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Precursors of dangerous substances formed in the loss of control of chemical systems

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Abstract

Article 2 of Directive 96/82/EC on the control of major accident hazards caused by dangerous substances requires to consider also the hazards due to the dangerous substances ''which it is believed may be generated during loss of control of an industrial chemical process'', although no generally accepted guidelines are available for the identification of these substances. In the present study, the accidents involving the unwanted formation of dangerous substances as a consequence of the loss of control of chemical systems were investigated. A specifically developed database was used, containing data on more than 400 of these accidents and on the substances involved. The hazardous substances formed in the accidents and the precursors of these substances were identified. The influence of accident characteristics on the substances formed was investigated. In the context of the application of Directive 96/82/EC, an accident severity index and a hazard rating of the precursors of dangerous substances formed in the accidents were proposed. A lumping approach was used in order to develop schemes for the preliminary identification of substances that may be formed in the loss of control of chemical system. The results of accident analysis were used to test the schemes developed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Unforeseen reactions; Chemical hazards; Accident analysis; Hazardous substances; Major accident hazards

1. Introduction

Handling and processing of chemical substances may directly cause important hazards due to the substance characteristics. However, another important hazard factor comes from the possible formation of dangerous compounds by unwanted or unforeseen

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reactions. These events are usually associated to a loss of containment, thus resulting in a toxic release. As a matter of fact, the formation of dangerous substances as a consequence of the deviation of a process from the normal operating conditions was found to be the cause of severe accidents [1].

Although the dangerous characteristics of chemical substances involved in industrial processes are extensively investigated, less attention is paid to the chemical hazards posed by unwanted reactions. This is probably caused by the complexity of the problem. The chemical effects of ‘out of control’ conditions are more difficult to foresee, since a wide number of chemical substances and of chemical systems are involved in industrial operations.

Nevertheless, the hazards due to the formation of dangerous products by unwanted reactions are now taken into account in European Council Directive 96/82/EC (also known as ‘Seveso-II’ Directive) [2]. Article 2 of the Directive requires to consider also the hazards due to the dangerous substances ‘‘which it is believed may be generated during loss of control of an industrial chemical process’’. However, no well-accepted criteria are yet available for the identification of dangerous substances that may be formed from a chemical system undergoing ‘out of control’ conditions. Although several studies are present in the literature on single case-histories, and several research projects were carried out, mainly on the identification of hazardous products of fires (i.e. see Cole and Wicks [3], Petersen and Rasmussen [4], Bockhorn [5], and references cited therein), a systematic approach to the problem is still lacking.

This study analyzes the characteristics of accidents involving the loss of control of a chemical system. More than 400 accidents were thoroughly examined using a specifically developed database, named EUCLIDE (Emission of Unwanted Compounds Linked to Industrial Disasters and Emergencies) [6,7]. The substances from which the hazardous compounds were formed in the accidents, defined ‘precursors’ in the followings, were identified from accident data analysis. The characteristics of the accidents influencing the hazardous substances formed were also discussed.

A methodology for the preliminary identification of the hazardous substances that may be formed in industrial accidents was developed and tested using the database. The definition of an accident severity index and of an hazard rating of the precursors was found to be possible on the basis of Annex I of European Council Directive 96/82/EC.

2. Lumping approach to the description of chemical systems

A complete screening of all the hazardous substances that may be formed in all the chemical systems of industrial interest as a consequence of ‘out of control’ conditions is clearly impossible. The problem may be approached on one hand reducing the number of substances of interest to those that are considered more hazardous in Annex I of Directive 96/82/EC. An indirect hazard ranking of named substances and substance classes is given in Annex I by the threshold quantities for the application of Directive requirements. Only named substances and substance classes with thresholds lower than 10 t for the application of notification requirements (articles 6 and 7) were considered in the present study.

On the other hand, the problem may be further simplified using a lumping approach to the identification of reactants, products, and reaction pathways of concern. Lumping techniques have given important results in kinetic studies of complex chemical systems [8–10]. Applications of lumping approaches to the description of reacting chemical systems range from the analysis of cracking and visbreaking processes [11–13] to pyrolysis and combustion of biomass and wastes [14–16]. Lumping analysis consists in: (i) the definition of a limited number of 'macrocomponents' to represent the actual chemical system; (ii) the definition of a simplified reaction scheme to represent the actual network of possible reactions. Each macrocomponent represents all the chemical species present in the system that have some similar characteristics.

