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Problems of risk and safety in the chemical-forestry complex†

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Undertakings of the chemical-forestry complex in our country constitute a serious potential threat to the lives of the service personnel and the population in the adjoining regions. The principal trend in the development of such undertakings involves an increase in output from different plants, an improvement in technological parameters (temperature, pressure, and concentration), the processing of a large amount of materials, and the accumulation in technological areas of an appreciable amount of inflammable, explosive, and toxic chemicals.

This fact requires a serious analytical approach to the development of technological processes and of equipment used in the latter and also to the planning of industrial developments taking into account the consequences which may arise in incidents of various degrees of seriousness, starting from slight leakages, failure of hermetic seals in the reaction equipment, and going as far as large scale explosions and fires.

It is noteworthy that, unfortunately, in the Soviet Union there have been in this respect virtually no systematic studies based on unique scientifically well-founded principles and the results of incidents occurring in different undertakings are not considered as a whole. At best they are retained in the subdivisions of various ministries and are inaccessible. On the other hand, one cannot fail to note that in the industrially developed countries very much attention has been devoted to the problem of risk and safety, including the ecological safety of chemical undertakings— programmes are being developed at the governmental level, being financed both by the government and individual firms. For example, in the EEC countries alone three programmes have been realised recently and the fourth, concerned with problems of the safety of chemical industries and the prevention of accidents, is being carried out. A series of centres for the study and prediction of catastrophes have been created in the USA at well known universities and in major companies. Specialist journals are being published and specialists are being trained. The importance and urgency of this problem were emphasised at a conference held in 1987 in Rome, where more than 140 reports representing virtually all the industrially developed countries were delivered.

It is important to emphasise that the relevant research is based on a systematic approach to ensuring safety at all stages of planning and exploitation: in the normal, pre-accident, and accident regimes with localisation of the consequences of the accident including its organisational aspects.

The estimation of risk and the adoption of appropriate measures designed to diminish it constitute one of the main aspects of the procedures for ensuring the safety of the control of processes in devising plans for coping with accidents and in planning new industries. The stages in the assessment of risk are as follows:

1. Identification of the danger in which one usually employs "denial tree" and "events tree" methods or denials type analysis. The necessity to examine the entire spectrum of the possible types of danger (from minor frequently occurring breakdowns to major and rare accidents).

2. Analysis of the consequences of accident situations based on the mathematical models devised taking into account the severity, danger, and type of incident.

3. Analysis of the frequency of incidents in which "denials or events trees" are also used.

4. Estimation of the degree of risk as a combination of the frequency of the event and the severity of its consequences. Naturally, all the studies are being prosecuted with a wide-scale employment of computer systems.

More than 60 data banks concerning incidents in chemical undertakings as well as 120 data banks concerning dangerous chemicals are known to exist abroad at the present time. Programs for the abolition of major incidents in chemical plants for the manufacture of herbicides, in petrochemical complexes, etc. have been developed in detail. In individual instances the expenditure on the application of methods for the analysis of the risk in technological processes and industries reaches 20–25% of the total cost and yet it pays for itself in the course of a short period (5–6 years) of operation.

Unfortunately, the trends which can be clearly traced in the activities of the research organisations in the world are much less pronounced in the activities of the corresponding organisations of the Soviet Union, although the general trends in the development of the technosphere in chemical industries are approximately the same in our country. As an example, one can show that the proportion of factories and their output have been increasing in the petrochemical complexes of developed countries: in the USA, Canada, and the Soviet Union (Fig. 1).

It has to be said that petrochemical complexes constitute a very serious risk. For example, the petrochemical complex located close to Leningrad in the town of Kirishi contains approximately 500 000 tonnes of combustible petroleum products in an area of approximately 1.5 km^2. If one admits the theoretical possibility that these petroleum products can form a gas–air mixture, then the power of its overall explosion will be approximately equivalent to the explosion of a 3–5 megatonne nuclear device. Naturally, the consequences of such an accident would be felt over distances running into many tens of kilometres.

