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CHEMICAL RISK ASSESSMENT METHODOLOGY

Abstract: *The basic source of hazard in chemical industry is plants with hazardous substances. Exposure to hazardous substances may cause harm to humans, animals and/or the environment. Also, they are a great threat in case of inadequate treatment as well as during production, manipulation, storage, transport, utilization, or even in case of hazard or an accident. In this paper, a definition of a chemical accident has been given, followed by descriptions of accident phases and the zones of accident. Managing and assessing risks related to chemical accidents is a complex process that requires a systematic approach during risk identification, control and reduction.*

Key words: hazardous substances, chemical accidents, risk, risk assessment.

INTRODUCTION

Inadequate treatment of hazardous substances can lead to chemical mishaps or accidents.

An accident, a mishap, or a disaster is an emergency event or a series of events that occur as a consequence of uncontrolled releases, spilling, or spreading of hazardous substances in production, utilization, transport, storage, and cause damage to humans and the environment.

The cause of accidents (mishaps or disasters) related to chemical laboratories, chemical industry and companies using hazardous substances in production, storage or transport are most often: employees mistakes (due to ignorance or being irresponsible), accidents arising from conditions that are difficult to control, or natural disasters [1].

For example, the production of paints and varnish is a very complex and risky process since paint pigments of organic or non-organic origin get synthesized, and it contains polymers and solvents mostly used as a foundation for paints and varnish. The mentioned substances possess a higher or a lower level of toxicity and most of them have a characteristic of easy vaporescence which can influence their release, during the production process and/or during an accident. Therefore, they can represent a risk for human health and the environment.

It can be said that the technological process in the chemical industry is considered a risk. In other words, risk is a potential problem. It is present in all spheres of work within an organization, thus it is necessary to manage it. According to the terminology of the International Organization for Standardization - ISO [2], the risk is "A combination of the probability of an event and its consequences", and in some situations, the risk is "a deviation from the expected" [3]. Organizations face various forms of risk, so there is a need to develop the management system for risk monitoring and recommendations on how to treat the consequences of a risky event.

THE PHASES OF CHEMICAL ACCIDENTS

Stages of accident involve the time before the occurrence of an accident, the initiation, duration, accident development, termination and the time after the accident. It is essential to be familiar with the stages of an accident in order to adequately respond and to undertake activities to eliminate the negative consequences of an accident. In literature, there are four phases of an accident. It is considered that the classification which comprises four phases of an accident development is rather incomplete and inadequate, that is, it does not provide necessary temporal and spatial information about the accident. By the same criterion, a classification can involve seven phases of an accident in a facility [4]:

- Phase I - the time before the occurrence,
- Phase II - the time of the occurrence,
- Phase III - the time of the accident duration within the facility (production, storage, transport),
- Phase IV - the time of the accident duration outside the facility,
- Phase V- the termination of the accident,
- Phase VI - the time immediately after the accident, and
- Phase VII - the time after the accident.

In the first phase, all necessary measures should be taken to prevent the appearance of the accident. Knowing the time of the accident occurrence is significant in order to be prepared for the third phase and to be able to determine the priorities in saving lives and material goods. In the third phase, it is necessary to save employee lives and undertake technical and technological measures to prevent the accident occurrence outside the facility. The fourth phase is focused on providing conditions for saving the population, flora, fauna, economy and, most importantly, humans. In the fifth phase, the territory affected by the accident is determined. This phase also involves the preparations for the sixth phase. In the sixth phase, immediately after the accident, the first aid is given (food, accommodation and medical help) and the evacuation is organized with the aim to save people. The seventh phase comprises taking suitable measures for the localization, remediation, and elimination of consequences of the accident.

Temporal and spatial distribution of an accident depends on several factors: physical-chemical characteristics of the substance, temperature, meteorological and hydrological conditions, topographic characteristics of the locality, etc. The dynamics of the accident and the level of remediation depend on the type and the mass (quantity) of the discharge, characteristics of the substance, characteristics of the relief, and climatic conditions of the terrain, as well as on the preparedness and technical competence. Experiments have shown that bursting of reservoirs with hazardous matters in a solid or liquid state, lead only to the local impact in the place of the accident, or the close surroundings. Steam and gasses of hazardous substances can spread even to dozens of kilometres, which noticeably increases the proportions of hazard [4].

