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Contribution to the quantitative risk assessment of chemical processes

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Legislation concerning prevention of serious industrial accidents, known in the CR also under “Seveso II” [1], has been implemented since 2000. The Ministry of environment CR recommended application of so-called “Purple book” [2], [3] as a basis for the quantitative risk assessment (QRA). This paper deals with inofficial observations and considerations of authors participating in teams solving QRA problems in the CR. There is no doubt about usefulness of all the work done for process safety. However after some time has elapsed it seems to be lots of problems for further discussion remarks and recommendations, which might be taken into account in further development of the QRA. The existing methodology tends to focus attention to factors causing accidents with huge impact on fatalities and negative social environment’s reactions. Then a company management has to spend almost all safety expeditures in preventing events with very low frequencies. On the other hand so-called “short range failures” or “near misses“with greater probabilities of occurrence should deserve a corresponding attention and allocation of financial sources. Application of more advanced approaches to plant safety like safequarding, E/E/PE etc. would also be reflected. Three real industrial examples are presented to illustrate the situation encountered in practice.

1. Introduction

1.1 Some history

The Seveso II Directive was transposed into the Czech legislation as the Act No. 353/1999 Coll., on the prevention of major accidents caused by selected dangerous chemical substances and chemical preparations and on amendment of Act No. 425/1990 Coll., on District Authorities, outlining of their jurisdiction and some other related measures, in the wording of later regulations. The legislation concerning prevention of serious industrial accidents defines various safety measures and precautions, which must be respected. First the objects under concern are distinguished into category A and B according to amount of stored matters. Besides other obligations the liable persons have to work out a safety report about QRA for objects belonging into category B. Stress is laid upon evaluation of individual and societal risk outside the site, so as to enable elaboration of emergency plans for neighbouring community. Final results are required in form of boundaries or curves on the map depicting the level of both types of risk. Later on the authorities have tended to involve further aspects like synergy and domino effects, human factors and terrorism to mention just a few.

Experience with implementation has shown several problems. The elaboration of safety reports was fully given to special private authorized companies or agencies independent on assessed objects. In order to arrive at QRA according to the methodology some special software had to be adopted besides other tools. Unfortunately no unique standard commercial software was prescribed for this purpose by authorities. Therefore individual reports had no unique fashion and their supervision was difficult.
The evaluation of QRA according to [2] consists of several items like:

- Selection of equipment with major potential hazard.
- Calculation of amounts of released flammable and toxic materials at prescribed scenarios and with given annual frequencies for individual top events.
- Modelling of dispersions after release in form of puff or plume clouds according to Pasquill-Gifford model [4].
- Probability of encountering clouds with ignition sources.
- Calculation of causalities in case of fire, explosions and/or toxic exposures.
- Final evaluation of QRA in terms of annual frequencies of fatalities.

Just at the very beginning too many objects (about 140 objects) belonging to severe category B were found to have an unacceptable risk, despite their satisfactory existing and operating for many years. In most cases there were no easy and cheap solutions how to overcome this problem. One cannot simply move the object or people from the neighbourhood, decrease a number of operators, change the technologies, replace all hazardous substances and operations, re-commission the plant according to actual standards etc. In addition to this the objects with unacceptable risk cannot be properly insured but their insurance is obligatory.

During the time some original requirements were found to be too severe. For instance the authorities tended to require immediate retrofit of objects according to actual legislation despite they were designed and commissioned according to legislation valid in time of their realisation in the past. The new adopted Act No.59/2006 Coll. [2] on the prevention of serious accidents caused by selected hazardous chemical substances or chemical preparations and on amendments to Act 258/2000 Coll. on the protection of public health and on amendments to related legislation, as amended, and Act No.320/2002 Coll., on amendments to and the repeal of certain acts in relation to the termination of the activities of the district authorities, as amended (Act on the Prevention of Serious Accidents). On February 1st, 2005 there were 73 companies registered in category A and 81 companies in category B.

1.2. Remarks to the methodology of QRA

First, the methodology of QRA is based on amount of stored or contained matter rather than a technical level of its processing. It can simplify an initial selection of objects under concern but on the other hand it does not take into account more advanced methods of process control and prevention of accidents.

The second reason seems to follow from prescribed frequencies of events [2]. There is usually no clear justification for their very severe values besides the fact that their sharing or transfer among different objects or even countries is questionable. Despite an enormous number of investigated factors and their combinations causing accidents, the existing methodology of QRA finally focuses attention to big disasters at very low probabilities. On the other hand in everyday´s life another type of undesirable events prevail and namely those with lower consequences but higher frequencies of occurrence. They cannot be simply overseen and also deserve a proper attention and allocation of financial sources.

Let the third reason be omissions and oversights occurring usually due to lack of time and money for QRA analysis. Starting-up, shutting down of plant operations, maintenance as well as activities of outsourced agencies are mostly encountered in practice as problematic.