A preliminary analysis of the links between the hazardous substances formed and the chemical systems involved in accidents showed that in most of the accidents the system conditions experienced during the loss of control of the process caused important changes in the chemical structure of the substances that were present. This suggested a drastic lumping of reacting substances to macrocomponents defined on the basis of the presence of 'heteroatoms' (atoms different from carbon and hydrogen). Chemical systems were tentatively reduced to six reactant macrocomponents: hydrocarbons and oxygen-containing organic compounds; nitrogen-containing organic compounds; halogen-containing organic compounds; sulphur-containing organic compounds; phosphorus-containing organic compounds; organometallic and organometalloid compounds. A chemical system, where more than one heteroatom is present, may be

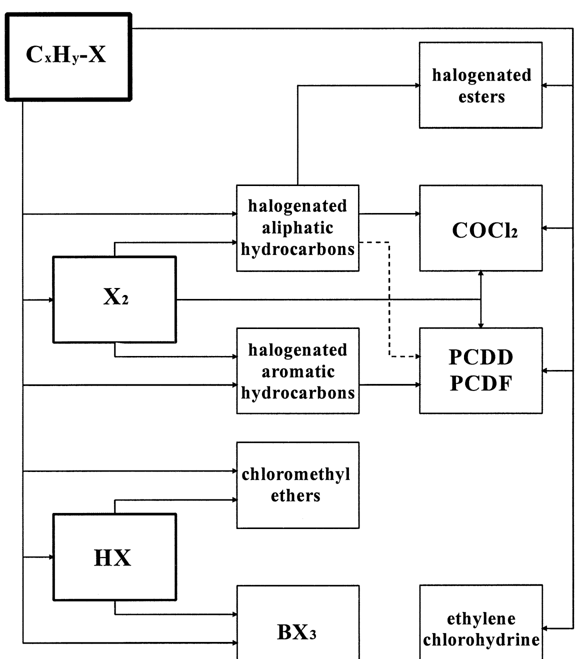

Fig. 1. Lumped reaction scheme for halogen-containing compounds (X_2:halogens; HX: hydrogen halides; BX_3: boron halides).

represented by more than one reactant macrocomponent. Inorganic substances are not directly represented in the reactant macrocomponents, but as a working hypothesis, may be aggregated to the corresponding organic macrocomponent. This is justified by the possible formation of the organic macrocomponent starting from organic substances present in the system and inorganic compounds containing the corresponding heteroatom.

The analysis of the chemical characteristics of the hazardous substances and substance classes identified by European Council Directive 96/82/EC and 67/548/EEC [17] was performed in order to define the product macrocomponents of concern [18]. This resulted in the production of a lumped reaction scheme for each of the 'reacting' macrocomponents. An example for the halogen-containing macrocomponent is given in Fig. 1. In the implementation of the reaction schemes, oxygen was always considered as present in the reacting system, since accidental events usually involve the loss of containment.

At a preliminary stage, all the product macrocomponents should be considered as possible hazardous products in 'out of control' conditions. However, the analysis of each

Table 1
Specific precursors of halogen-containing hazardous products identified in Fig. 1

Product	Specific precursors	Required coreactants	Conditions	*T* range
X_2	HX	Strong oxidizer	Oxidizing	Low
	Hypochlorous acid/salt	–	Acid	Low
	Trichloroisocyanuric acid	–	Acid	Low
	Chlorates, oxides	–		Low
HX	Alog. aliph. hydroc.	–		Low–medium
Halogenated aliphatic hydroc.	X_2	Aliphatic hydrocarbon		Low–medium
	HX	Unsaturated hydroc.		Low
Halogenated aromatic hydroc.	X_2	Aromatic hydrocarbon	Acid	Low
Chloromethyl ethers	Hydrochloric acid	Formaldehyde	Acid	Low
	Thionil chloride	Dimethoxymethylene	Acid	Low
BX_3	Boron compounds	Halogenated comp.		Medium–high
	HX	Boron compounds	Acid	Medium
halogenated esters	Halogenated alcohol	Halogenated acid		Low
	X_2	Non-halogenated ester		Low
	Halog. aliph. hydroc., ox.	–		Low
$COCl_2$	X_2	Carbon monoxide		Low
	X_2	Hydrocarbons, oxygen		Low
	Carbon tetrachloride	Acetaldehyde	Oxidizing	Low
	Chloroform	Oxygen		Low
	Halog. aliphatic hydroc.	–	Oxidizing	Low
PCDD/PCDF	PCB		Oxidizing	Medium
	Chlor. phenoxyacids	–		Low–medium
	Chlorinated phenols	–		Low–medium
	Chlor. diphenyl ethers	–		Medium
	Chlorinated phenyl esters	–		Low–medium
	Chlorinated hydroc.	Oxygen	Oxidizing	Low–medium
	X_2	Aromatic hydroc.	Oxidizing	Low–medium
Ethylene chlorhydrine	HX	Ethylene oxide		Low

of the reaction pathways indicated in the figure allowed the identification of the specific precursors and of the reaction conditions that may lead to relevant yields of the hazardous products. These data were obtained for each of the macrocomponent reaction schemes. Table 1 summarizes the data obtained for the halogen-containing macrocomponents.

