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Formation of hazardous compounds by unwanted reactions in industrial accidents

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Abstract

'Unwanted reactions' caused by the accidental contact of reactive substances may result in either physical effects, such as fire or explosions, or chemical effects, as the formation and release of hazardous reaction products. To help to develop criteria for identifying such reactions, a number of industrial accidents caused by 'unwanted reactions' were analyzed. The chemical systems more frequently involved in these accidents and the substances released were identified. The process operations during which the accidents took place and the immediate causes of the accidents were also examined. Simple criteria for the identification of hazard conditions with respect to 'unwanted reaction' accidents were derived from European Council Directive 67/548/EEC for the classification, packaging and labelling of dangerous substances. The validity of these criteria was verified using the data on accidental events.

Keywords: Hazardous substances; Accident analysis; Hazard criteria; Chemical hazards; Unwanted reactions

1. Introduction

Chemical reaction hazards are important elements of the risk connected to the handling of chemical substances. A relevant amount of work is reported in the literature on the study of the physical effects (fires, explosions, etc.) caused by the accidental contact of reacting substances (i.e. see Lees [1] and references cited therein). Several

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criteria are reported for the identification of categories of these 'incompatible' substances, and are widely used, i.e. for the arrangement of storages of chemical substances. However, less attention has been given to the development of criteria for the prevention of chemical effects, such as the formation of hazardous substances. This was possibly because these hazards are difficult to foresee and prevent using general criteria. In fact, a wide number of combinations of chemical substances are present that may result in the unwanted formation of hazardous compounds in 'out-of-control' conditions. However, European Council Directive 96/82/EC (commonly referred to as the 'Seveso-II' Directive) on the control of major accident hazards involving dangerous substances [2] was recently adopted by the European Council. The Directive requires to take into account these effects, stating that ''the presence of dangerous substances shall mean the actual or anticipated presence of such substances in the establishment, or the presence of those which it is believed may be generated during loss of control of an industrial chemical process''.

This paper is focused on the analysis of the hazards coming from the unwanted formation of hazardous substances as a consequence of the accidental mixing of 'incompatible' compounds in industrial accidents. A relevant number of industrial accidents were examined. Although very simple safety criteria may be followed to prevent many of these accidents, they were found to be still an important cause of injuries and damages. The characteristics of the chemical system involved in these accidents and of the substances formed by 'unwanted reactions' were studied. The results were used to identify the categories of reactive substances that should be considered of major concern with respect to the unwanted formation of hazardous compounds.

This study was carried out as a part of a more general research project concerning the analysis of the hazards caused by the unwanted formation of dangerous substances in accidental events with respect to the implementation of the European Council Directive 96/82/EC [3–5].

2. EUCLIDE database

Data on accidental events involving the unwanted formation of hazardous substances by unforeseen reactions were obtained from the literature and interrogating the four more important European databases of industrial accidents [5]: ARIA, managed by the BARPI, a sector of the French Ministry of the Environment; FACTS, managed by the TNO (NL); MARS, run by the Major Accident Hazards Bureau of the European Community (I); and MHIDAS, managed by AEA Technology (UK) on behalf of the Health and Safety Executive. Accidental events having the following characteristics were selected:

(i) the accident should involve the formation of hazardous substances not present on the site in normal conditions;

(ii) the accident should involve substances used in the chemical industry (i.e., raw materials, intermediates, final products); and

(iii) sufficient data on the chemical system involved in the accidental event (i.e. substances involved and released) should be reported in accident description files.

A specific database (named EUCLIDE: Emission of Unwanted Compounds Linked to Industrial Disasters and Emergencies) was developed in order to organize and analyze the data on the 406 accidental events selected. Information on the chemical characteristics and the hazard classification of the about 300 substances involved in the accidents was also included in the database. Further details on database characteristics are reported elsewhere [3].