Finally let be mentioned know-how for the QRA of chemical plants as applied by insurance companies. It can serve as an example how to combine both economical and technical approaches. The insurance agents usually try to create a map of frequencies and consequencies of potential accidents and determine a tolerance of risk. If the risk is quite unacceptable the objects or activities are not insured and must be outsorced. However this shift of responsibility to another subject can cause further consequencies, which are carefully analysed from various management´s points of view. Participation of the subject on insurance costs also reflects the level of risk. A regularly repeated detailed risk analysis takes into account all aspects of company´s management and attitude of personnel to safety issues etc. Despite the emergency planning is usually at disposal, technical and financial conditions of plant restoration after accident is also an important item of insurance policy.

1.3. Example 1

A racking and filling station of propane-butane (PB) bottles has area of 270 x 210 m and is situated at the edge of a great city. The site is surrounded by a factory manufacturing wood, football stadium, road and fields in a plain landscape. A prevailing direction of winds is from West to East. There are about 36 objects (buildings and structures) important from the point of view of potential fire and explosion hazard.

The QRA analysis has been carried out according to guidelines published in [2]. First it is necessary to define relatively separated parts or sections of equipment as sources of hazard. Those are parts which are either not mutually connected or can be quickly separated. It is necessary to distinguish storage and process devices as well as pipelines. Special attention is to be paid to railroad tank wagons and road tank cars. They are considered as storage tanks if stay more than 1 day on one place, otherwise they are considered to be more reliable than simple storage tank if handled with care because of construction intended for transport.

The QRA analysis is started with evaluation of a so-called indication number A_F which is to be evaluated for each part of equipment. It is valid $A_F = Q*O_1*O_2*O_3/G$
where Q is amount of matter under concern. In our case the mixture of PB is a flammable flushing liquid under the pressure of saturated vapours. The outlined factors O_1, O_2, O_3, mean:

O_1= 1 for process and 0.1 for storage equipment

O_2 =1 for unconfined and 0.1 for confined (capsulated) equipment
O_3 =1 when the saturated vapour pressure at normal temperature is greater than 3 barg.
G=10000 kg is a limit value for inventory of flammable liquid.

In addition to this a selection number for fire and explosion hazard is calculated as
$S_F = (100/L)^3 * A_F$,
where L is a distance of the device from the site boundary. In practice individual points are defined on the site boundary and L is related to these points. This distance should be 100 m at least. S_F is evaluated for each part of equipment in 8 nearest points at least. Then the sources of hazard are listed according to magnitude of S_F.

It follows from this selection that the major hazard concerns of two spherical PB storage tanks with diameter 12,5 m, volume 1000 m^3 and mass 430 tonnes. They belong to a category of pressurised stationary storage tanks and vessels. Quidelines for evaluation of QRA [2] prescribe the following scenarios for this type of equipment:
G1) Instantaneous escape of the total inventory. The basic annual frequency of this event is $5x10^{-7}$.
G2) Continuous escape of the total inventory during 10 min by a constant rate (annual frequency $5x10^{-7}$).
G3) Continuous escapes from the hole with effective diameter 10 mm (annual frequency $1x10^{-5}$).

The case G1 seems to be the most consequential BLEVE scenario assuming fire in a vicinity of the storage tank. Heat flux due to radiation on the walls of the storage tank should be sufficient for evaporation of the whole liquid content combined with simultaneous failure of the relief valves. Lower annual frequencies of events (e.g. $1x10^{-7}$ or even less) can be applied for storage tanks provided with special additional device in addition to standard ones. For instance there can be remote automatic switch off a closing valve without personnel approaching in case of fire. Another measure is slowing down the evaporation by spraying the walls by water. Despite these facts the storage tanks are far the most risky equipment in comparison with other ones in the site. There is hardly any other way how to decrease a fire and explosion hazard than to take a less amount of substance Q and/or to confine it (O_2 = 0.1). However is it really reasonable to confine the tank despite PB vapours are heavier than air? There is also a great discrepancy between the limit value 10 tonnes of flammable liquid and 460 tonnes of actual inventory. The second most risky equipment is the racking platform for railroad tanker (43 tonnes) and for road tanker cars (15 tonnes) both with greater inventory than 10 tonnes. And what about the fact that the tanks are only 60 m far from the site boundary but not required 100 m at least? The tanks can hardly be moved and there is seemingly no urgent need to re-build them and to spend huge investments in order to satisfy (not transparantely justified) legislation.

1.4. Example 2

A chemical factory in the CR with about 1000 employees located on a boundary of a city with about 100000 inhabitants has more than 140 years tradition of manufacturing inorganic and organic chemicals. A following statistics illustrates an occurrence of leakage failures at various places for various substances within the chemical plant during one year. While for the total rupture of vessel can the prescribed annual frequency achieve $1x10^{-7}$ or even less, the prescribed annual frequency of pipelines breakdown, which is more then 10^{-4}. Nevertheless these accidents often belong to the category of "short range failures" or „near misses" and their impact on e.g. societal risk would be negligible if compared to above mentioned example of huge accident. The statistics is depicted on Fig.1.