Jointly to the macrocomponent reaction schemes, the tables may be used for the identification of hazardous products possibly formed in a known chemical system running in 'out of control' conditions. These data are important either for accident prevention and for post-accident investigation. The information given by the macrocomponent reaction schemes may be used to identify the possible hazardous products and unwanted reactions that should be considered in process safety assessment. On the other hand, the schemes may be used to orient further investigation on the consequences of accidental events. Macrocomponent reaction schemes may also be used as tools for the effective organization of data on substances formed in accidental events and on quantitative yields of hazardous substances that should be expected [18].

The application of lumping approach to the description of a chemical system has obviously some limitations. The main one with respect to the proposed application is that all the components that are present in the chemical system, or that may be present during the loss of control (i.e. as a consequence of loss of containment or contamination) should be identified and considered in order to correctly apply the methodology. In particular, hazardous products formed during accidents involving mixtures of substances whose composition is not certain or unknown may not be addressed with this methodology.

3. EUCLIDE database

In order to test the validity of the lumping approach to the identification of hazardous substances formed in accidents, the EUCLIDE database was used. EUCLIDE is a homogeneous data set that stores information on the characteristics of accidents that resulted in the formation of hazardous substances and on the chemical and toxicological characteristics of substances involved and formed in the accidents. The database contains data on more than 400 accidents that resulted in the release of hazardous substances formed as a consequence of 'out of control' conditions. EUCLIDE data were derived from the analysis of accident data files collected from the main European electronic databases (ARIA [19], FACTS [20], MARS [21], and MHIDAS [22]) and from the Community Documentation Centre on Industrial Risk [23]. Further details on EUCLIDE database are given elsewhere [6,7,18].

4. Results and discussion

4.1. Validation of macrocomponent reacting schemes

The hazardous substances that were formed in the accidental events present in EUCLIDE database are shown in Fig. 2. Among the dangerous substance classes more

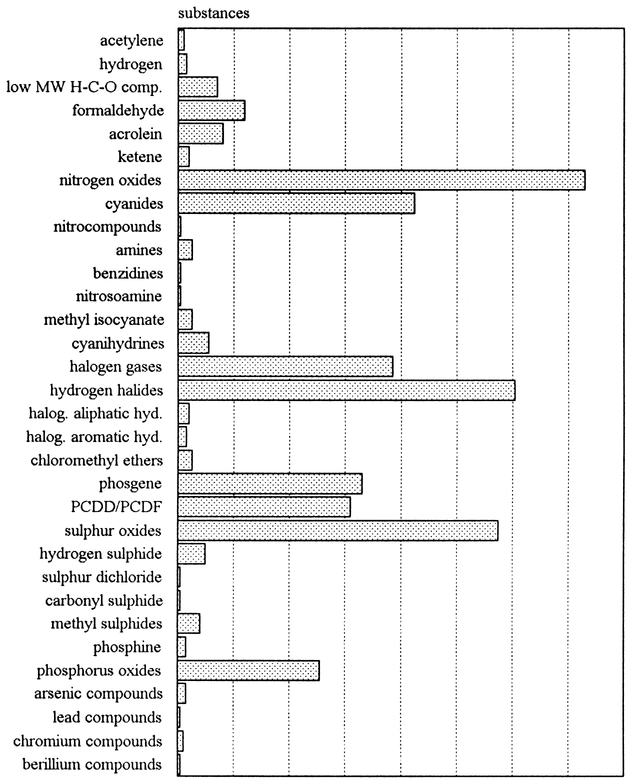

Fig. 2. Substances and substance classes formed as a consequence of the loss of control of chemical systems in the industrial accidents present in EUCLIDE.

