied to the water in chlorine instrument on the inlet to this plant then its availability can be calculated.

If the failure rate = 6 per year and the repair time = 2 days:

The probability that the instrument will be in working order at any time Pw is 0.96.

Clearly this is a very simplistic statement. If a multi-component system is involved the Markov diagram gets extremely complicated.

The Markov model for the two absorber feed CTC pumps on the plant is shown in figure 5. In order to resolve an availability for such a system with redundancy a series of differential equations similar to that above need to be generated. Clearly for even a relatively simple system this quickly involves complex mathematics and a computer programme is advisable.

Failure Mode, Effects and Criticality Analysis (FMECA)

If a detailed study of all the possible failure modes of a piece of equipment or number of pieces is required then failure mode effect and criticality analysis is a technique that allows this depth of study.

The technique consists of examining the possibility of a component failing to function as specified, examining in detail the manner of potential failure and the cause of the failure. This information is then used to evaluate the effect of this failure on the surrounding plant or equipment. An index can be applied to the effect of the failure to indicate its degree of importance. The final step of the analysis is to review the items with the highest index of criticality and recommend design changes or precautions which limit the effect of the failure.

The technique is essentially very simple, but, it is important to organise the data in a readily presentable form. A typical FMECA is shown in Table 4 based on our example plant.

	Item C.T.C. Absorber Feed Pump							
	Sub Part	Failure Mode	Failure Cause	Criticality	Improvement			
1.	Pump Body	Overheats	Pump against closed head	Н	Temp Trips			
		Leaks	Overpressure/ Corrosion	I	Routine Insp.			
2.	Pump Seal	Overheat	Run Dry	Н	Seal temp ind.			
		Leak	Wear	I	Inspection			
		Sieze	Excessive Wear	I	Inspection			
3.	Pump Motor	Overspeed	Control Failure	н	Redundancy			
		Stall	Winding Failure	I	Redundancy			
		Run Slow	Pump Seizing	I	Redundancy			
		Burn Out	Pump Seized	I	Redundancy			
		Stopped	Contactor problems	I	Redundancy			
4.	Pump Impeller	Wear	Not inspected	N	Routine Insp.			
	Shaft & Bearing	Sieze	Bearing Failure	I	Routine Insp.			
		1	1	1				

- H Hazardous
- 1 Inconvenient
- N Negligible

Table 4 Typical FMECA Sheet.

Simulation Techniques

When a number of redundancy paths are available for a system and there is interaction between pieces of equipment with regard to maintenance then the most appropriate technique for examining reliability of the overall system is simulation. The technique is most often referred to as Monte Carlo simulation because of its use of random numbers. The technique is to define the system, its failure and repair characteristics, and any restraints. The operation of the plant is then considered over a short time interval. The probability that the first piece of equipment in the system will fail is calculated and this is compared with a randomly generated number in the range 0-1: if the random number is less than the failure probability then the equipment is assumed to have failed. This is repeated for the whole system to constitute a single time step. This is repeated for a number of incremental time steps up to the whole time interval that we wish to cover. This represents a single trial. The whole approach then has to be repeated many times until a relatively constant ratio of successful trials to failures is reached.

The approach is most easily understood by an extremely simple example for which one would not normally use the technique.

A single component such as a trip switch on a pump motor is considered having a failure rate of 0.1/year and the period of interest is 1 year.

Then the probability of failure (q) can be calculated for each month incrementally.

i.e. q₁ = 0.1 x 1/12

= .0083

for end much $2 = \frac{0.1 \times 2}{12} = .016$

Table 5 shows a 10 test series using a random number generator for the 12 month run of each test and shows whether the equipment succeeds or fails; in this series there are 5 successes and 5 failures, however, many more tests perhaps up to 100 would be required to reach a steady state failure figure.