All the data on accidental events and on substances involved shown below were obtained from EUCLIDE database. As most of the other existing accident databases, EUCLIDE includes only a limited number of accidents. Therefore, all the information on frequencies that may be obtained from the data given below should be considered only as indicative values. However, a quite high number of accidental events with similar characteristics was included in EUCLIDE database. Thus, it is believed that the analysis of these data may be significant, at least from a qualitative point of view.

3. Results and discussion

3.1. Accidental scenarios causing the formation and the release of hazardous compounds

The analysis of the accidents included in the EUCLIDE database allowed the identification of three quite different scenarios leading to the unwanted formation of hazardous compounds as a consequence of the 'loss of control' of an industrial facility. These were: (i) fires, (ii) runaway reactions, and (iii) unwanted reactions.

A detailed analysis of the different accident scenarios is reported elsewhere [5]. The characteristics of fires and runaway accidents are well-known and will not be further discussed. 'Unwanted reaction' accidents were defined in this study as the consequence of the accidental reaction of 'incompatible' substances, and were shown to involve mainly inorganic compounds. These events usually originated from the erroneous mixing of substances that react violently, thereby generating heat.

It is clear that from a general point of view, the identification of the hazards caused by the unwanted formation of dangerous substances is very complex. The chemical reactions that may take place during fire and runaway accidents are quite difficult to foresee. System conditions during the accidents may cause drastic changes in the structures of chemicals involved. Furthermore, the chemical complexity of the systems involved in runaway or fire accidents is high. Both these factors require the development of specific techniques for the identification of hazardous products that may be formed in these accidents. A preliminary approach to this problem is reported elsewhere [6] and will not be discussed in this paper.

However, a significant number of the accidents included in the EUCLIDE database (78 out of 406) were found to be caused by 'unwanted reactions', even if these accidents seem to be more simple to analyse and prevent. Accidents caused by 'unwanted reactions' are a subset of data with many common features. A separate analysis of this

kind of accidents will be presented below, in order to identify the categories of substances that should be considered of concern with respect to these events.

3.2. Characteristics of 'unwanted reaction' accidents

'Unwanted reaction' accidents were mainly caused by the accidental contact of reacting substances. Not surprisingly, these accidents took place mainly during transfer operations in chemical plants, as shown in Fig. 1. A relevant number of accidents also took place during transport, as a consequence of the loss of containment, or during storage, mainly as a consequence of contamination. The immediate causes of these accidents were mainly operator errors, as shown in Fig. 2. The results shown in Figs. 1 and 2 point out that 'unwanted reaction' accidents arose mainly from the neglect of safety measures and from the inexperience and insufficient training of the operators.

Table 1 lists the substances present in the chemical systems involved in the accidents. Only a limited number of chemicals were found to undergo this kind of accident. While about 300 substances are present in the EUCLIDE database, only about 50 were involved in 'Unwanted Reaction' accidents. However, the substances more frequently involved in these events have a wide use in the chemical industry and also in other activities (water treatment plants, swimming pools, etc.).