frequently formed in accidents are nitrogen and sulphur oxides, hydrogen halides, but also extremely hazardous compounds as phosgene and poly-chlorinated-dibenzo-dioxins (PCDD). The analysis of the accidental events stored in the database allowed in most cases the identification of the precursors of the hazardous substances that were formed in the accident. Significant data could be obtained only for the substances that were formed in a relevant number of events. Fig. 3 shows the data obtained for four of the more hazardous compounds that were formed in the accidents examined: PCDD, phosgene, chlorine and hydrogen cyanide. From the analysis of the figure the substances and substance categories more likely to yield these hazardous products may be identified. The data reported in the figure may also be used to estimate the frequency with which the different precursors were involved in accidental events. The data shown in Figs. 2 and 3 were used to test the macrocomponent reaction schemes developed for the identification of hazardous substances formed in 'out of control' conditions. The substance classes defined in the lumping approach were used to organize the data reported in Fig. 2. As a matter of fact, the product macrocomponents were able to represent the actual components of the chemical systems. The comparison of Figs. 1 and 2 shows that all the more hazardous chlorinated substances formed in the accidents are

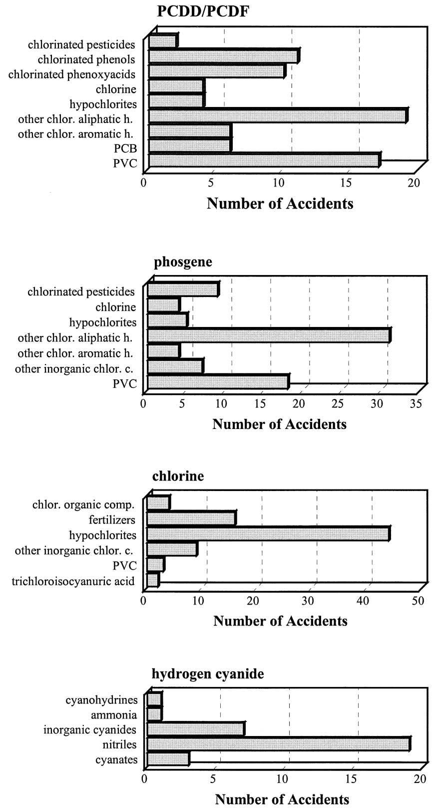

Fig. 3. Precursors of different hazardous substances formed in ‘out of control’ conditions in the accidental events present in EUCLIDE.

included within the possible reaction products present in Fig. 1. The comparison of data in Fig. 3 and Table 1 for chlorinated compounds shows that the actual precursors of hazardous substances formed in accidents were identified by the lumping methods. Most of these compounds are listed as ‘specific precursors’ in Table 1, and were identified by the preliminary analysis of reaction pathways performed for the production of the macrocomponent schemes [18,24]. This was verified for all the accidents analyzed.

The actual unwanted hazardous products formed in the accidental events were always included within the hazardous products identified by lumping analysis. On the other hand, the comparison of accident data to macrocomponent reaction schemes made possible the identification of hazardous products, whose formation was theoretically possible but that actually were not formed (or at least not in significant quantities) in the accidents examined. This is in part caused by the loss of details that is inherently associated to lumping techniques. Lumping approach may give information on the main product categories that may be obtained in accidents, but may be quite inaccurate with respect to the identification of the products obtained with higher yields. Very important factors as the roles of temperature and pressure, and the presence and persistency of reaction intermediates may be underestimated by lumping techniques. These factors, which are widely variable in accidents, influence significantly the products formed in ‘out of control’ conditions. However, the results obtained thus confirmed that the lumping approach may be used as an analysis tool in order to get at least some preliminary information on the possible hazardous products formed in a chemical system in ‘out of control’ conditions.

4.2. Influence of accident characteristics on hazardous substances formed

The chemical species formed in the accidents are influenced mainly by the characteristics of the chemical system involved. As shown above, knowing the normal components of a chemical system may be sufficient to identify the more hazardous substances or substance classes that may be formed in accidents by a priori methods. Having in mind the limitations discussed above, the macrocomponent reaction schemes developed in the present study proved to give quite reliable indications on the possible hazardous products for all the accidents examined. However, the results obtained by lumping techniques may be further refined. Other factors may be taken into account in order to obtain less generic information on the hazardous products of concern that may be formed. One of the more important of these factors was found to be the accident scenario. As a matter of fact, three distinct and quite well defined scenarios were found to cause the unwanted formation of hazardous substances as a consequence of ‘out of control’ conditions. These were: runaway reactions (125 accidents over 406 in EUCLIDE database), fires involving chemical substances (203 accidents), and unwanted reactions (78 accidents). The characteristics of fires and runaway reactions are well known. ‘Unwanted reaction’ accidents were defined as the accidental interaction of two reacting compounds, generally originated by the erroneous mixing of substances that react violently. A typical example of this kind of accidents is the accidental mixing of hydrochloric acid and sodium hypochlorite that causes the formation of chlorine. Further details on accident scenarios are reported elsewhere [18].

