Risk Analysis and Emergency Management of Ammonia Installations

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Quantitative Risk Assessment (QRA) is increasingly used, worldwide, for evaluating the risk of handling hazardous materials in the process industry and for land-use planning purposes. Techniques and methods are also used in the development of emergency management tools.
Much experience, also related to possible ammonia releases, has been achieved in this field. Several studies concerning the risk of handling, storage and transport of ammonia have been carried out. This paper describes some state-of-the-art experience in the Netherlands.

INTRODUCTION

In 1982, the European Communities issued the 'Council Directive on the major accident hazards of certain industrial activities'. The direct inducement for this was the release of toxic dioxins from a pesticides factory in Seveso, Italy, in 1976. The said directive is therefore better known as the 'Post Seveso Directive' [1].

The implementation of the Directive in the Netherlands requires from the (about 80) notified industries the drafting of an external safety report, including a Quantitative Risk Assessment for major hazards [2]. Also for ammonia and fertilizer producing plants such investigations have been carried out.

Risk assessment is always carried out for smaller scale applications of ammonia, like cooling facilities in icecream, dairy products, fruit and vegetables stores and for ice-skating courts. Environmental licenses and regulations to prevent hazard, damage and nuisance, often require quantified hazard analysis.

The application of ammonia also requires a judgement from 'pressure vessel' regulations. Although these regulations were originally developed with regard to occupational safety, several installations which are located near populated areas, are also judged from external safety point of view. The need for a universal and simple evaluation of, often relatively old, existing installations resulted in the development of a general method for certification of ammonia cooling systems.

Quantitative Risk Assessment is a relatively new technique for determination of the acceptability of industrial activities in populated areas. The extended use of QRA's, for environmental licences, land-use planning and risk reduction, has led to the development of several standard methods and tools. They are also widely applied in emergency response planning for both on-site and off-site purposes.
Especially for ammonia, both for large and small scale application, experience has been built up in TNO in the past years. Several studies and consultancies were carried out, not only in the Netherlands but also abroad.

This paper aims to give an overview of these experiences, illustrated with some case studies.
Although much published research on ammonia releases is available, the uncertainties about the physical behaviour and the potential toxic impact of ammonia vapours still appear obvious. Also the knowledge and quantification of the influence of management and material factors on the reliability of technical systems in the chemical industry ought to be given increased attention, in order to include site-specific circumstances into risk-determining failure probabilities.
Industrial support in the enhancement of knowledge is vital.

QUANTITATIVE RISK ASSESSMENT: OBJECTIVES AND METHODS

General

Responsive industrial companies will always be engaged in improving the safety of their processes, in order to prevent incidents which may cause a serious threat to life and health of workers, to the environment or to material property. Both technical and procedural measures are taken and management and training are intensified in order to reduce the risk of potentially hazardous activities.

Authorities often take their responsibility with respect to people outside the companies and to the ecological environment, by setting environmental conditions to licences for the industry. Setting criteria to the risk of exposure to hazardous materials, due to accidental release of such material, is one of the targets the authorities can use in these conditions. Quantitative Risk Assessment (QRA) is one of the tools available to 'measure' the risk of industrial activities.

Quantitative Risk Assessment can be used for:
(1) Prioritizing possibilities for risk reduction.
(2) Prioritizing accident scenarios for which emergency preparedness planning should be considered;
(3) Land-use planning: where is extension of housing or industry possible and where should this be avoided?

Attributes of risk quantification

First we define the meaning of 'RISK' as:

*Risk is the **likelihood** of an **adverse outcome**.*

So, risk is determined by two factors: the adverse effects ('consequences') of an exposure to hazard and the probability or frequency that these consequences occur.

In a Quantitative Risk Assessment for hazardous materials (industry or transport), two criteria for risk are used [3]:
(1) Individual risk: the frequency per year (the measure of likelihood) of death of an individual due to an accident involving hazardous industry (the adverse outcome).
This measure is a function of the location in the surroundings of the industry, regardless whether actually people are living there. It presents the risk in an area.
(2) Societal risk: the cumulative frequency of a certain number of simultaneous deaths due to expected accidents in a specific industrial activity.
Here, the actual presence of people in the surroundings is taken into account.

Risk analysis for industrial companies can be carried out in several ways and with differing depths.
Very detailed system analyses can be carried out, for instance using Hazard and Operability (HazOp) studies or Fault Tree Analysis (FTA), for structured evaluation of the design of a process or for ruling out possible large scale incidents. FTA is a very well known technique in nuclear power plant design.

For an overall Quantitative Risk Assessment for industrial plants, however, generally the conceptual break approach is followed to identify and define accident scenarios. This approach means that for all selected installations system ruptures and leaks are identified which are considered credible. This credibility is based on engineering judgement and on accident casuistry from the past. The risk for the surroundings and the environment is calculated for all the identified scenarios, accounting for system reactions (detection and shut down systems), operator intervention, etc.

For the determination of the risk, several aspects have to be quantified. For the sake of comparability of studies, standard methods have been developed, to a large extend by TNO, which are applied now by many industrial and consultancy companies and authorities all over the world. We distinguish:
(1) *Physical effects* following upon a release of hazardous material: release rate, evaporation, dispersion, etc; the socalled Yellow Book [4] contains standard models for these physical effects.
(2) *Consequences* (damage, injury) due to the exposure of humans or constructions to the physical effects: fire, explosion, toxic effects; the vulnerability models for consequence assessments are given in the Green Book [5].
(3) The *probability* of each of the events and developments: accident frequency, failure probability of system reactions, weather distribution, probability of ignition, probability of the adverse effects, etc; methods for probability estimation are given in the socalled Red Book [6] and an overview of generic failure probabilities and reliability figures is compiled in the Probability Figures Book [7]. Casuistry and case histories, among others, can be derived from accident databanks like FACTS [8].

Much research has been put into development of models, consequence criteria and probability assessment in the last one or two decades. Several models however, do not have the capability to account for specific circumstances with regard to material behaviour and the physics of the environment. That is why more research is still going on [9, 10].

For probability assessment in QRA's, many data are based on generic failure frequencies, e.g. [11, 12, 13]. This implies that from case histories related to the experience time, statistical values for the expected accident frequency have been derived. It may be obvious that this approach gives only a few possibilities to include site-specific aspects and management factors like training, inspection and material selection. Further research in this field is also envisaged.

The uncertainties or unaccountable specific aspects have led to discussions between authorities and industry, with regard to the application of quantitative criteria for acceptability of risk which have been proposed for the Netherlands.
Several attempts have been made to quantify the uncertainties.

Dutch legislation on the Post Seveso Directive

The EC's Post Seveso Directive (1982) [1] has the following objectives, to be implemented in all member states:

(1) It prompts certain industries to draw up an External Safety Report (ESR) for those activities where, in the event of a major release of hazardous materials, serious threat to life of people and/or the environment could be caused.
(2) The report should contain information about the possible effects of incidents, in what way the probability of undesired events is limited and how mitigation/repression of consequences is assured.
(3) The Directive prompts the industry and the responsible authorities to give information to the community, about the potential hazards and on how people should act in the event of an incident.
(4) For the authorities there is the obligation to inform neighbouring countries in case the incident might also affect areas across the country border.

The installations which fall under the Post Seveso Directive (PSD) obligations are selected on the basis of the quantities of hazardous materials present.