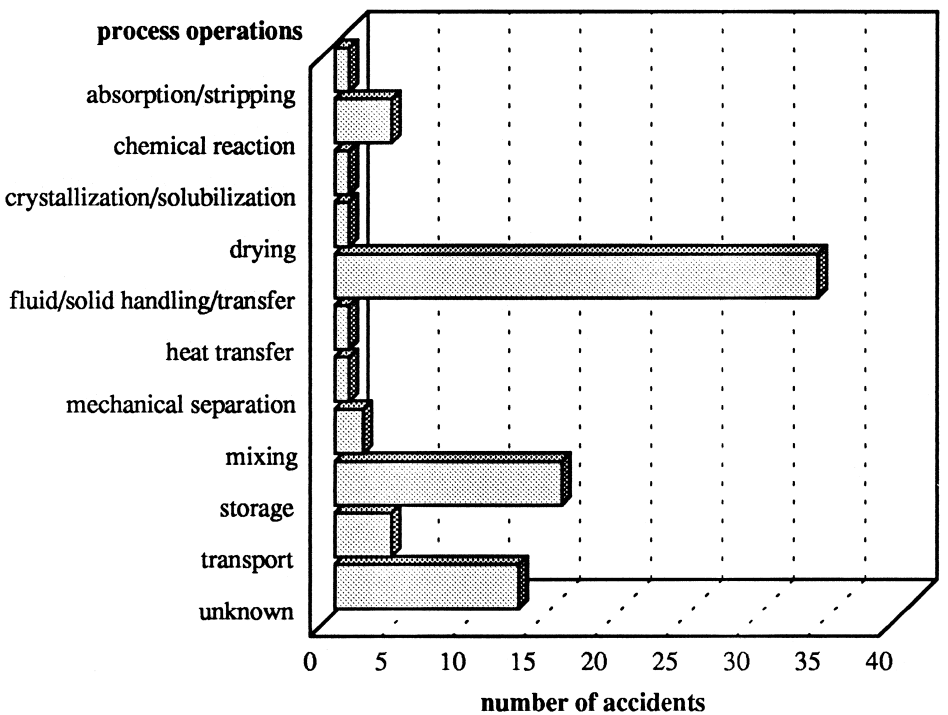

Fig. 1. Process operation during which 'unwanted reaction' accidents took place.

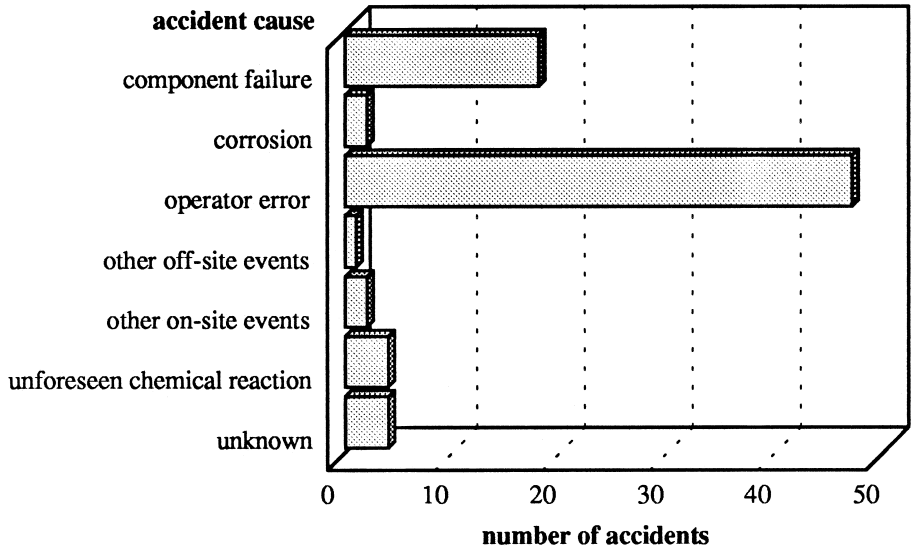

Fig. 2. Immediate causes of 'unwanted reaction' accidents.

As shown in the table, 'unwanted reaction' accidents usually involve substances of quite simple structure and of low molecular weight. The exothermic reactions that started the accidents resulted from the direct or indirect (i.e. by decomposition reactions caused by the temperature rise) formation and release of hazardous products. The very simple chemistry of the reactions that took place in these accidents caused the almost complete conversion of the substances involved to the unwanted products.

The substances that were formed in the 'unwanted reaction' accidents included in the EUCLIDE database are listed in Fig. 3. The figure shows the number of events in which the formation of these compounds was detected. The total number of events in which the formation of the substance was likely due to the characteristics of the chemical system involved in the accident was also reported.

Among the substances more frequently formed in 'unwanted reaction' accidents, there are chlorine, hydrogen chloride, nitrogen dioxide, and sulphur trioxide. However, other very hazardous compounds as hydrogen cyanide, hydrogen fluoride, hydrogen sulphide, and arsine were formed in the accidents.