The different characteristics of the accident scenarios are likely to influence the chemical processes that take place during the accident. Fig. 4 shows the data obtained from EUCLIDE database for PCDD, phosgene, chlorine and hydrogen cyanide. The influence of the accident scenario can be observed comparing the data reported in the figure for the three chlorinated compounds. PCDD and phosgene are formed mainly in runaway and fire accidents, while chlorine is formed also in a relevant number of ‘unwanted reaction’ accidents. The influence of accident scenario is mainly due to the different system conditions during the accident. In particular, runaway and fire accidents usually cause the system to reach higher values of temperature and pressure with respect to ‘unwanted reaction’ accidents. Although the chemical pathways involved in the heat generation during fires and runaway reactions may be widely different, the more severe temperature and pressure conditions achieved during these accidents are likely to result in more drastic changes in the chemical structure of the substances involved. Thus, in spite of the very different conditions experienced in runaway reactions and fires, it may be expected that both these accident types may frequently cause the formation of substances of quite complex chemical structure as dioxins.

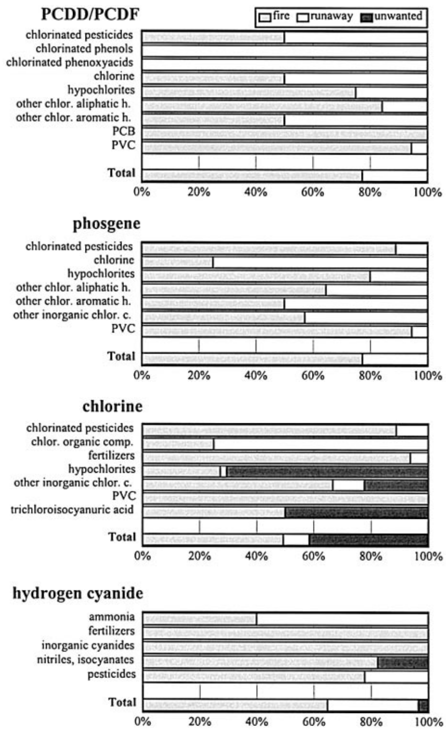

Fig. 4. Accident scenarios causing the unwanted formation of hazardous substances from different precursors.

Therefore, the hazardous substances that may be formed in a given chemical system in ‘out of control’ conditions may be strongly influenced by the accident scenario that is more likely to take place. The different ranges of system conditions may allow quite specific reactions to take place. This is the case of PCDD formed in runaway conditions from chlorinated phenols, or of chlorine formed from hypochlorites and hydrochloric acid in ‘unwanted reaction’ accidents. Moreover, also the precursors of the hazardous substances formed in the accident are different in the different types of accident. In Fig. 4, the relative importance of the accident scenarios is reported for the precursors of PCDD, phosgene, chlorine and hydrogen cyanide. The figure clearly shows, i.e. that chlorophenols are likely to cause the formation of PCDD mostly in runaway accidents, while poly-chloro-biphenyls (PCB) in fire accidents. This is caused by two factors: the specific reaction conditions associated to the different accident scenarios; and the characteristics of industrial activities or operations involving the different precursors, that in turn influence the accident scenario that is more likely to take place. The accident scenarios that may take place in a process plant can be identified using well-known hazard analysis techniques, as hazop and event trees. Thus, knowing the components of a chemical system and the more likely accident scenarios, the data shown in Fig. 4 may be used to identify the hazardous substances whose formation is more probable within those identified by macrocomponent reaction schemes.

4.3. Severity index of accidents involving the formation of hazardous substances

The identification of the precursors of hazardous substances formed in industrial accidents is important not only for the scientific and technological aspects of the problem, but also for the application of the legislation for the control of major accident hazards. In particular, Directive 96/82/EC states that also the substances that ''may be generated during loss of control of an industrial chemical process'' should be considered as present in the establishment inventory. Therefore, the identification and the hazard ranking of the specific precursors of dangerous substances is of fundamental importance for the correct implementation of the Directive.

The risk related to the different precursors is dependent on two factors: (i) the frequency of accidents involving the precursor; and (ii) the severity of these accidents. The first factor is mainly related to the industrial importance of the precursor (i.e. expressed by the global production per year). Frequencies of accidents involving the precursors may be evaluated using the data obtained from EUCLIDE, as those shown in Fig. 3.

On the other hand, accident severity is mostly related to the hazard of the products formed in 'out of control' conditions and to the yields that should be expected in accidents. Accident severity data are more difficult to obtain. The definition of either a hazard rating of chemical substances and of a generally accepted accident gravity scale are still open problems [25]. Furthermore, data on accident consequences are often not precise or omitted in accident reports.