In the Netherlands the PSD implementation has been brought under the jurisdiction of the 'Nuisance Act', which can demand for conditions to danger - or hindrance causing installations, in order to limit such adverse effects. A Nuisance Act licence is required, before such an installation may be taken into operation. The responsibility for control and maintenance of (compliance with) this Act and the specific conditions have been given to local authorities: community or province.
The External Safety Reports in the Netherlands require a Quantitative Risk Assessment to be carried out and included in the report. The results of such an analysis, to be presented in iso-risk contours and societal risk curves, are used by the responsible authorities for evaluation of the risk to the surroundings. Preliminary risk criteria have been set with respect to maximum tolerable risk in residential areas.

Approximately eighty companies in the Netherlands were obliged to submit an External Safety Report as per Post Seveso Directive. Four of these companies comprised of ammonia producing facilities and/or related fertilizer production.

Ammonia facilities are selected for the PSD obligation if the amount present in the installation exceeds 500 tons. According to the Dutch regulations, the Safety Report must concern all the activities within the notified installation; not only the ones where this quantity is present. The QRA however, may be restricted to the activities from which major hazard might be possible. A special system for sub-selection has been developed for that purpose [14, 15].

The proposed criteria for risk in residential areas in the Netherlands are [3]:

(1) Individual Risk: maximum tolerable 10^{-6}/year for new installations; 10^{-5} for existing ones.
The individual risk level of 10^{-8}/year is recognized as 'negligable', which should be strived for in all situations. If the risk is more than 10^{-8}/year, possibilities for risk reduction should be investigated or building new housing should be avoided.
(2) Societal Risk: the probability of ten simultaneous fatalities should not exceed 10^{-5}/year. N times as much fatalities should correspond with a lower probability by a factor N-square.

RISK STUDIES RELATED TO AMMONIA INSTALLATIONS

Examples of ammonia risk studies

The Department of Industrial Safety of TNO Environmental and Energy Research, has executed or contributed to several studies in which safety and risk of ammonia was involved. Below a non-exhaustive list is given:

— Gujarat State Fertilizers Company Ltd, Baroda, India. Maximum Credible Accident (MCA) Analysis for ammonia plants, storage and transport, Urea, Melamine, DAP, H_2SO_4, combustibles, Caprolactam, Nylon, etc.

— Hindustan Lever Ltd, Haldia, India.
MCA analysis, HazOp, Engineering Review and full Risk Analysis for Di-AmmoniumPhosphate plant and the related Ammonia storage and feed.

- Hydro Agri Sluiskil B.V., Sluiskil, The Netherlands. *)
  Quantitative Risk Analysis for the External Safety Report (Post Seveso Directive), for ammonia production, storage, pipeline transport and loading/unloading ship, road tanker and rail tanker; Urea, AmmoniumNitrate, Nitric Acid.

- Dutch Ministry of Transport and Public Works, The Netherlands.
  Transportation of Ammonia by inland waterway vessels, across the 'Van Starkenborghkanaal', in the north of the country.

- Rashtriya Chemicals and Fertilizers Ltd, Bombay, India.
  MCA analysis and (review of) emergency preparedness plan for ammonia production, storage, pipeline transport, road and rail tankers.

- European Communities. *)
  Benchmark Exercise on Major Industrial Hazards:
  A comparison of quantitative risk assessment methods and results among 11 European organisations.
  The study object comprised a sea-side atmospheric ammonia storage, including the loading/unloading activities and pipeline transport to a pressurized storage tank.
  Main aim was to gain more insight into the (sources of) uncertainties in risk analysis.

- Research into the efficiency of water spray curtains for the absorption of ammonia clouds upon a release (own TNO research programme). *)

- Several companies in the Netherlands, involved in processing of food and dairy products, where ammonia is applied as a cooling medium. *)
  Technical inspections and pressure vessel certification have been carried out by TNO. Also a general method for assaying these type of installations has been developed.

- A.B.C. Pvt. Ltd., Bombay, India.
  MCA-analysis and risk evaluation for the transportation of ammonia by inland waterway vessels, including the loading/ unloading activities, in the Cochin harbour area; and the environmental risk for fishery in rivers.

The subjects indicated with an asterisk (*) are described in more detail in this paper.

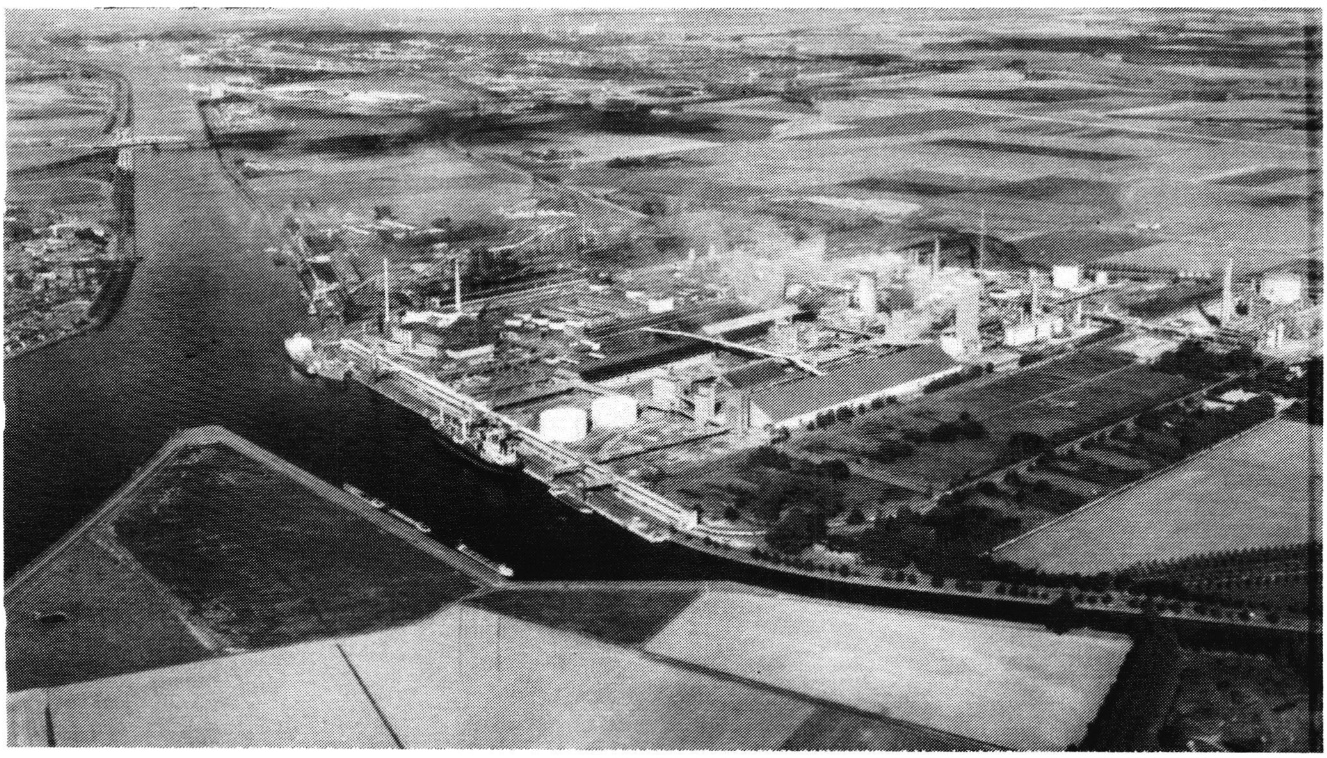

Figure 1 Birds-view of Hydro Agri Sluiskil
Sluiskil-town at opposite side of canal

A full quantitative risk analysis for an industrial plant

Description of the plant

The study concerned the facilities of Hydro Agri Sluiskil BV, which is a subsidiary of Norsk Hydro A/S.
Hydro Agri Sluiskil (H.A.S.) was founded about 60 years ago in Sluiskil, a small town in the south-western part of the Netherlands. The residential area is at a distance of about 300 m from the company's boundary, opposite a canal.