At the same time one cannot fail to note that experience gained in the work of organisations associated with the creation of specialist engineering techniques in our country and in the first place in space rocket engineering (much experience has been accumulated in a series of organisations associated with the creation of the space rocket technology in our country including the safe exploitation of both the rocket themselves and of the launching equipment) merits continuous attention specially under the conditions of the developing changes. It is now appropriate and necessary to pose the question concerning the use of this experience for reducing the degree of risk and increasing the safety of chemical industries. For example, at the State Institute of Applied Chemistry Scientific-Industrial Association (SIAC SIA‡) and also in the organisations working in cooperation with the latter, extensive researches have been conducted and are

†This seems to be a euphemism for the rocket fuel industry (Ed. of Translation).

‡Russian abbreviation NPO GIPKh (Ed. of Translation).

being conducted, including large-scale experiments, into the potential danger of chemical compounds used in specialist technology (rocket fuel, etc.). A broad spectrum of inflammable and explosive properties of various metallic and non-metallic materials is being investigated; systems have been created whereby one can analyse the possibility of the development of a thermal explosion as the most typical cause of many accidents; programs have been developed whereby it is possible to create mathematical models which effectively reproduce the real situations frequently observed in reality. Thus, detailed fundamental studies on the interaction of self-inflammable components with nitrate oxidants made it possible to demonstrate clearly the impossibility of the detonation of this system even when the components are mixed rapidly. This in turn led to a multibillion economic gain in the creation of a whole series of launching systems.

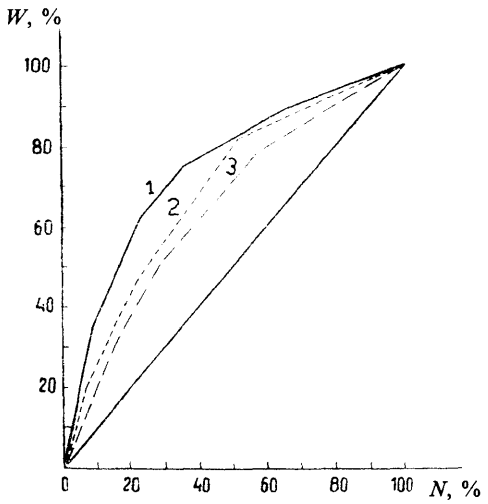


Figure 1. The increase in the power (W) and the fraction of factories (N) in petrochemical industries throughout the world: (*1*) USA, 1985; (*2*) Canada, 1984; (*3*) USSR, 1985.

In many accidents which have occurred in our country on military firing ranges and in the course of special large-scale experiments (for example, in the simulation of the break up of a rocket in the tube of a submarine) a virtually complete agreement between prediction and the real consequences of accidents of this kind was demonstrated. Detailed investigation of the transient processes in the combustion and detonation of liquid and gaseous oxygen and hydrogen led to the creation of reliable fire and explosion warning systems in the "Energy"–"Storm" complex known throughout the world.

As regards considerations with a direct bearing on chemical industries, one should note that the most typical cause of accidents is inadequate knowledge of the relevant chemistry and also of the physical processes in various stages of potentially dangerous industries. For example, in the manufacture of hydrogen peroxide by the isopropyl method (Kuibyshev) there have been several accidents of various degrees of severity associated with the fact that in the various stages of the study of this process the side products arising from the oxidation of isopropyl alcohol by hydrogen peroxide were undetected. These peroxide compounds are typical initiating explosives as regards their characteristics and their accumulation in the stagnant zones of any kind of apparatus, starting with columns and extending to pumps, inevitably leads to an accident. The understanding of the mechanism of this phenomenon made it possible to take necessary technical measures which reduced the risk and danger in this industry and in recent years we have fortunately not had any such incidents.

A similar typical error, made in the research stage, consists in the fact that sometimes no account is taken of the possibility of the formation of explosives in other systems. For example, in 1988 an explosion occurred at the Kropotkin chemical factory. Studies conducted at the SIAC SIA showed that, apart from the target reaction designed to produce polyfurite, a polyfurite–sodium perchlorate explosive mixture is also formed. Perchlorates accumulated and, in combination with the combustible substances, generated an explosive substance which was the cause of the explosion. The use of perchloric acid in this industry is the main source of risk.