An attempt was made in order to point out the differences in accident consequences with respect to the hazardous substances that were formed. Fig. 5 reports the consequences of the accidents involving the formation of PCDD, phosgene, hydrogen cyanide, chlorine and hydrogen chloride. In the figure, for each of the hazardous substances considered, the percentage of accidents that caused the evacuation of population, traffic disruption or ground/water contamination are reported. These were the only reliable data on consequences that could be obtained, also because the number of accidents involving fatalities was too low to yield significant data. Nevertheless, it can be observed from the figure that limited differences in the data on accident consequences are present with respect to the different hazardous substances formed. Thus, it may be concluded that the data available do not allow an hazard ranking directly based on accident consequences.

An alternative method for the hazard ranking of the substances formed in the accidents may be based on the criteria given by Annex I of Directive 96/82/EC for the identification of dangerous substances to be considered in the control of major accident hazards. As discussed above, the threshold quantities given in Annex I for the different hazardous substances and substance classes may be used as an indirect hazard ranking of the substances considered. A severity index of the accidents involving the formation of hazardous substances may thus be defined as the sum of the ratios between the quantities formed in the accident and the thresholds with respect to the Directive:

$$SI = \sum_{i=1}^{n} \frac{q_i}{T_i} \qquad (1)$$

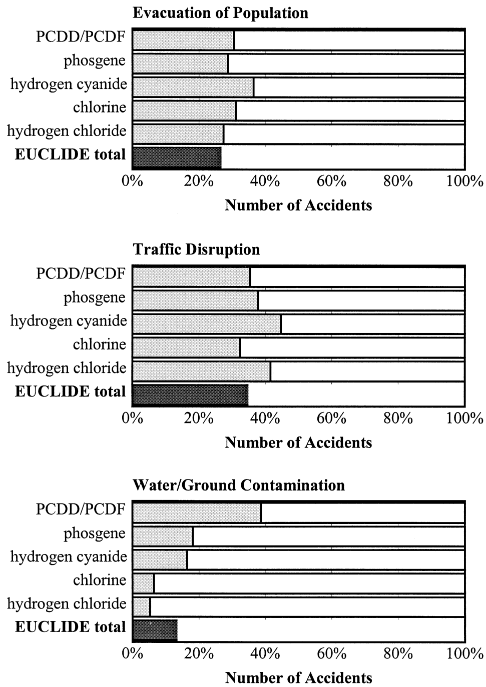

Fig. 5. Consequences of accidents involving the unwanted formation of different hazardous substances.

where SI is the index of accident severity, q_i is the quantity of substance i formed in the accident, and T_i substance i threshold value for the application of articles 6/7 of the Directive, given in Annex I. Unfortunately reliable information on the quantities of hazardous substances formed in the accidents could be obtained from accident data only for a limited number of events [1,6]. Fig. 6 reports the calculated severity index for 21 accidents involving the formation of chlorine and for 11 accidents involving the formation of phosgene, for which it was possible to estimate the quantities of hazardous substances actually formed. The figure shows the accident fraction (expressed as a ratio between the number of accidents, N, and the total number of accidents examined, N_t) with respect to the severity index. As expected, the values of the severity index are higher for accidents involving the formation of phosgene. The presence of a maximum in the curves is probably due to the under-reporting of low severity accidents.

It is interesting to observe the effect of the quantities of hazardous substances formed in the accidents, and thus of accident severity, on the application of 'Seveso-II' Directive. As discussed above, Directive 96/82/EC requires that also the dangerous substances formed in the loss of control of processes are taken into account in site hazard evaluation. Therefore, if the quantities of hazardous substances formed are higher than the threshold values given in Annex I, the requirements of Articles 6 and 7 or 9 of the Directive shall be applied to the site even if in normal conditions the thresholds are not exceeded. Although only for a small number of accidents enough data were reported,

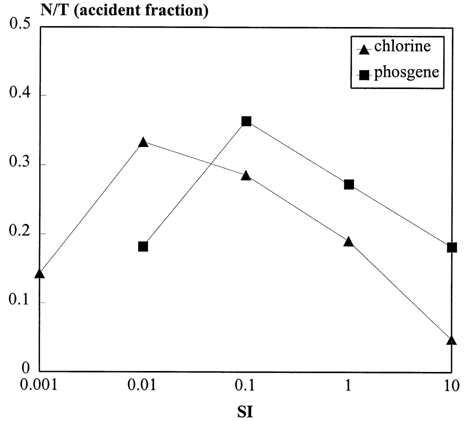

Fig. 6. Accident severity index calculated for 21 accidents invoving the unwanted formation of chlorine and for 11 accidents involving the unwanted formation of phosgene.

the effect of the formation of several hazardous substances on plant classification was estimated. The results are shown in Fig. 7. The figure reports the percentage of accidents (calculated on the events for which sufficient information was available) in which the unwanted formation of PCDD, phosgene, chlorine and hydrogen cyanide took place and resulted in the formation of quantities of substances above the thresholds given in Annex I, thus affecting Directive application to the site. As expected, the formation of the more hazardous substances as PCDD and phosgene, having lower threshold values, resulted more frequently in effects on plant classification. Furthermore, the results reported show that the potential formation of hazardous substances shall not be neglected in the application of the Directive.