MON	TH	1	2	3	4	5	6	7	8	9	10	11	12	
Failu Prob- abili	ure - ity	.008	.016	.025	.033	.041	•050	.058	.066	.074	.083	.091	.100	Success or failure
TEST	1	.035	.937	.869	.350	.513	. 890	.099	.642	.939	.959	.111	.201	s
TEST	2	.724	.464	.254	.046	.626	.706	. 941	. 993	.003	.164	.047	.487	F
TEST	3	.340	. 952	.543	.674	.006	. 520	. 389	.734	.276	.608	.678	.457	F
TEST	4	.593	.451	.019	.071	.084	.228	.187	.322	.326	.770	.004	.797	F
TEST	5	.365	.506	.488	.512	.974	.677	.238	.728	.175	.777	.078	.038	F
TEST	6	.003	.265	.946	. 692	.521	.514	.032	.176	.087	.016	.177	.038	F
TEST	7	.867	.835	.503	. 967	. 602	.306	.312	.126	.625	. 994	.221	.720	s
TEST	8	.125	.896	. 558	.834	. 663	. 891	. 996	.505	. 939	.443	.450	. 550	s
TEST	9	.803	.561	.215	. 662	.528	. 892	. 354	.197	.319	.683	.342	.295	s
TEST	10	.081	.479	.959	.686	.437	.076	. 423	.774	. 988	.230	.787	.461	S

Table 5. Monte Carlo Simulation of Failure of Pump Motor Trip Switch

Typical applications of simulation include situations such as the chlorine compression on our example plant which uses four compressors of two different types. Normally the two newer compressors are used in parallel and the remaining pair act as off-line spares. Because of limitations of the older compressor the plant cannot operate at full capacity with the two older compressors on line. In addition because of space limitations only one compressor can be serviced at a time. This type of availability situation can only be handled using simulation techniques.

A further rather different chemical plant use of simulation techniques is on a plant such as our example where a variety of gas strengths and volumes may be input and the plant operating parameters have a number of variables. These can be studied using a Monte Carlo simulation technique to examine the operation of the system under varying loads.

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DATA AND ITS COLLECTION

All of the techniques discussed require information about the reliability of items of process equipment. In some cases this may require only simple failure frequency data, but with more advanced techniques the nature of the failure rate and the repair rate together with the total outage time may be required. Information is also likely to be needed on the mode of failure and the cause of failure.

These data are never easy to obtain. The figures quoted in this paper are based on plant experience using system failure data from abnormal occurrence records. Where component level data are used these are estimated based on the system figures.

Generic data are available from a number of sources. Perhaps the best of these sources is the data bank operated by Systems Reliability Services (SRS) which is a branch of the United Kingdom Atomic Energy Authority (UKAEA). Data from the data bank are available to associate members of SRS either directly via a computer link or indirectly through SRS staff.

There are also data available in the technical press (eg. ref. 18) however these data are more difficult to assemble. Generic data have to be treated with great care since they can only be properly applied to the specific situation in which they were collected.

A detailed assessment of possible leak sources and the potential leak frequency was carried out in the early 1970's resulting in a number of recommendations for improvements. While the improvements resulted in a substantial reduction in the leakage frequency the original target figures were not reached. A second study revealed that the generic figures used for the earlier study were in some cases optimistic for the environment of a chlorine unit. A second phase of review based on plant historical data has resulted in further improvements and has reduced emissions to the pre-defined target levels.

The best data will always be those which are collected on the plant under consideration. Collecting such data will always be an expensive exercise. One reported large study in Italy used 15,000 man hours alone in setting up the collection scheme.

Where costs can be shared however, significant cost saving can be made. Several such collection exercises have been carried out by Engineering students working for SRS on Associated Octel's Plants.

The compressors on the example plant were examined as one small part of the data collection exercise. The two older compressors were found to be relatively unreliable in a general study and were examined in greater detail over a three year history.

The utilisation factor = 11% Failure rate/calendar year = 8.83 Failure rate/operating year = 76.37

The breakdown of the failure modes and causes is shown in Table 6.