The problem of the formation of hazardous substances in industrial accidents is important, not only from the scientific and technological point of view, but also for the application of the European legislation. Article 2 of Directive 96/82/EC, reported above, requires to consider the hazards due to 'dangerous' substances (identified in Annex I of the Directive) actually present in the establishment inventory or likely to be formed in the 'loss of control' of a process. An example will better illustrate this point. A typical accident caused by an 'unwanted reaction' is the inadvertent mixing of hydrochloric acid and sodium hypochlorite. This may result in the formation of chlorine with yields that may be considered stoichiometric. Neither hydrochloric acid nor sodium hypochlorite (substances actually present) is considered in Annex I of the Directive.

Table 1
Substances involved in 'unwanted reaction' accidents

Substance	Classification (Directive 67/548/EEC)		Number of events
	Hazard label	Risk phrases (R)	
acetic acid	C	10, 35	1
acetic anhydride	C	10, 35	2
acetone	F	11	1
acetone cyanohydrin	N, T+	26/27/28, 50	1
acrylonitrile	F, T	11, 23/24/25, 38, 45	1
aluminum chloride	C	34	1
aluminum sulphate	Xn	20/21/22	1
aluminum		10, 15	1
ammonia	T	10, 23	1
ammonium dichromate	E, N, T+	1, 8, 21, 25/26, 41, 43, 46, 49, 50/53	1
ammonium nitrate	O, Xi	8, 36/37/38	1
ammonium thiocyanate	Xn	20/21/22, 32	1
arsenic	T	23/25	1
beryllium	T+	25, 26, 36/37/38	1
bromine	T+	26, 35	1
butyl acetate	F	11	1
calcium carbide	F	11, 15	1
calcium hypochlorite	C, O	8, 31, 34	4
chlorine	T	23, 36/37/38	1
chlorosulphonic acid	C	14, 35, 37	4
dimethyldichlorosilane	F, Xi	11, 36/37/38	1
ferric chloride	C, Xn	20/21/22, 34	2
formic acid	C	35	1
hydrochloric acid	C	34	17
hydrofluoric acid	C, T+	26/27/28, 35	1
hydrogen peroxide	C, O	8, 34	2
lithium aluminum hydride	F	15	1
methyltrichlorosilane	F, Xi	11, 14	1
nitric acid	C, O	8, 35	11
phosphorus trichloride	C	34, 37	1
potassium bichromate	N, T+	21, 25, 26, 37/38, 41, 43, 50/53	1
silicon tetrachloride	Xi	14, 36/37/38	2
sodium bifluoride	C, T	25, 34	1
sodium bisulphite	Xn	20/21/22, 36/37/38	1
sodium hydrosulphite	Xn	7, 22, 31	3
sodium hydroxide	C	35	2
sodium hypochlorite	C	31, 34	27
sodium nitrate	O, T	8, 23/24/25	2
sodium nitrite	O, T	8, 25	1
sodium sulphate	Xi	36/37/38	1
sulphur	Xi	36/37/38	1
sulphur chloride	C	14, 34, 37	1
sulphuric acid	C	35	12
tin tetrachloride	Xi	14, 34, 37	1
titanium tetrachloride	C, Xi	14, 34, 36/37	2
trichlorisocyanuric acid	O, Xn	8, 22, 31, 36/37	1
zinc		10, 15	1