The main installations in the H.A.S. premises are:

- three ammonia plants
- two urea plants
- two ammoniumnitrate plants
- two nitric acid plants
- related storages and transfer systems.

The total capacity of the NH_3 synthesis plants is more than the required feed to the consumers: Urea, HNO_3 and NH_4NO_3. The excess NH_3 production is exported, both at pressurized conditions (road- and rail tankers and ship) and refrigerated (ship). Regarding the short distance between the ship's loading facilities and the town of Sluiskil and the related risk of the activity, limitations had been set in the environmental licence for the frequency of transshipment of pressurized ammonia to ship: maximum 200 hours per year.
For intermediate storage of ammonia, both for feed stock to plants and to export facilities, storage tanks were built:

(1) Three spherical tanks for pressurized ammonia, capacity 500 MT (2x) and 150 MT (1x).
(2) Two cylindrical tanks for refrigerated ammonia, capacity 10,000 MT and 20,000 MT.

For the transfer of ammonia all over the area, pipeline systems have been constructed with a total length of about 5 km. The largest pipelines are the ones from the refrigerated storages to the ship loadings docks, with diameters up to 500 mm (~ 20").

Approach in the QRA

Hydro Agri Sluiskil was selected for PSD notification on the basis of the quantity of ammonia present in the installation. For the QRA the following installations were selected [16]:

(1) Ammonia let-down vessel of the two largest NH_3-Synthesis Loops.
(2) Both atmospheric ammonia storage tanks.
(3) The two 500 MT spherical storages.
(4) Rail tanker loading.
(5) Ship loading, both for pressurized and for refrigerated ammonia.
(6) The complete pipeline transfer system.
(7) The Nitric-acid plants.

Accident scenarios were identified for these activities using the conceptional rupture approach. The following adoptions were made:

a. process- and storage vessels:
   - tank rupture, characterized as a full bore break of the largest connection;
   - leakages in other connections, probability related to the pipeline length;
   - catastrophic rupture of concrete containment of atmospheric storages (very low probability);
b. (un)loading facilities for ships and rail tankers:
   - rupture and leakages of the loading arms;
   - catastrophic rupture of tank lorry;
c. nitric acid plants, release of nitric oxydes:
   - major leakage in heat-exchangers of low pressure circuit;
   - major leakage in heat-exchangers of high pressure circuit;
d. ammonia transfer pipeline system:
   - full bore rupture, only for diam <= 6";
   - large leakage, hole area 10 % of pipe cross sectional area;
   - small leakage, hole area 1 % of pipe area.

Using the Event tree approach, for all scenarios the following system reactions were adopted:

1. Automatic shut-down, if pertinent, successful after 1 minute; failure probability 0.01.
2. Operator intervention in case of large leak (> 5 kg/s):
   - successful after 2 minutes if leakage in own section, probability of failure (no early detection) 0.01;
   - successful after 5 minutes if leakage in other section (late detection), failure probability 0.01.
3. Operator intervention in case of small leak (< 5 kg/s):
   - successful after 2 minutes if leakage in own section, probability of failure (no early detection) 0.05;
   - successful after 5 minutes if leakage in other section (late detection), failure probability 0.05.
4. Availability of water curtains to reduce NH_3 cloud dispersion after 10 minutes (company's fire brigade), to 10% of the evaporated amount.

With regard to the source terms of ammonia dispersion, the following was adopted:

1. Release rate calculated as fully liquid outflow.
2. Evaporation rate equals the sum of
   - twice the flash-off potential (heat capacity between operation temperature and boiling temperature);
   - pool-evaporation due to heat from substrate;
   - pool-evaporation due to diffusion, for average pool temperature of -50°C.

The aspect of evaporation was a point of debate with the parties involved. Like in earlier discussions in the AIChE - ammonia committee [17], the question on how to assess the source terms of semi-refrigerated releases was raised.

Consensus was found by adopting the 'two-times-flash' approach. Eventually this approach was laid down in general recommendations for application of physical effect calculations for liquified gas releases in QRAs.
Some aspects of uncertainties about ammonia release source terms will be further discussed.

Results of the QRA

The total number of accident scenarios that were identified for the risk assessment for H.A.S., amounted about 900. This high number was mainly due to the transfer pipeline systems: these were divided in sections of about 100 m length with regard to possible leakage locations and related probabilities. For each leakage location the source term (evaporation) and the accident frequency (development) were determined.

Using TNO's software programs EFFECTS and RISKCURVES [18, 19], the following calculations were carried out:

- gas-concentration and exposure duration in the surroundings, as a function of distance;
- toxic load due to inhalation of ammonia or NO_2;
- probability of fatal injury due to the toxic load;
- probability of receiving this toxic load, accounting for the accident probability, the frequency distribution of weather conditions (atmospheric stability, wind velocity and wind direction);
- population distribution in an area of 6 km x 6 km around H.A.S..

The calculations resulted in:

1. Individual risk contours, for risk of 10^{-4} to 10^{-8} /yr.
2. Societal risk curve.

Both are given in Figure 2 and 3.