The second cause of accidents is that the probability of the occurrence and thermodynamics of reactions leading to side products, whose heats are sometimes greater than that of the main reaction, are not always accurately calculated. We again refer to the experience gained at the SIAC SIA: a serious explosion with the breakup of the apparatus and of the building in the manufacture of perfluoro-oenanthic acid occurred in October, 1986 at the experimental factory in Dzerzhinsk. The heat of the main reaction, for which the apparatus was designed and in relation to which the entire technological process had been tested, did not exceed 6 kcal mol^{-1}:

$$2CF_3(CF_2)_5COOCH_3 + KBH_4 + 2CH_3OH \rightarrow$$
$$2CF_3(CF_2)_5CH_2OH + KBO_2 + 2C_2H_5OH + 6 \text{ kcal mol}^{-1}.$$

It has now been established that, together with the main reaction, there is a possibility of a side reaction between methyl perfluoro-oenanthate and potassium perborate in the presence of methanol, whose heat is 50 kcal mol^{-1}:

$$2CF_3(CF_2)_5COOCH_3 + KBH_4 + 3CH_3OH \rightarrow KF + BF_3 +$$
$$+ C_6F_{14} + C_3F_8 + H_2O + 6CO + 4CH_4 + 2H_2 + 50 \text{ kcal mol}^{-1}.$$

The reaction takes place when the synthetic process is carried out in a reactor whose size differs significantly from that of the analogous reactor used in the laboratory method and leads to a thermal explosion in air of the products of the synthesis.

In research and particularly in planning studies, very little account is taken of secondary factors in accidents. In particular, the failure of the hermetic seal in a 50 m^3 vessel (and this is still a very small volume) filled with a combustible gas, for example, natural gas or any other hydrocarbon, leads to burns and damage felt over a distance of approximately 3 km.

Fig. 2 presents curves for the variation of pressure in the shock wave front on detonation and the explosive pulse in this case. Here no account was taken of the fact that many factors — temperature inversion, wind, accidental ground features, secondary fragments, etc. — make an additional "contribution" and intensify the effect of the explosion and hence must be taken into account in assessing the risk of a real accident of this kind.