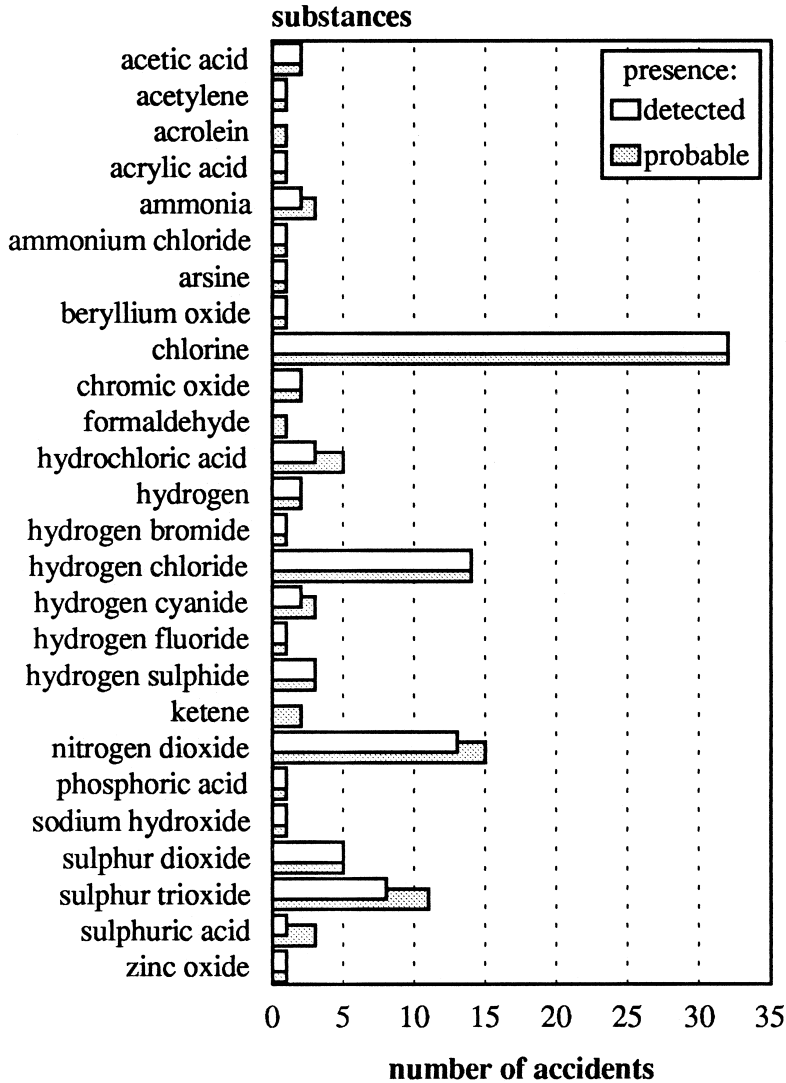

Fig. 3. Substances formed in 'unwanted reaction' accidents.

Thus, these substances should not be included in the establishment inventory. However, chlorine (likely to be formed as a consequence of the loss of control of the process) is considered in Annex I of the Directive with thresholds of 10/25t for the application of the requirements in Articles 6/7 and 9, respectively. Thus, also considering the summative criteria introduced by the Directive, an establishment may fall under the requirements of the Directive as a consequence of the presence of sodium hypochlorite and hydrochloric acid, since these substances may form chlorine as a consequence of

'the loss of control of an industrial chemical process'. Therefore, general criteria for the identification of chemical systems likely to undergo the formation of hazardous substances in 'out-of-control' conditions will be needed for the correct implementation of the Directive. It's worth noting, however, that exactly what should be considered as an 'industrial chemical process' could possibly be better defined. A relevant number of 'unwanted reaction' accidents took place in storage installations, to which the application of Article 2 is not clear [5].

3.3. Criteria for the identification of hazardous conditions with respect to 'unwanted reactions' accidents

The quite simple chemical structure of the compounds usually involved in 'unwanted reaction' accidents reduces the possible reaction pathways in the chemical system that undergoes the accident. Thus, the number of unwanted hazardous products that may be formed is also limited. Furthermore, 'unwanted reaction' accidents generally take place during fluid handling and transfer. Since no relevant external energy source is usually present during transfer operations, unwanted reactions should have a low activation energy. The possible reactions that may take place in 'out-of-control' conditions are further reduced by these factors. Both these elements confirm that the criteria for the identification of hazardous substances generated in 'unwanted reaction' accidents should be different and may allow for a simplified approach with respect to that proposed for 'fire' and 'runaway reaction' accidents.

Table 1 reports the classification of the substances involved in 'Unwanted Reaction' accidents with respect to the European Council Directive 67/548/EEC [7]. Table 2 reports the meaning of the hazard symbols and risk phrases used in Table 1. Almost all the substances in the table may be considered hazardous. Many have corrosive or irritant characteristics due to their acid or basic properties, while others are oxidizing or flammable.