CHEMICAL ACCIDENT RISK

Chemical-industrial complexes are very compound systems that comprise various equipment, managing-controlling devices, and operating procedures necessary for the regular production and processing. Industrial plants from this field use a large number of various hazardous matters which can be in the form of raw materials and/or finished products. The presence of hazardous matters in industrial plants, warehouses, means of transport, or during activities poses a risk of occurrence of a chemical accident. Hazard can be defined as a physical event, a process or phenomenon which can cause damage. According to the genesis, it can be geological, hydrometeorological, or biological, and it can differ by its magnitude or intensity, frequency, duration, space it affects, the speed of its occurrence, spreading, and the reversible period (UNISDR, 2004).

Satisfying all the requirements and standards by the legislation in order to prevent the potential hazard does not fully secure the occurrence of a chemical accident. However, for the chemical accidents to appear two conditions must be fulfilled - the necessary and sufficient conditions. The necessary activity implies the existence of a hazard and its activity at the potential development of the unwanted event, while the sufficient condition relates to the unfavourable outcome of hazard activity involving all risk factors. The necessary condition is always present in the system of hazardous substances and its degree of action varies depending on the risk factors which are in function of the sum of magnitude or intensity, frequency, duration, the speed of appearance, the reversible period of action and the surface of the space comprised by the hazard. There are hazards probability categories which can change in space and time. If, in certain circumstances, the hazard is manifested through a combination of events H_1, H_2,...,H_n; afterward, the probability can be expressed through an equation (1) of total probability [4]:

$$P = \sum_i P\frac{G}{H_i} \cdot P(H_i) \tag{1}$$

where the following are: $P(G/H_i)$ – the conditional probability of danger, G - danger; $P(H_i)$ – the probability of the i-event, H_i – i-event, P - probability.

The sufficient condition, the appearance of the chemical accident depends on four basic groups of risk factors: characteristics of the substance used in industrial production, means of work, human factor and the management.

In chemical industry, the products can have certain characteristics (toxicity, flammability, explosivity, etc.) based on which they are classified into the group of hazardous substances. At certain conditions, the above characteristics may pose risks for both people and the environment. The level of hazard from the toxic activity of substances is conditioned by its toxic potential, while the hazard from fire and explosion is conditioned by the energy potential [4].

In conditions of fast and sudden manifestation of the highly toxic potential of substances, we speak about toxic accident. The release of energy in substances can lead to the existing hazard which, as a consequence, may turn into a fire and/or an explosion. The accident may involve a combination of activities of a substance ac: toxic - fire – explosive actions. For this reason, various combined accidents may occur, for example: fire that releases the emission of toxic substances when the flammable substance is toxic at the same time or when a non-toxic substance or its compound turns into a toxic substance in conditions of combustion. Mutual connection and conditionality between various kinds of chemical hazards create combined chemical accidents and risk for a man and the environment to a greater or lesser extent [4].

When a chemical accident is a technical-technological accident, which is a condition for risk occurrence, the risk can be defined as a function of the probability of occurrence and consequence of a specific hazardous event, occurrence, a process which happens or can happen and which causes a hazard for life, people and the environment. Although the attempts to give a unique definition of risk are suitable in all scientific disciplines did not lead to the wanted goal. There have been various definitions across the scientific disciplines [4]. The Law on Emergencies ("The Official Gazette of the Republic of Serbia" No. 111/2009, 92/2011 and 93/2012) defines the technical-technological accident as a sudden and uncontrolled event which is a consequence of the lack of management control of means of work, handling hazardous matters in production, transport, storage, and logistics, and whose aftermaths can jeopardize the safety of people, goods and the ecosystem. This definition relates to the static and dynamic conditions and that it comprises all the technological processes during the manipulation of hazardous matters [5].

CHEMICAL ACCIDENTS HAZARD ZONES

As it has been already stated, there is an ever-present risk of accidents during the processes of production, transport, and storage of hazardous substances. Therefore, the places of accident occurrence can be the following:

- production and technological plants where hazardous substances are involved;
- warehouses, stockrooms, and facilities where hazardous matters are deposited and kept;
- landfills, and
- means and communications by which hazardous matters are transported.

In case of an accident in facilities with hazardous substances, we distinguish the following:

- *The hotspot of the accident* represents an imagined space where there is a spill of the hazardous substance and the aerial space above that ground where the primary cloud with hazardous substances is being formed. In the term meaning, the accident hotspot suits the *primarily affected region* (PAR), which is formed at chemical impacts.

- *The primary cloud* is the cloud of steam of the hazardous substance which appeared during dehermetization (or an explosion) of a reservoir with the hazardous substance, by transforming the hazardous substance from the liquid to the steam phase. With the simple dehermetization of the reservoir with hazardous matters (without the effect of explosion or a sudden increase in temperature in the reservoir), the primary cloud is formed only by that hazardous substance whose boiling temperature is lower than the temperature of the environment.