Failure Mode/Cause	No. of Failures	% of Total Failures
Degradation/Component	4	15.37
Degradation/Liquid Ingress	2	7.69
External Leak/Component	7	26.92
Fractured/Component	1	3.85
Fractured/Freezing	1	3.85
Instrument/Component	3	11.54
Misaligned/Component	3	11.54
Noisy/Component	2	7.69
Overheated/Undiagnosed	1	3.85
Seized/Undiagnosed	1	3.85
Slipping/Component	1	3.85
	26	100

Table 6. Breakdown of Failure Modes and Causes for a Chlorine Compressor

These data were extracted from a variety of sources by a student mechanical engineer from Liverpool Polytechnic. Typical sources included daily process log sheets, process foreman's reports, maintenance foreman's reports, defect notes, safety notes, stores withdrawal records, personal note books belonging to operators and works monthly records. Where possible attempts were made to corroborate information by using more than one source.

The end result is a series of history sheets. A typical sheet is included as Table 7. These event data can be processed to give failure data for application by the analyst. Table 7. History Data Sheet

ITEM DESCRIPTION:- Snift Gas Compressors LOCATION:- Chlorine Works

Event No.	Event Date	Equip. No.	Failure Mode	Failure Cause	Outrage Time(hrs)	Operating Time(hrs)	Description of Event
012	25/4/82	4480/1	External	Component	96	40	The discharge valves were found to be badly pitted. The valve seats were repaired and the valves rejointed.
013	25/4/82	4480/2	Degraded	Component	: 432	536	The compressor was inefficient. The valves were overhauled and refitted. Compressor seized on test run due to contaminated oil. Piston found to be cracked. Piston, rings, rod, glands and valves all renewed.
014	30/4/82	4480/1	Seized	Undiag- nosed	96	8	Compressor seized and was freed. Oil found contami- nated. Oil changed also absorption vent valve which was passing.

In this case the compressors are used as stand-by equipment which clearly has an impact on their reliability. The study indicated possible reliability improvements by modifications to the valve systems. None of the failures listed however resulted in a chlorine release to atmosphere.

The difficulties of using generic data can be seen in Table 8 where generic compressor data from differing sources are compared with the on-plant data.

IChemE SYMPOSIUM SERIES No. 93

Source		Compressor	Medium	Pressure	Failure Rate per operating year		
SRS		Reciprocating	Cryogenic	100 psi	26		
SRS		Reciprocating	Air	100 psi	1.9		
ICI	(Heckle)	Reciprocating	Refrigerating	?	0.48		
AOC	(Plant)	Reciprocating	Chlorine	100 psi	76		

Table 8. Failure Data on Compressors

CONCLUSIONS

The introduction of major hazard legislation requires management to examine the hazards posed by their plant and to show that the safeguards that they have installed are adequate. A number of techniques which may assist in this task have been identified.

The chemical hazard properties of any materials being handled must first be established either through literature search or by experiment. The hazards posed by processing of the material can be identified by a number of techniques including check lists, safety audits, reviews of codes of practice, hazard and operability studies. In many cases the qualitative review of safety produced using such techniques will be sufficient to assure the authorities of the safety of the plant. In the case of the most hazardous plants it may be necessary to develop the assessment further using quantitative techniques.

The techniques for analysis used by the nuclear industries for many years including fault tree, Markov, failure mode, effect and criticality and Monte Carlo simulation can all be adapted for use in the process industries to quantify hazard frequencies.

The prime limitation of these quantitative techniques is the availability of data on the failure characteristics of process plant. Generic data are not readily available for many process items. Where such quantitative approaches are required, management would be well advised to identify what sources of plant data and experience are available. Action should then be taken to ensure that such data is recorded in an easily retrievable form to assist in quantitative hazard studies.

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FIGURE 1

LOGICAL CONSTRUCTION OF A FAULT TREE.





SECTION OF FAULT TREE BEFORE MODIFICATION.



FIGURE 3 SECTION OF FAULT TREE AFTER MODIFICATION.







 $\lambda_{A} \& \lambda_{B} = FAILURE RATE FROM WORKING STATE$ $\lambda_{SA} \& \lambda_{SB} = FAILURE RATE FROM STANDBY STATE$ $\mu_{A} \& \mu_{B} = REPAIR RATE$