4.4. Hazard ranking of precursors of dangerous substances formed in accidents

The severity index defined in Eq. (1) may be used to compare the hazards due to the unwanted formation of different dangerous substances. However, even more important with respect to the application of Directive 96/82/EC is the hazard ranking of the precursors of hazardous substances. In normal operating conditions, only the potential

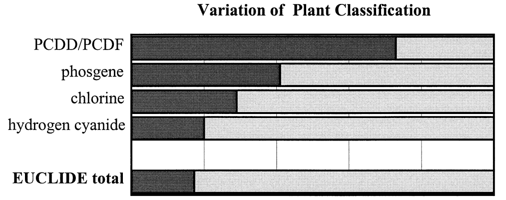

Fig. 7. Changes in plant classification with respect to Directive 96/82/EC due to the formation of hazardous substances in accidental events causing 'out of control' conditions.

precursors are present in the chemical system. Thus, the presence of the precursors in the site inventory is the starting point in the evaluation of the hazards due to the possible formation of dangerous substances in the loss of control of chemical systems. Data reported in Figs. 3 and 4 may be used to identify the more important precursors of the hazardous substances that were formed in the accidents. However, in the hazard ranking of the precursors, the yield of dangerous products that should be expected is a very important factor. An example is given by the data on the precursors of PCDD reported in Fig. 3. From the figure it can be observed that PVC and chlorinated aliphatic hydrocarbons are the precursors that more frequently yielded dioxins in accidental events. This is probably caused by the wide use of these compounds in the activities of chemical industry. On the other hand, chlorinated phenols and PCB are involved in a lesser amount of events, but the yields of PCDD generated in these accidents are probably much higher, and thus are likely to result in more critical accidents. As a matter of fact, in the accident of Seveso [26], presently the more severe accident reported involving the formation of PCDD, the precursor of PCDD was 2,4,5-trichlorophenol.

Data on the quantities of hazardous substances formed in the accidents from the different precursors are scarce. Furthermore, information is present on a limited number of events and thus may not be significant to correctly evaluate at least the order of magnitude of the yields that should be expected. The yields of hazardous substances likely to be formed from the different precursors should be estimated by other methods, i.e., using available experimental data obtained from medium and large scale experiments [27,28]. The organization of data present in the literature on expected yields of hazardous products is the object of the current work of the authors. Although this is a quite complex task, the availability of at least indicative values of the yields may be used to evaluate the hazard of the precursors. Combining the hazard ranking of dangerous substances based on the criteria given in Annex I with data on the expected yields, a rough risk index of the precursors may be obtained. This may be defined, on the basis of the threshold quantity values given in Annex I of the Directive, as:

$$R^* = 1 - \frac{M_u}{My} \tag{2}$$

where R^* is the risk index, M_u is the threshold value for the application of Articles 6 and 7 expressed in kilomoles of the unwanted product, M the corresponding threshold value of the precursor, y the estimated yield (defined as the molar fraction of the precursor converted to the hazardous product). The values of M and M_u may be calculated from the threshold values reported in Annex I using the following expression:

$$M = \frac{T}{\mathrm{MW}} \tag{3}$$

where T is the threshold value in t reported in Annex I and MW is the molecular weight of the compound expressed in t/kmol.

Since the values of y are between 0 and 1, the values of the risk index R^* range between $-\infty$ (for $y \to 0$ or $M_u \gg M$) and 1 (for $M_u \ll My$). M is the maximum quantity of precursor, expressed in moles, that may be present in a chemical plant or storage without causing the application of the requirements of Articles 6 and 7 (notification) of Directive 96/82/EC. Thus, My is the estimated quantity of the precursor that may be converted to the hazardous product as a consequence of an accident in an establishment to which the requirements of 'Seveso-II' Directive are not applied.