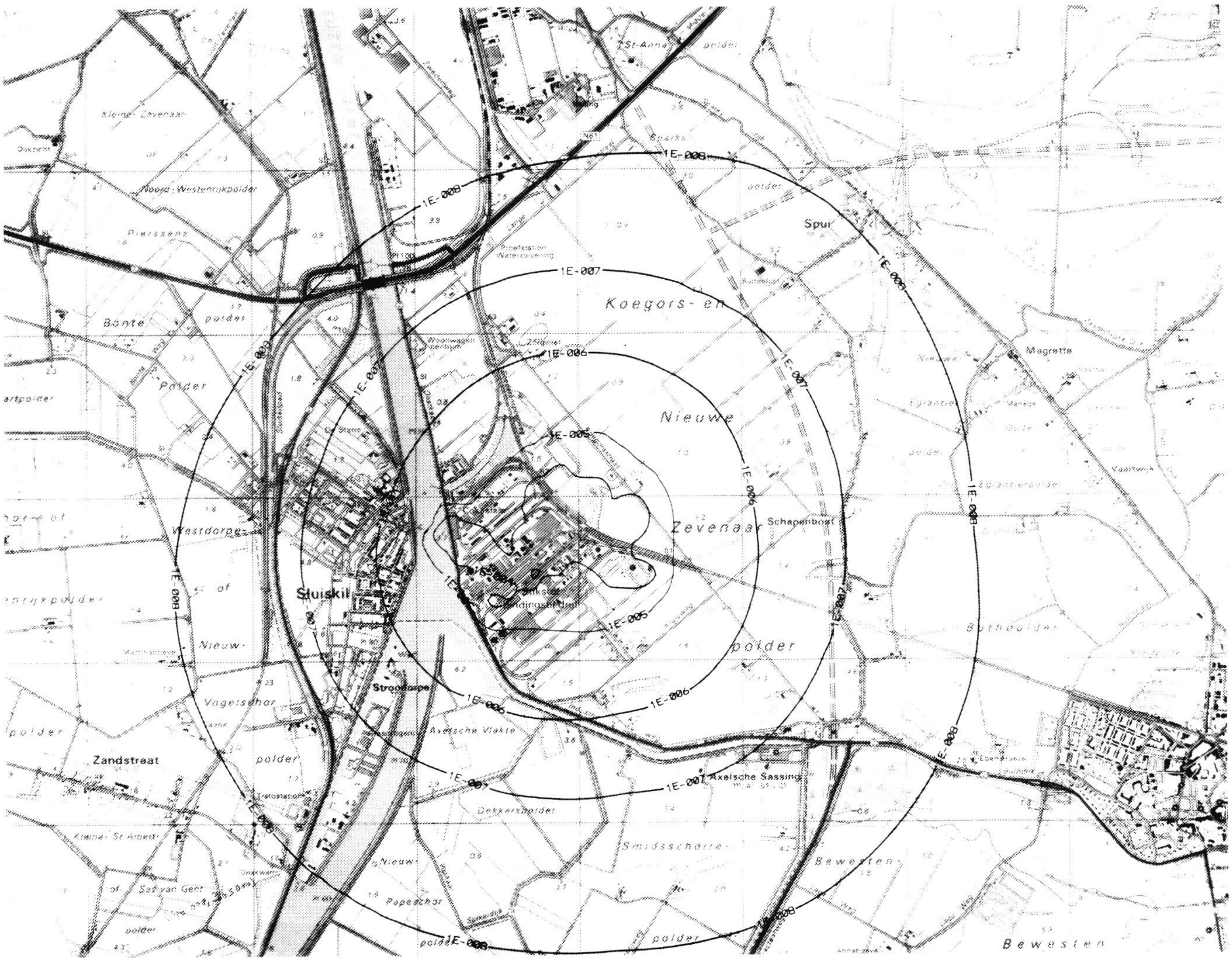

Figure 2 Individual risk contours, in [yr^{-1}], for Hydro Agri (Scale: 1 km ≙ 23 mm)

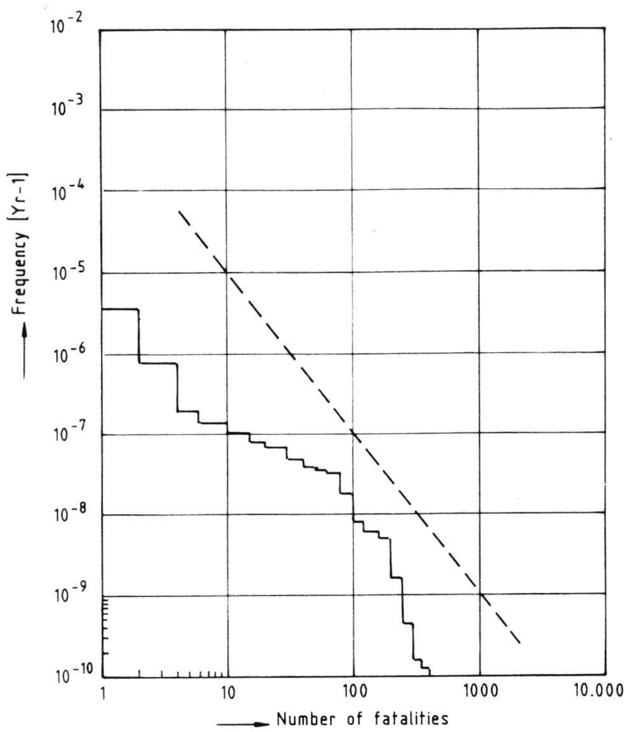

Figure 3 Societal risk curve for Hydro Agri

The Individual Risk contour of 10^{-6}, which is the upper target criterion for living areas in the Netherlands, appears to reach up to 200 m within the town area of Sluiskil. Although, according to [3], for existing installations a less stringent risk criterion could be adopted (10^{-5}/year), the local authorities initially considered that the calculated situation should be improved.
The Societal Risk curve shows that the expected frequency of 100 or more fatalities is less than 10^{-8}/yr, which is within the acceptable limits.

The fact that the individual risk is beyond the anticipated criteria, made it necessary to evaluate possibilities for risk reduction. An analysis was performed of the relative contribution of the accident scenarios to the total risk. This analysis yielded the following global distribution:
- activities (transport) with pressurized ammonia: 75-85%
- nitric acid production: 5-15%
- activities (transport) with refrigerated ammonia: 5-10%

The contribution of single scenarios however, was never more than 2%. Consequently, significant risk reduction by specific measures is very difficult.

Simultaneously with the QRA study for H.A.S., also a regional environmental study was carried out for the whole area around the canal. This study involved odour, noise and risk. The results of the QRA-study for H.A.S. were included in risk contours for the whole area, of about 5 x 20 km. The results showed that, although H.A.S. is locally a significant risk factor, the overall risk contours are determined by transportation of hazardous materials via road, rail and waterways in the area. These conclusions called for further evaluation of the application of the risk criteria for single installations.

The final conclusions about the futural environmental situation around Sluiskil, are presently under discussion with the authorities. Recent recommendations from the Dutch ministry for Environment for regional environmental studies will probably result in:
1. Industrial expansion will be accepted upto a maximum risk in existing living areas of 10^{-5}/year.
2. In residential areas expansions and new houses are not permitted within the 10^{-6}/year risk area; however, renewal of housing is permitted within the 10^{-5}/year area.

Presently, the final decisions can not be given.

TYPICAL UNCERTAINTIES IN RISK ASSESSMENT STUDIES

In the above, some aspects of uncertainties in QRAs have been mentioned. They were also recognized in the study for H.A.S.. Although several research projects and uncertainty evaluations have been carried out in the past few years, there still is no full agreement on all aspects.
Also the socalled Benchmark Exercise on Major Hazard Analysis, which was initiated by the EC and in which eleven organisations participated in a QRA for an ammonia facility, did not result in complete consensus, neither from effects and consequences point of view, nor for the likelihood assessment [20].
It would go beyond the scope of this paper to present results of the Exercise in detail. Some lessons from uncertainty point of view are however given here.

In Figure 4 one of the comparisons among the eleven results is given in a graph. It is obvious that large differences exist among the participants.
From the evaluation by JRC-Ispra, who was project leader for this Benchmark Exercise, a remarkable difference was recognized between two groups of participants:
1. Those who followed the 'conceptional break' approach (Teams 6, 7, 9, 11), resulting in a large number of accident scenarios that were included with respect to severity, accident locations and system reactions.
2. Those who followed more the 'system analysis' approach, where for a limited number of *major* hazard scenarios a detailed analysis with HazOp-s and/or Fault Trees was carried out.