- *The secondary cloud* is a cloud of steam of hazardous matter which appeared because of the evaporation of a spilled hazardous matter into the protective pool or on the surrounding ground (Figure 1) [5].

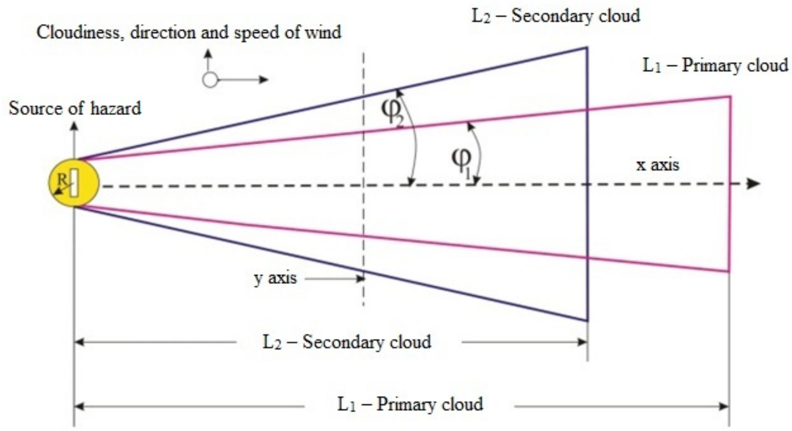

Figure 1. *The main elements of a chemical accident*

The main elements of the description of a chemical accident, φ1andφ2–half of the angle of the spreading sector of the primary, i.e. the secondary cloud; the x-axis -the wind direction or the direction of spreading of the cloud (the wind direction is defined in degrees or the sides of the world where the wind "blows" from, and the direction of steam spreading is defined by degrees or the sides of the world toward which the cloud of contamination is moving); they-axis–the direction vertical on the wind direction (used in determining the width of the hotspot and the primary and the secondary contamination cloud).

After proper risk analysis and assessment, it is possible to determine the hazard zones after the accident for each new case. The main zones are the following:

- *The first zone* is the zone in which the accident occurred and where providing first aid to the endangered population implies the efficient application of protective means;

- *The second zone* can be defined in 10-30 minutes interval from the moment of the accident occurrence, and how much time it takes for the intensive spread of toxic substances. The space covered depends on the accident range, the kind of hazardous substance, and conditions in that area (meteorological, topographic, etc.). In this zone, it is possible to carry out certain measures in order to reduce the break-through of toxic substances in the facilities, with the simultaneous evacuation of the endangered population.

- *The third zone* is determined by the territory on which the chemical substance appears after 30 minutes. This zone is considered as a real hazard zone of chemical accident. In this zone, the measures for population protection, evacuation, and other procedures are defined by protection plans [4].

THE STAGES OF CHEMICAL ACCIDENT DEVELOPMENT

Regardless of the kind or the character, all accidental situations pass four stages of development: occurrence, initiation, culmination, and the end of an accident.

In the stage of **occurrence,** there are preconditions for the future accidental situation: there are many disadvantages in processes, technological failures and omissions as well as shortcomings in production; there is a burden to both the equipment and the employees, extreme physical conditions of the production appear (such as high and low temperatures, high-pressure shocks), various chemical substances are stored changes (flammable, explosive, corrosive, highly reactive, powdery substances), all followed by the negative anthropogenic influences on the environment.

In the stage of **initiation**, technological breakdowns appear due to the change of process parameters (pressure, temperature, concentrations of hazardous matters, the speed of reaction, and the consumption of substances), unfavourable or extreme weather conditions, natural disasters, diversions. The initiation of the accident happens due to deviation from the normal process or the uncontrolled coincidence due to which the system becomes unstable. Accidents in warehouses and technological processes are a consequence of defects in the equipment: errors during design, building and equipment assembly; errors in equipment exploitation; malfunctions in the technological process. The accidents during transport happen due to bad conditions of railway tracks, poor-quality of overhaul works, the defects on a transport vehicle; crashes, collisions; corrosion of pipelines, etc.

The stage of **culmination** is followed by the release of a large quantity of mass and energy. An insignificant initial event usually starts up a mechanism of chain events, with multiple increases in the initial power and the size of the event. As a consequence of accidents in warehouses and technological processes, fires, explosions, and emissions of hazardous substances are transmitted into the environment occur. In transport accidents, the accidents which may happen are falling off from tank rails, fires, explosions, and emissions of hazardous substances into the environment.