If the risk index ranges between $-\infty$ and 0 (and thus: $M_u \geqslant My$) the possible formation of the hazardous substance from the precursor is of limited concern, at least following the criteria given in the Directive. In this range of R^* values, the quantity of hazardous substances that may be formed in an accidental event is estimated to be under the threshold for the application of Directive requirements. However, plant classification may change due to the summation criteria introduced by the Directive even if the quantity of hazardous substances formed is under Directive thresholds.

On the other hand, when the risk index ranges between 0 and 1, the hazards due to the formation of the dangerous substances should be considered of great concern. If $0 < R^* \leqslant 1$ then $M_u < My$. Therefore, in this range the estimated quantity of hazardous substance that may be formed in an accidental event is above the Directive thresholds and, applying the criteria given in Article 2, is sufficient to change the site classification with respect to the Directive.

The values of R^* calculated assigning an arbitrary value of $y = 0.1$ to the yield are reported in Table 2 for several possible precursors of phosgene. A value of $T = 5 \times 10^5$ t (corresponding to the maximum value of T present in Annex I multiplied by 100) was used to calculate M when the precursor was not considered in Annex I of Directive 96/82/EC. The differences in the risk index present in the table are due only to the differences in the threshold values and molar weights of the different precursors, since the same value of the yield was used. Thus, precursors classified 'very toxic' by Directive 67/548/EEC, as some chlorinated pesticides (i.e. chlorfenvinphos), have a risk index lower than less hazardous substances as trichloroethylene. This should be expected, since using Eq. (2) the hazard of precursors was defined as a function of the difference in the hazard classification of the substance formed with respect to that of the precursor. Obviously, the use of estimated yield values may introduce important differences even for the precursors having the same hazard classification.

Table 2
Hazard ranking of possible precursors of phosgene ($T_u = 0.3$ t; $M_u = 3.03$ kmol)

Substance	CAS	Substance type	Classification	T (t)	M (kmol)
Chlorfenvinphos	470-90-6	Pesticide, phosph. ester	T+, N, R24, R28, R50/53	5	13.9
Chlorthalonil	1897-45-6	Pesticide	Xn, R40	n.c./5×10^5	3.85×10^6
Ethylene dichloride	107-06-2	Chlor. aliphatic hydroc.	T, F, R11, R22, R36/37/38, R45	50	505.3
Lindane	58-89-9	Pesticide	T, N, R23/24/25, R36/38, R50/53	50	171.9
Tetrachloroethylene	127-18-4	Chlor. aliphatic hydroc.	Xn, R40, R51/53	500	3014.8
Trichloroethylene	79-01-6	Chlor. aliphatic hydroc.	Xn, R40	n.c./5×10^5	1.88×10^6
Vinyl chloride	75-01-4	Chlor. aliphatic hydroc.	F+, T, R12, R45	10	161.3

The proposed hazard ranking of the precursors, although valid only in the context of the application of Directive 96/82/EC, seems suitable in order to identify the precursors of most concern with respect to the formation of hazardous products in the loss of control of chemical systems.

5. Conclusions

The data on accidental events involving the formation of hazardous substances in ‘out of control’ conditions present in a specifically developed database were analyzed in order to identify the substances and the substance classes more frequently formed in these accidents. The accident scenario resulted one of the more important factors influencing the hazardous substances formed in the accidents.

A lumping approach was used to develop macrocomponent reaction schemes for the identification of the possible hazardous products that may be formed in the loss of control of a chemical system. The macrocomponent reaction schemes were tested using accident data. The results obtained from accident analysis confirmed that lumping analysis gives quite reliable indications for the preliminary identification of the possible hazardous products formed in the accidents examined. However, lumping approach has some limitations: the composition of the chemical system should be exactly determined, and the influence on hazardous product yields of factors as temperature, pressure and intermediates persistency may be underestimated. Thus the use of macrocomponent schemes should be combined to other information as the characteristics of the chemical system in normal operating conditions and data on the likely accident scenario. These may be used to obtain reliable information on the hazardous products that may be formed in the loss of control of the system.

An accident severity index was proposed for the unwanted formation of hazardous compounds. The precursors of the hazardous substances formed in the accidents were identified. A hazard ranking of the precursors was developed in the context of Directive 96/82/EC application. The results obtained show that both the severity index and the precursor hazard ranking proposed seem to be acceptable tools for the description of the characteristics of accidents involving the formation of dangerous substances as a consequence of ‘out of control’ conditions.

Even if important topics in the field still need to be addressed, as the availability of reliable values of the yields of hazardous substances in accidental events, the results obtained may be a first step to orient further work in the field. The approach proposed proved to be effective at least to obtain some preliminary information on the more hazardous products that may be formed in accidental events, also in the perspective of the application of Article 2 of Directive 96/82/EC.

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