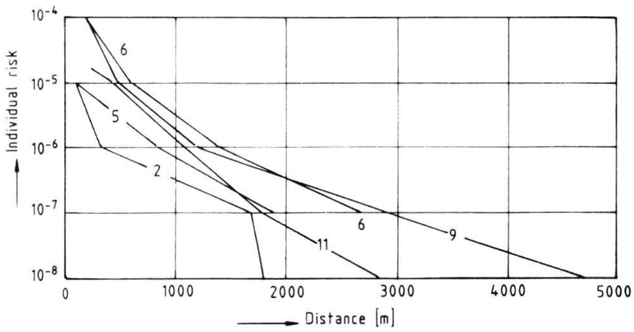

Figure 4 *Results of Benchmark Exercise 'Major Hazard Analysis' for all scenarios at the refrigerated storage site*

The basic information of all the participants appeared to be too exhaustive to evaluate all the sources of uncertainty and their causes. Some typical ones are listed below:

a. *Effects / source term assessment*
For estimation of the source rate, i.e. the amount of ammonia which goes into the dispersing vapour cloud per unit of time, dominating factors are the release hole size, the system pressure, the possibility of two-phase outflow formation and the ambient conditions.
Depending on the physical conditions, the differences in the source term among the teams could vary by a factor of 10 or more. The adopted fraction ammonia rain-out varied from 0% to 80%, for pressurized releases, and consequently the initial evaporation from 20% to 100%. Based on this observation, and realizing that total initial evaporation of semi-refrigerated ammonia is probably not realistic, in the H.A.S. study and others the two-times-flash approach was chosen.

b. *Effects / dispersion*
Although much research [17] has been devoted to ammonia behaviour after a release, there still appeared to be much confusion about the dispersion behaviour of ammonia: is an ammonia cloud buoyant or heavy? The formation of a heavy cloud is mainly explained by the cooling of the ammonia-air mixture that occurs upon a release. Heat of evaporation is extracted from the air and its moisture, resulting in a cold and thus dense cloud-mixture. In most models it is assumed that just enough air is mixed in (instantaneously) to evaporate all ammonia that does not flash-off.
In view of the uncertainties as mentioned under a), with regard to the fraction of rain-out, it is obvious that the potential density is directly related to the assumptions made in the first step.
This, and the fact that different models and software codes were used by the different participants in the BE-MHA, was another source for uncertainties in the results of the risk calculations. It would be fruitful to carry out further validation analyses for this aspect.

c. *Consequences / vulnerability models*
In QRAs, consequence calculations are based on damage models for lethality of people due to exposure to toxic doses. Generally, these consequence models are of the Probit function type:
Pr = $A + B \cdot \ln (c^N \cdot t)$;
where:
Pr = probit value, a representation for the fraction of the population that shows a certain effect, here lethality;
A, B, N = specific factors, determining the type of consequence and depending on the material;
c = gas concentration, in [ppm] or [mg/m^3];
t = exposure duration, in [min].
Figure 5 shows the relation between Pr and fraction.

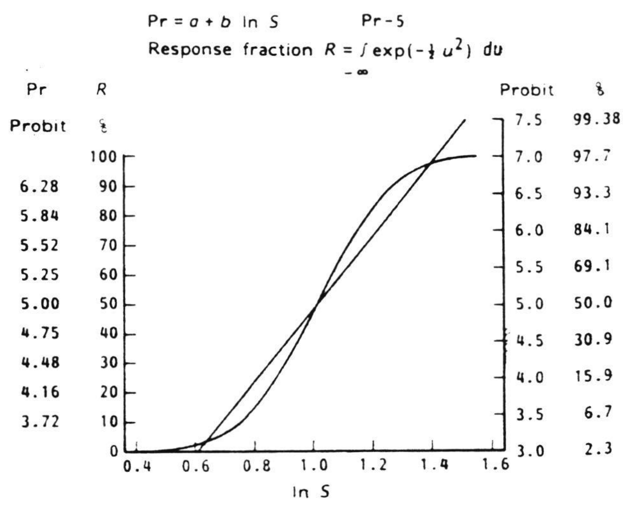

Figure 5 *Relation between Probit [-] and Probability [%]*

Most available probit functions have been determined from the results of animal experiments which are extrapolated to expected human response. Often safety factors are used. The method is described in [5].
In Figure 6 graphs are given of the probit functions used by the different participants in the Benchmark Exercise. It shows the critical NH_3 concentrations as a function of the probit (probability of death), for an exposure duration of 30 minutes. Some observations:

— the LC-50 (Pr = 5.00) varies between 3300 and 11,000 ppm; the LC-01 (Pr = 2.67) between 1200 and 6000 ppm;

— the probit value for a specific NH_3 concentration, e.g. 6000 ppm, may vary between 2.5 and 7.5, or between 1% and 99% lethality; this implies a factor of 100 (!) difference in the risk at the location where this concentration occurs.

These results show that there still exists scope for consensus about the aspect of ammonia toxicity.

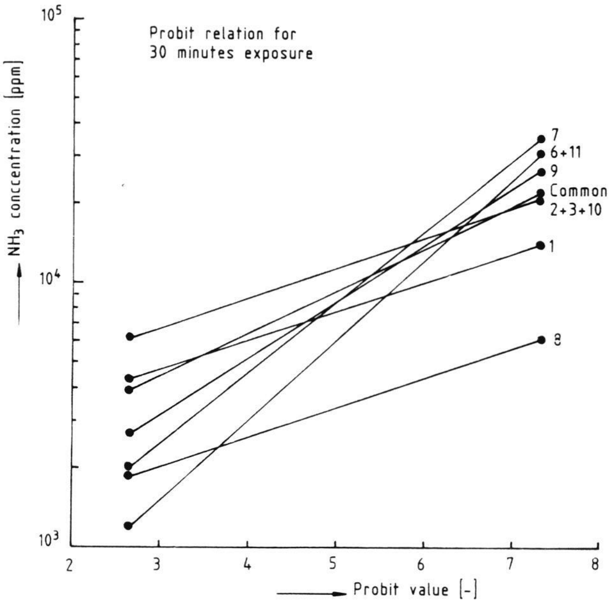

Figure 6 Graphical representation of the NH_3-probit functions, used in the BE-MHA

d. *Failure probabilities*

As mentioned before, most of the accident frequencies in QRA-studies are based upon generic figures. In that respect, the differences between different studies are mostly limited, since most risk analysis studies refer to the same standard literature on this field [11, 12, 13].

This however, does not mean that the uncertainties in the absolute validity of the figures are low as well. The fact that failure and reliability data are based on old systems and have been generalized to all comparable systems, leads to question marks concerning the applicability in a present system. For instance, all failure rates for transfer pipelines in QRAs are based on casuistry from underground LPG- and gasoline long range transport pipelines, over the period 1950 - 1970. As main causes for leak or rupture, digging/drilling and corrosion were identified. It is very much questionable whether such figures are characteristic for overground, well-inspected pipelines in industrial plants as well.

An evaluation of experience with ammonia pipe systems, worldwide, would be a worthwhile suggestion.

Also with respect to the general level of maintenance, operator training, management factors and emergency response, further distinguishes in the generic figures would be very welcome. TNO recently started an investigation into management factors, together with SRD. Also industrial partners are asked to cooperate. The industry could provide the information and quantitative data for this,which can be very much of use in developing more justified failure data, which is also in the interest of industry.

e. *Risk presentation*

The Benchmark study has shown that differences existed between participants about how exactly Individual Risk is defined, which aspects are required to be included in the risk and how it should be presented. Especially the probability of exposure versus the geometry of the toxic cloud and as a function of weather conditions, appeared to be complicated phenomena which could only be dealt with using dedicated computer software, like SAFETY or RISKCURVES. More development in this field is certainly envisaged.

Summarizing the above, it is obvious that, although Quantitative Risk Assessment is a very useful instrument, both for industry and for authorities, further development of knowledge and specific data is required to make studies more site-specific, thus also satisfying the efforts that plant owners take to make their installations as safe as possible.