For the whole description of this phenomenon it is evidently not possible to generalize the situation to the number of relieves only and it is necessary to consider the potential hazard of released matter and to the relevant equipment. Considered compounds have also impact on the number of leakages within various parts of processes in the site. It follows from the statistics that there is a significant leakage of petroleum compounds through transport. On the other side all other compounds escape mostly within the pipeline system and therefore the stress should be laid upon it.

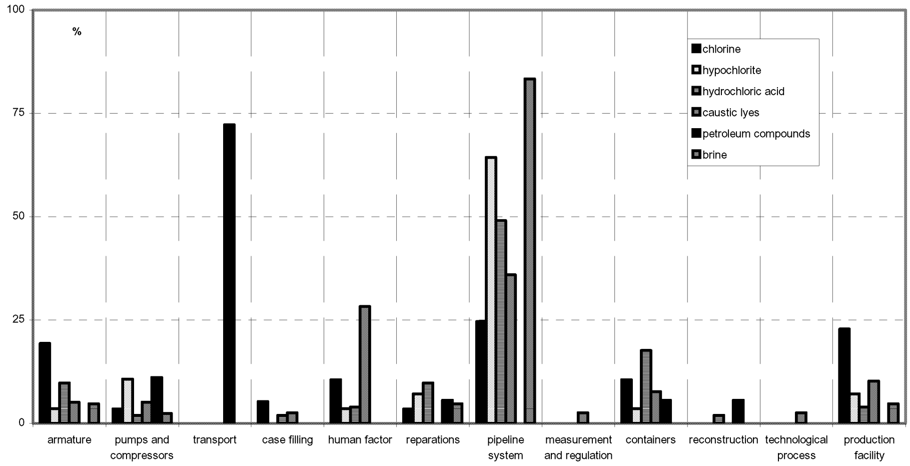

Fig.1. Frequency of leaks of individual compounds within different parts of process

Another important factor is the role of the season of the process performing (i.e. quarters). It takes into account weather, holidays, maintenance and the services periods, etc. which are not negligible as one can see on Fig. 2. Again it is evident that the pipeline system has the largest number of breakdowns in all quarters. Nevertheless it can be also seen that the particular frequencies of events for particular parts of process are different for each quarter of the year. The analysis of near misses in chemical plants provides a good opportunity for companies to determine that a problem exists and to correct it before a more serious accident occurs [6]. Accidents of this type are due to various breakdowns of pipeline system, armatures, production facilities, and failures in technological process etc. And result in relieves and spills of toxic, flammable, and explosive chemical materials. In addition to this a human factor is hidden in major cases, corrosion plays an important role (not particulary involved in QRA) and HAZOP would be used to elaboration of reglements for reparations and maintenance.

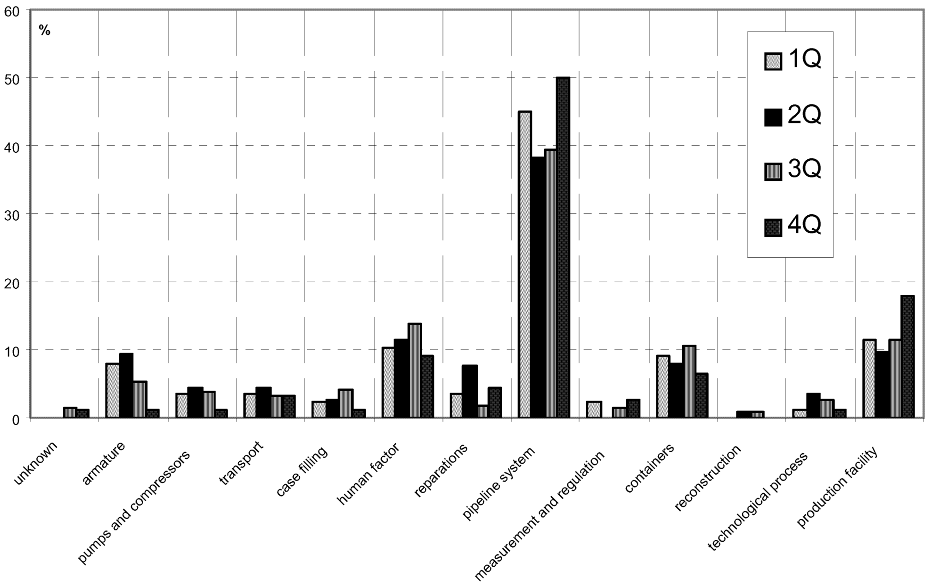

Figure 2. Quarter impact on number of leaks within the whole facility

Safeguarding is any means of preventing personnel from coming in contact with the moving parts of machinery or equipment during operation or during maintenance and servicing. Machine safeguarding improves productivity and morale because of the protection offered. Application of all these methods could further increase the accuracy of the QRA.

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3. References

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