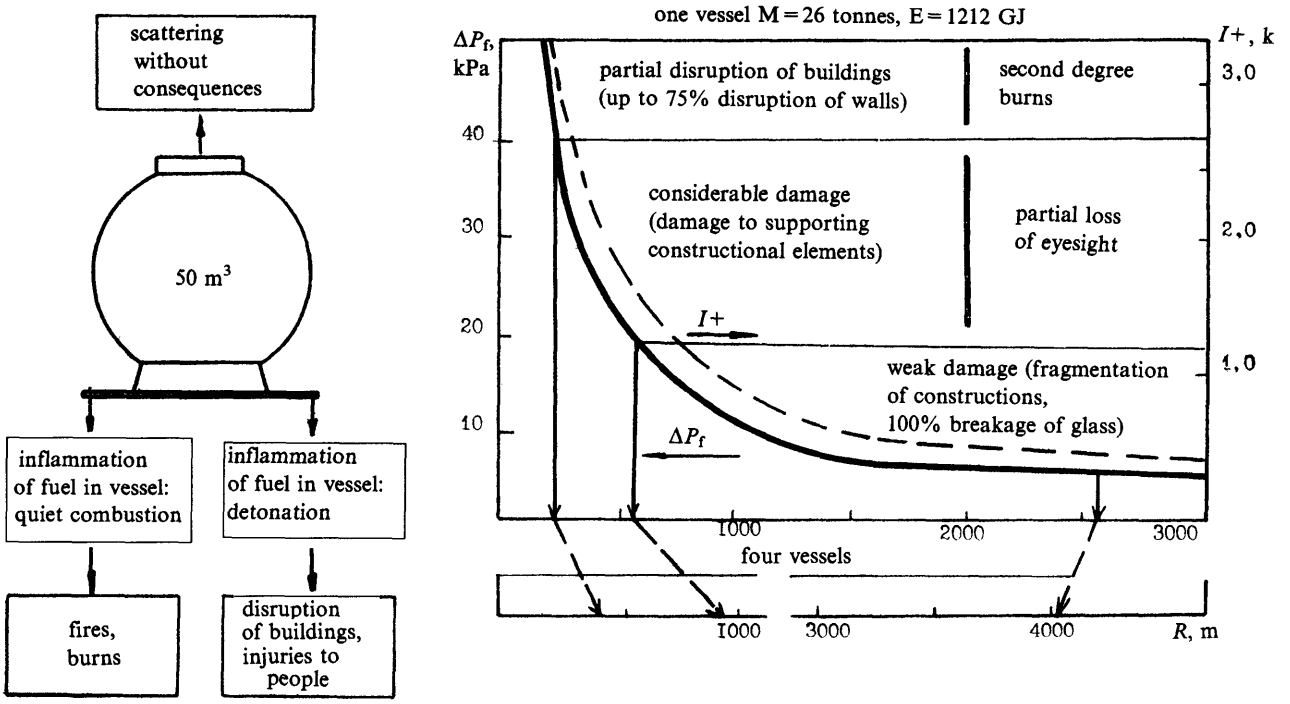


Figure 2. Danger of failure of the hermetic seal and explosion of a container (V = 50 m^3); Δ_{p_f}, change in pressure in shock wave front; I, explosion pulse; R, radius of action.

The pollution of the environment by chemical products during various accidents is also a serious risk factor and requires continuous study.

The most important field of research, which in our country also lags in its development, involves the creation of systems for the automated control of processes which would make it possible to assess not only the occurrence of a process "post factum" but also the onset of a pre-accident situation and on a time scale such that it would be possible to localise these accident situations by altering the technical parameters.

Thus one is dealing with the creation of not simply automated control systems but systems for the early identification of processes, especially in those stages where they are potentially dangerous. It is noteworthy that, for the solution of the set of problems listed above, concerning the questions of safety of industry, including chemical industries, it will be desirable to make use of the existing experience in the organisation of similar studies already gained abroad.

Such experience also exists in the Soviet Union. In particular, methods for dealing with leakages of rocket fuels have been developed in the course of many years at the SIAC SIA. These methods included both technical aspects for the abolition of the consequences of such leakages and provided for all the organisational measures. It has to be said that the many breakdowns which have occurred, for example, as a result of railway accidents, were made good fairly rapidly and without human casualties. Such experience should be transferred also to chemical undertakings.

Here it is useful to point to the relationship between the conditions governing the occurence of modern accidents and the structure and expenditure on their prevention. We may note that the present expenditure does not yield the required effect because it is concentrated on technical systems and there has been virtually no expenditure on the training of directing personnel to take control of safety measures. The tragic events in Chernobyl and the earthquake in Armenia showed how important it is, in the initial stages of the development of catastrophes, to establish control by means of a set of measures and to control large masses of people in a state of psychological stress in order to diminish the consequences of the catastrophe.

Thus it is evident that we are faced by the necessity to develop significantly the studies in the field of risk and safety in the industries of the chemical-forestry complex. Such studies should be given priority by the government. One may propose the following subdivisions of research of this kind:

1. The construction of computational-theoretical models and the determination of risk factors in accident situations in chemical industries.

2. The creation of a data bank of starting materials, intermediates, and final products designed to ensure the construction of a safety system.

3. The improvement of existing methods and means and creation of new ones for the determination of the characteristics of the danger associated with chemicals.

4. The creation of a single methodology for the localisation and abolition of the consequences of explosions and emissions of toxic substances.

5. Estimation of the economic effectiveness of the measures designed to ensure the safety of chemical industries.

6. Analysis and expert assessment of measures designed to improve the ecological aspects and safety of the existing chemical undertakings. Events of recent years — numerous accidents and even catastrophes — which we have witnessed and in which we have participated, demonstrate that the development of this priority field of research can not be put off.