A METHOD FOR CERTIFICATION OF AMMONIA VESSELS

Large ammonia plants, both producing and consuming ones, generally fall under the Post Seveso obligations.

There are however a large number of other ammonia handling facilities, especially where this substance is used as a refrigerant. These installations generally do not fall under the PSD jurisdiction. Nevertheless, they do have to comply with environmental regulations and occupational safety.

The Dutch Commission for Prevention of Disasters (CPR) issued a guideline CPR-13, entitled "Ammonia: Transport, Storage and Application" [21, in Dutch], in which conditions and safety facilities for ammonia cooling installations are proposed which are also regarded appropriate for environmental demands. However, in some aspects they appear to contradict with the "Pressure Vessel Act" and its corresponding "Rules for the certification of pressure equipment". Stringent application of these Rules sometimes requires complete decommissioning of the installation for an inspection of all vessels and pipelines and X-ray control of the whole system. Another complication is the enormous administrative effort.

TNO has developed a method for simplification of the periodical inspection and certification, by selecting criteria for the extent and depth of such an inspection, depending on the type of installation and the sub-systems. This method is mentioned here as the "Plan van Aanpak" (Dutch for:

Scheme of Approach). A short description of the philosophy and background is given here.

Background
Both for new installations and for existing ones which were not inspected and certified earlier by the "Dienst van het Stoomwezen (DSW)" (Pressure Vessel Inspectorate), an assay and certificate of acceptance are required.

In one of the provinces in the Netherlands, the DSW accepted the following approach:

1. The assay and inspection belong to the responsibilities of the installation owner. He may either put out this work to an external consultant or install his own company inspection service.
   First the consultant draws up a socalled "Plan van Aanpak (PvA)", taking into account the requirements from the Nuisance Act and from the Rules for pressure vessels.
   The PvA prescribes the way the inspection is going to be carried out and the criteria of judgement.
2. Under certain conditions, the technical assay may deviate from what the "Rules" prescribe for that. Therefore, the PvA requires the acceptance by the DSW.
   When the installation is found in safe condition, after carrying out the whole PvA, the assaying consultant provides a certificate. The DSW can always request for a second check whether the inspection has been carried out in compliance with the agreed PvA.

Outlines of 'Plan van Aanpak' by TNO
TNO has an assignment from a large dairy products company in the Netherlands, with several factories in the mentioned province, to draw up a general PvA for all ammonia installations of the company. The work resulted in a method in which both the principles of the "Rules" and those of 'External Risk' were combined. This means that the assay of the installation and its facilities meets both the safety requirements for workers and for residents. In order to satisfy both, the requirements from CPR-13 are the main guideline.

With respect to safety for the surroundings, in some occasions the PvA deviates from the 'Rules', because the Rules sometimes appear to be less appropriate for safety to outside. In those occasions some elements of an inspection, which are demanded by the Rules, are neglected or evaluated with less stringent criteria. In other occasions the Rules appear to be not stringent enough for maximum protection of the environment, e.g. forced ventilation of the machine room in case of leakage. In those cases additional actions are proposed for the installation, which go beyond the requirements of the Rules.
The additional requirements are based on consequence and risk calculations.

The safety of the employees of the installation is generally brought at an acceptable level by full compliance with the 'Rules', which were primarily drawn up for that purpose: preventing failure of vessels, also in fire conditions. However, the 'Rules', originating for pressure vessels in general, hardly account for the toxic properties of ammonia. It is a fact that minor leaks can already cause dangerous concentrations inside a building. That is why the ammonia vapour detection system, which is required from an external risk point of view, must also be used to initiate actions to protect workers: alarm, activation of isolation valves, etc.

The most important deviations from the 'Rules' are:

1. Equipment which has been inspected before, e.g. by the manufacturer, may be adopted as valid and appropriate.
2. Existing vessels for which no inspection certificate exists, may be inspected as yet; it does not lead to disapproval of the whole installation, which could be the case for the original DSW inspections.
3. Contrary to the 'Rules', a manhole on each vessel is not mandatory, regarding the low corrosion potential of NH_3.
4. Material investigation is only required for the equipment with process temperatures less than -20 °C.
5. Compared to the 'Rules', the schedule for random sampling of weld inspections deviates. The proposed sampling procedure accounts for the credibility of damage to piping (small diameters) and the potential severity of the damage (inside or outside a building; liquid or vapour line). Generally less stringent criteria for approval are applied.
6. In order to reduce the release of ammonia to the atmosphere, in case of a leakage inside the machine room, installment of a water curtain in the ventilation discharge, initiated by the ammonia detection system, is mandatory.

Recently, TNO's proposal for the PvA for the dairy products company, was approved for application in all the factories of the company and also for other similar installations in the same province. TNO came into the possibility to act as a certifying organisation in that region.
Presently, we are trying to get the same approval in other Districts of the DSW and for environmental regulations for the whole country.

EMERGENCY MANAGEMENT

For large scale ammonia production or application, major hazards remain possible. Emergency preparedness planning and mitigation possibilities are required.
TNO has developed several methods and tools for disaster management planning, mostly in an assignment from the Dutch authorities.
The following aspects can be distinguished:

1. *Preparation*: selection of activities and required resources.
2. *Real-time decision support*: helps aid services during the course of a disaster in deciding their actions.
3. *Repression*: technical measures to reduce the extent of the disaster.

For each of these aspects, one or two results of TNO's developments are described in this chapter.

Emergency preparation

For establishing an emergency response organisation, especially for off-site emergencies, one of the first requirements is an identification of the (industrial) activities for which such an emergency could be expected. What is needed then is a method for selection and prioritizing the installations.
TNO has developed a method for categorizing chemicals with toxic hazard potential, using socalled toxicity indices [22]. The method is based on both the toxicity of the chemical, in LC-50 values, and the potential source strength, based on the vaporisation potential (vapour pressure at 20°C). About 130 chemicals, among which ammonia, were selected for a priority list for emergency response planning.

To identify the activities (industries or transport routes), a Guideline was developed [23]. This 'Guide to hazardous industrial activities' distinguishes between types of material (gas, liquid, liquefied gas, solids), type of hazard (toxic, flammable, explosive) and way of storage (pressurized, refrigerated, etc). Categories of materials have been identified, and by the use of graphs the potential damage distance (lethality and serious injury) are found as a function of the system inventory. An example is given in Figure 7.
The potential damage area can be drawn on a map of the surroundings, from which the potential number of victims can be assessed. This, together with a global indication of the accident probability and of specific demographical circumstances, gives the local authorities an instrument for deciding whether emergency preparedness is required.
The Guide is not only used in the Netherlands, but has been proposed for application in Canada, Soviet Union and Taiwan R.O.C.. Apart from Dutch and English, the Guide has also been translated into the Spanish, Russian and Chinese language.

TNO has evaluated different possible 'Warning and Monitoring Services', for implementation in the Netherlands. This has considerably contributed in building up the Emergency Response Organisation in the country.