Criteria for the identification of categories of incompatible substances may be obtained on the basis of the hazard categories given by European Council Directive 67/548/EEC for the classification, packaging and labelling of dangerous substances [7]. The Directive may be used to evaluate the dangerous reaction potential of the different combinations of substances. This is directly related to the hazard of 'unwanted reaction' accidents, since the severity of the accidents depends mainly on the quantities of substances involved, as found in the analysis of accidental events.

Two different hazard levels with respect to the unwanted formation of dangerous substances may be identified: (i) nonspecific hazard, and (ii) specific hazard.

The nonspecific hazard condition arises when categories of 'incompatible' substances are simultaneously present on a chemical plant: substances classified as 'Flammable' together with 'Oxidant'; or substances with acid properties together with substances with basic properties, both usually classified as 'Corrosive' or 'Irritant'. The unwanted contact of these substances may cause exothermic reactions that have low activation energies.

The simultaneous presence of substances belonging to incompatible categories is a well-known hazard. The inadvertent and uncontrolled contact of these substances may

Table 2
Hazard symbols and risk phrases of substances listed in Table 1

Hazard	
C	corrosive
E	explosive
F	flammable
N	dangerous for the environment
O	oxidizing
T	toxic
T+	very toxic
Xi	irritant
Xn	harmful
Risk phrase	
1	explosive when dry
8	contact with combustible material may cause fire
10	flammable
11	highly flammable
14	reacts violently with water
15	contact with water liberates extremely flammable gases
20	harmful by inhalation
21	harmful in contact with skin
22	harmful if swallowed
23	toxic by inhalation
24	toxic in contact with skin
25	toxic if swallowed
26	very toxic by inhalation
27	very toxic in contact with skin
28	very toxic if swallowed
29	contact with water liberates toxic gas
31	contact with acids liberates toxic gas
32	contact with acids liberates very toxic gas
34	causes burns
35	causes severe burns
36	irritating to eyes
37	irritating to respiratory system
38	irritating to skin
41	risk of serious damage to eyes
43	may cause sensitization by skin contact
45	may cause cancer
46	may cause heritable genetic damage
49	may cause cancer by inhalation
50	very toxic to aquatic organisms
53	may cause long-term adverse effects in the environment

be the cause of an accident. The accident may lead to the unwanted formation of dangerous compounds in ‘out-of-control’ conditions, although this possibility also depends on the characteristics of the substances involved.

The analysis of the risk phrases given by European Council Directive 67/548/EEC also identifies a specific hazard condition, related to the unwanted formation of

hazardous substances. This is given by the simultaneous presence of substances with acid properties and of substances to which risk phrase (R) 31 (contact with acid liberates toxic gas) or R32 (contact with acid liberates very toxic gas) is given. The latter, which is simply derived from the classification scheme in the Directive, identifies a specific chemical hazard derived from the simultaneous presence of these two categories of substances.

The presence of substances classified R14 (reacts violently with water), R15 (contact with water liberates extremely flammable gas), and R29 (contact with water liberates toxic gas) needs to be separately considered. All these categories of substances react with water. Since water or aqueous solutions are almost universally present in chemical plants, the presence of these substances is sufficient to create a chemical hazard. The presence of substances classified R14 and R15 results in a nonspecific hazard, comparable to that created by the simultaneous presence of flammable/oxidant or acid/basic substances. The presence of substances classified R29 creates a specific chemical hazard comparable to that resulting from the presence of acids and substances classified R31 or R32.

On the basis of European Council Directive 67/548/EEC and considering the two hazard levels identified, it was possible to obtain a hazard rating of the combinations of the different substance categories. This refers to the hazards due to chemical effects, and specifically to the unwanted formation of hazardous substances. Four different hazard ratings were given, ranging from low to extremely high on the basis of the evaluated reaction potential and of the possible unwanted formation of hazardous substances. The results of this analysis are shown in Table 3(a).