The stage denoting **the end of an accident** starts from the moment of elimination of the source of hazard and it lasts until the total elimination of consequences of the emergency. The duration of this stage depends on the type, intensity, and size of the consequences and can be measured even in decades (for example, the Chernobyl disaster). It comprises measures of chemical protection applied in the localization and liquidation of the source of pollution [4].

CLASSIFICATION AND CATEGORIZATION OF CHEMICAL ACCIDENTS

Chemical accidents are conditioned by the existence of an accidental event which is an opportunity for exposure to chemical substances. The understanding of the nature of a chemical event and the choice of criteria for the categorization and classification of a chemical accident requires consideration and knowledge of characteristics of hazardous matters.

Categorization of chemical accidents represents a systematized approach to all relevant techniques (methods, rulebooks, practical experience, software, etc.).

Classification of chemical accidents implies their alignment in groups with identical or very similar characteristics. Categorization of chemical accidents is carried out based on the results of their classification and it is significant for a unique system of risk assessment. It means that every chemical accident is characterized by a certain group of parameters that do not have the same influence on the outcome of the accident (consequence).

The most general division of chemical accidents is according to their origin. They can be:

- natural and
- artificial (anthropogenic)

The classification of chemical accidents according to the place of their appearance comprises:

- production (fixed) plants for production and processing of hazardous matters,
- transportation means for the transport of hazardous matters,
- warehouses with hazardous matters (industrial, distributive and other),
- waste landfills which have characteristics of hazardous waste,
- households in everyday use (for example, propane-butane, hydrochloric acid, etc.)

Depending on the scope of the geographical prevalence of the contaminated zone, chemical accidents can be local, regional, national and global.

According to the consequences with fatal outcome, chemical accidents are divided into:

- Technological disasters (≥ 25 casualties),
- Large chemical accidents (≥ 5 casualties) and
- Significant chemical accidents (≥ 3casualties).

Basic processes which can appear after the initiation of a chemical accident comprise:

- explosions,
- fires and
- spilling (leaking) of hazardous matters [6].

RISK ASSESSMENT FROM A CHEMICAL ACCIDENT

Technogenic risk is conditioned by the development of hazard which appears in accidents or breakdowns in the technosphere, and it comprises emissions of hazardous matters from industry in working and living environment, fires, contamination with radioactive substances as well as contamination with toxic substances during their transport and storage.

Based on the aforesaid, it arises that qualitative-quantitative assessment of the technogenic risk should be used to determine the risk in utilization, handling, transport, and storage of hazardous substances, if it is concluded that on a certain location (for example the industrial zone or on traffic routes) certain ecological elements will be exposed to hazardous substances, which will, as a consequence lead to the degradation of the environment.

The purpose of qualitative-quantitative risk assessment is to provide a report of the risk within the plant and evaluate the level of acceptable risk, as well as to inform the competent institutions and the public about the increased risk at the spot or in the close vicinity.

During qualitative ad quantitative risk assessment, the starting point is to present the risk as a quantified size of the occurring or expected side effects on people, things, or certain elements of the environment, which are the consequence of certain accidents. So, the risk (R) is viewed as the frequency function of the activity of stressors and the occurrence of side effects with the assessment of the level of consequences, the equation (2) [7].

$$R = f(F, G) \tag{2}$$

where: *R*–is the numeric representation of the risk related to the accidental event; *F*–the frequency of the activity of stressors and the appearance of side effects; *G*–the level of consequences on the corresponding element.

The risk assessment can be carried out by the application of suitable methods and techniques used to define the nature and degree of risk from a potential accident, the state of hazard and the consequences which can cause damage, losses and jeopardize people, the environment and material goods.

The analysis of hazard develops through three phases, and they are: identification and analysis of consequences, measures of preventive activities, and measures of the response to the accident and remediation plans for the consequences of the accident. Production and technological plants with hazardous substances used in production are the most important places where these measures should be applied, followed by warehouses, stock rooms, and other facilities where such substances are stored, as well as the means of their transportation.

Here we have tried to define the notion of "endangered space", which is an area where we could expect to find

Accident risk assessment is the activity used to identify hazards, carry out the analysis, and determine the levels of risk from uncontrolled events in industrial plants and installations, facilities and warehouses. It represents an assessment of the probability of whether a certain hazard shall turn into risk [8].