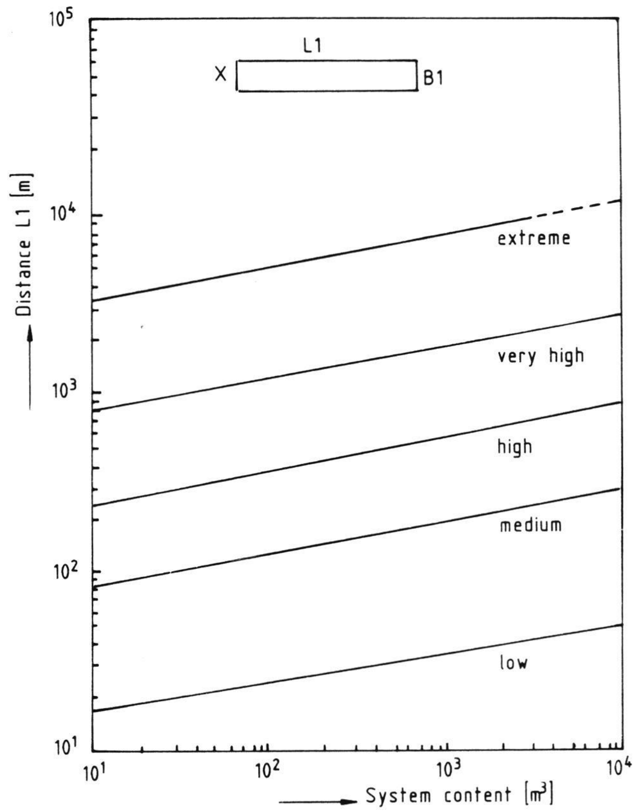

Figure 7 Example of damage distances from the 'Guide to Hazardous Industrial Activities'

Real-time decision support

During the course of a disaster and in the disaster relief phase, the aid services require quick and reliable information about the situation in the surroundings and the possible development of the accident: where will the toxic cloud go to, when will it be there, how many people may be involved and what is the most effective measure to reduce the consequences?

The Dutch Fire Inspectorate, which is part of the Ministry for Home Affairs, assigned TNO to build a computerized decision support system for quick, real-time evaluation of the development of a toxic disaster. The system is called 'IRIS', which is a Dutch acronym for 'Information and Calculation system for Incidents involving Hazardous Substances'.
It has the capability to calculate the consequences (injuries) of a toxic release as a function of time, including the evaluation of alternatives in emergency response measures like source reduction, mitigation (stay indoors) and evacuation.The real-time weather conditions are elaborated in the calculation system, and also has IRIS the capability of feed back of measurements in the surroundings, should they deviate from the prediction of the calculation module.

The system also contains the mapping of the surroundings and the industrial activities present there, in order to prepare credible accidents at locations where they exist.

IRIS is presently in the implementation phase and should be operable in the, highly industrialized, Rijnmond area by the beginning of 1992. Afterwards it will be implemented in other areas of the Netherlands.

Prior to the development of IRIS, which took a few years, a simplified system of 'damage contours' was made for the Fire Inspectorate. They aim to be used for identifying the damage area in disaster cases where the IRIS system has not been implemented yet. Transparency damage contours have been drawn for the typical material categories which are distinguished in the Guide to Hazardous Industrial Activities. An example of such a contour is given in Figure 8.

Source mitigation: Absorbing water curtains

In general, the most effective way to reduce the consequences of a release of hazardous (toxic) material, is reduction of the amount of vapour that is dispersed into the atmosphere: source mitigation.

During the past few years, several industries have installed (water) spray systems in cases where hazardous material releases might be possible. Both small-scale and full-scale experiments are described in literature, about vapour cloud dilution, by mixing-in air into the cloud using the spray momentum. Several experiments have been carried out to investigate the effects of nozzle types and either upward or downward directed sprays.
In many occasions an effective dilution to below flammability limits could be achieved.

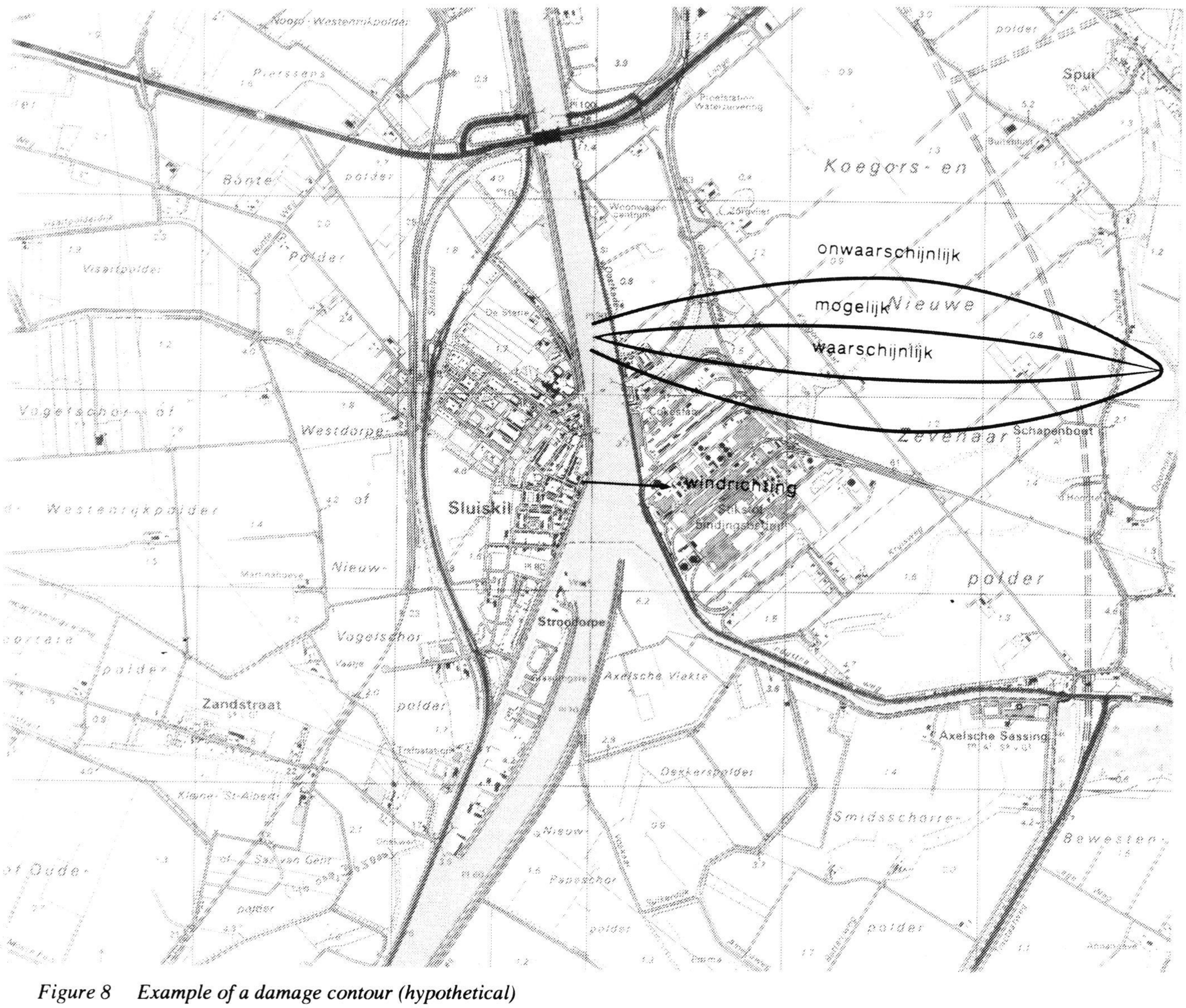

Figure 8 Example of a damage contour (hypothetical)

Using these spray systems also for absorbing vapours, which seems more appropriate in case of toxic vapour releases, was less well known. That is why TNO, after a literature survey, has started a research program to investigate the effectiveness of such water curtains for limiting toxic vapour dispersion. A first phase of small-scale experiments has been carried out, in which ammonia was applied as the test vapour. So far the results appear to be very promising [24].