Table 3(b) shows the distribution of the 'unwanted reaction' accidents examined with respect to the hazard categories of the substances involved. Sixty out of the 78 accidents were the consequence of the two hazard conditions defined above. Thirty-two of these were caused by the contact of acids with substances classified R31 and R32 (specific hazard). Twenty-seven accidents started from the contact of flammable/oxidant, acid/basic substances or by substances classified R14 or R15 (nonspecific hazard).

Therefore, the simple hazard conditions derived from Directive 67/548/EEC may explain almost all the 'unwanted reaction' accidents. Great attention is usually paid to the prevention of contacts between flammable/oxidant and acid/basic substances. However, the chemical hazards derived from substances classified R29, R31, or R32 were possibly underestimated. The high number of accidents involving substances classified R31, R32, or R29 (32 of the 78 accidents examined in the present study) and the severity of the chemical effects following the accident, resulting in the formation and release of hazardous gaseous compounds, suggests that improved risk management strategies should be applied to the storage and handling of these substances. The careful evaluation of the procedures used for the storage, handling and transfer of substances, and of the adequacy of safety systems is of fundamental importance in order to estimate the possibility of 'unwanted reaction' accidents due to accidental mixing of reactive substances, and to limit the severity of the consequences.

The presence of 'unwanted reaction' hazards and in particular of R29, acid/R31, acid/R32 categories of substances in an industrial establishment should be considered for the complete application of Article 2 of European Council Directive 96/82/EC. If

Table 3
Hazardous conditions with respect to 'unwanted reaction' accidents (a) and number of accidents in EUCLIDE database for each hazard condition (b)

(a)

F	m					
O	h	m				
A	u	u	m			
B	u	u	h	l		
R14 R15	u	u	u	u	h	
R31,32 R29	u	u	e	l	u	e
hazard	F	O	A	B	R14 R15	R31,32 R29

(b)

F	3					
O	4	8				
A	-	-	4			
B	-	-	7	-		
R14 R15	-	-	-	-	16	
R31,32 R29	-	1	32	-	-	3
hazard	F	O	A	B	R14 R15	R31,32 R29

Symbol: l, low; m, medium; h, high; e, extremely high; u, unknown on a general basis (to be evaluated on a case-by-case approach).
Hazard: A, acid; B, basic; F, flammable; O, oxidant; R, risk phrase (see Table 2).

these hazards are present, the substances evolved by the accidental contact of the reactants should be considered in the site inventory, using stoichiometric ratios for the evaluation of the quantities that may be formed and released.

4. Conclusions

Details of 78 industrial accidents involving 'unwanted reactions' were extracted from the EUCLIDE database [3] and analysed. The chemical systems involved, and the hazardous substances formed, in these accidents were identified. 'Unwanted reaction' accidents were found to take place mainly during fluid and solid transfer operations.

Simple criteria for the identification of hazards due to the 'chemical effects' of unwanted reaction accidents were examined. These were derived from the hazardous substance classification given in Directive 67/548/EEC [7]. Hazards are present when substances belonging to 'incompatible' categories (flammable/oxidant, acid/basic; substances classified R14 or R15) are simultaneously present in plant inventory. A specific hazard is caused by the substances classified R29 (contact with water liberates toxic gas) or by the simultaneous presence of acids and substances classified R31 (contact with acid liberates toxic gas), or R32 (contact with acid liberates very toxic gas). Accidents involving the inadvertent contact of these compounds usually result in the formation and release of hazardous substances. On the basis of European Council Directive 67/548/EEC and considering the two hazard conditions identified, it was possible to obtain a hazard rating of the combinations of the different substance categories.

The analysis of accident data suggests that the procedures for managing the safety of storage, transport, and handling of the substances classified R31, R32, or R29 should be improved to reduce the risk from these hazards. This will be necessary also in the perspective of the application of the European Council Directive 96/82/EC [2], that requires to consider the hazards caused by the possible formation of dangerous substances in the loss of control of chemical processes.

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