Figure 9 shows a scheme of the test facilities. The ammonia is evaporated underneath the spray nozzle, placed together in a laboratory fume cupboard. Both water flow and ammonia flow are measured and so are the ammonia concentration in the sprayed water and in the foam cupboards discharge air.
Variable parameters in the experiments were:

- water flow rate: 33, 64 and 141 l/hr;
- ammonia vapour flow rate: 12, 30, 48 and 66 l/hr, @ 25°C;
- type of spray nozzle: full cone and hollow cone;
- height of nozzle above ammonia release point: 0.1-0.4 m.

The duration of each test was about 15 min. Steady state of the ammonia concentration was reached after a few minutes. Each experiment was carried out in duplicate.

The efficiency of the water spray was calculated as:

$$\eta = 1 - \frac{CNH_3 \text{ with spray}}{CNH_3 \text{ without spray}},$$

where C NH_3 is ammonia concentration in the outlet air.

In Figure 10 the results for the efficiency are given in a graph, showing the relation with the type of nozzle and the height of it relative to the ammonia release point.
Obviously, the absorption efficiency varies between 60% and 80%, where the hollow cone nozzles generally yield the best results.

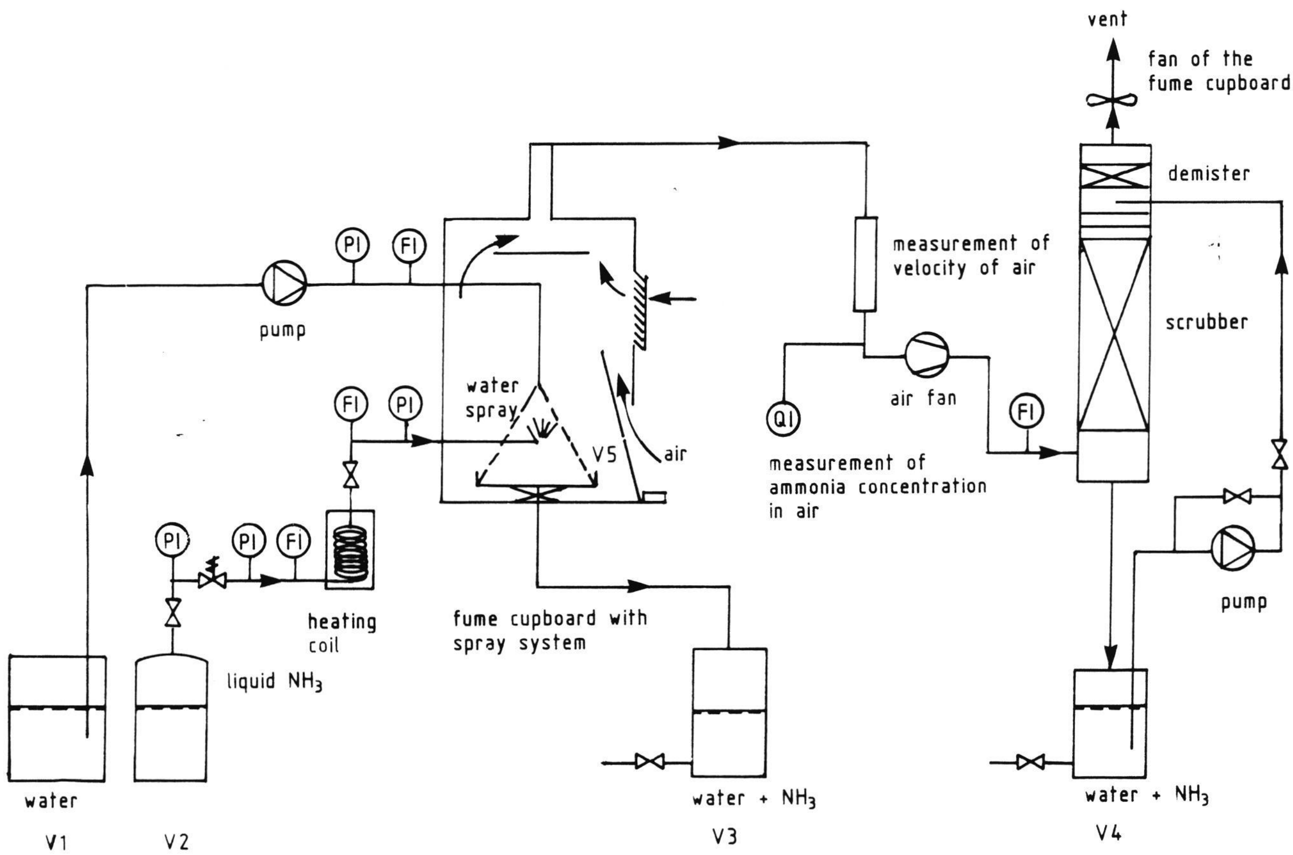

Figure 9 Test facility for water spray experiments

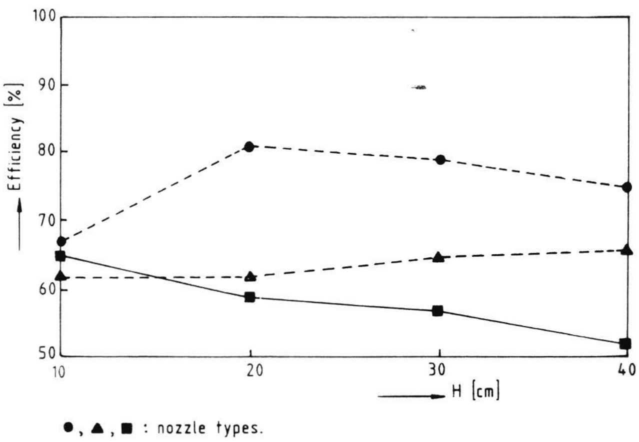

Figure 10 Absorption efficiency as a function of nozzle type and nozzle height

Most experiments were carried out with ammonia concentrations in the order of 200 - 500 ppm(v). Due to some problems with the ammonia detector, it was not possible to carry out these experiments for the higher ammonia concentrations, say 5000 ppm(v), which are concentration levels of relevance in hazardous releases.
Not all mass balance calculations appeared to match. The ammonia concentration as measured in the sprayed and recaptured water would indicate that all efficiencies were over 80%.
The results as a whole however, give us reason for carrying on with larger scale experiments, next year.

It is to be expected that the experience with spray systems for absorption of hazardous gases can prove its benefit in emergency response by industry and by community fire services.

CONCLUSIONS

Quantitative Risk Assessment has proven to be a useful tool for decisions on environmental licensing, land-use planning, industrial site selection and emergency management planning.
Also can the method be used for prioritizing areas for risk reduction.

However, the benefit of QRAs should not be overestimated. The technical realisation of risk reduction requires more structured techniques like HAZOP, FMECA and Fault Tree analysis. Large uncertainties in the quantification of specific effects and of failure probabilities in a QRA, which are generally approached from the pessimistic side, might lead to unnecessary high efforts and expenses to meet statutory criteria. Further research into these aspects is plead for. Involvement of the expertise of the chemical industry itself in this, is essential.

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