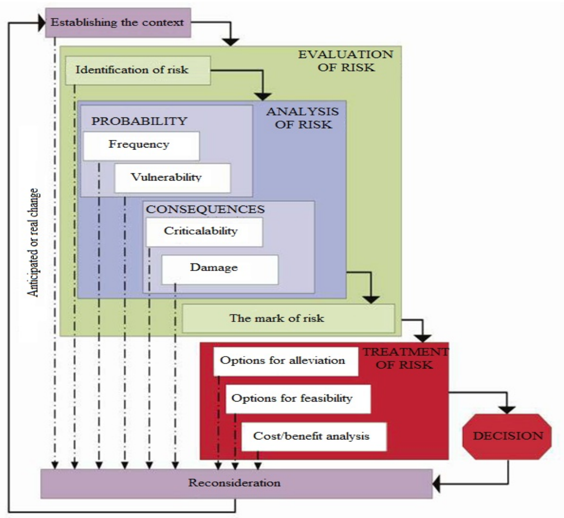

Figure 2. *Graphical presentation of risk assessment methodology*

The process of an accident risk assessment is broken into three phases: the preparation phase, development of a risk assessment program, and the implementation phase. In the first phase, an action plan should be made and it should contain data on the organizational structure in the facility, the branch of industry, data on persons responsible for risk assessment and data about the members of the risk assessment team, decisions and conclusions on the use of the information important for the assessment, details on resources needed for carrying out this process, cooperation and coordination between the persons who perform the assessment, the director, employed and all other relevant participants, the ways of documenting all the decisions, measures and plans in the assessment process and the ways of informing and reporting. The second phase is the phase of carrying out a risk assessment program. The third phase is the phase for the implementation of decisions, solutions and measures which were taken in the process of chemical risk assessment [8].

hazardous substances during an accident. Apart from this, we must take into consideration the assessment of possible chemical accidents occurred within individual technological processes and systems. That is why it is extremely important to provide all the data about the plant where a potential accident can occur [9].

The analysis of consequences is done by assuming the possible effects of hazardous substances on people, property, and the environment in the case of an accident. To successfully manage preventive measures and suppress the harmful activity of hazardous chemical substances, one must get acquainted with regularities as well as with unfavourable activities which can create harmful effects. The analysis of consequences uses data on the characteristics of chemicals and their maximum allowable concentrations (MAC) [10].

Preventive measures represent the implementation of more complex procedures intended to develop safe conditions in the whole technological system, establishing safety in production by which it is possible to prevent the occurrence of an accident.

Response to an accident is in charge of the services of The Ministry of Internal Affairs (Emergency Management Department), then the specialized ABCD (Atomic Biological Chemical Defence) units of the Army of the Republic of Serbia, state authorities, health services, fire protection services, communal services, units of civil protection, units for remediation, specialized laboratories, information support centres, hydrometeorological services, transport services and other relevant specialized organizations, institutions, and associations. The main goal of the remediation is the recovery of the injured, prevention of further pollution, and returning the living and working environment to the initial state.

MANAGING RISKS

The goal of risk management in the environment is to get an insight into the state of the environment and to reach the level of preparedness for all the subjects in preventing occurrence, processes, and events which jeopardize the life and health of people, and to evaluate the suggestions for further system development in managing environmental risks.

Figure 3. *Managing accidental risks*

There are various definitions of risk management [11]:

- Managing risk is an aspect of managing quality which has a supporting role in accomplishing the demanded quality of the system. The primary goal of managing quality is an implementation of the strategic management plan of which provides the requested system quality, while the goal of managing risk is maintaining the system quality even in the case of possible realizations of risky events. Managing risk should provide the continual existence of the system.
- Risk management implies managing which achieves a suitable balance between the creation of possibilities for profit and minimization of losses.
- Risk management is an approach that is based on the identification and control of those fields and events which are potential causes of unwanted changes in the system.
- Managing risk from an accident implies a group of measures and prevention procedures, readiness, response to the accident and remediations for reducing the probability of its occurrence and possible consequences, and has a goal to create conditions under which the risk from plants and work of hazardous installations is acceptable on a certain space.
- Managing risk is an organized process of identifying and measuring risk, choices, development, and application of options for treatment and following of risk.

In scientific and expert public there are common cases when in managing risk the risk itself is emphasized together with its quantitative identification, while in the methodological approach in the process control and a suitable response for its monitoring of state almost none of the significance is given.

Misunderstanding of goals in the process of risk management is often mystified and connected to the complex models for the quantitative risk assessment. It points out that the phenomenon of risk management should not be viewed as an independent category, but as a practical mechanism for realization of functions anticipated by suitable strategies.

THE METHODS USED IN RISK ASSESSMENT

Production, logistic, and transport activities with hazardous substances can be exposed to high risk from the occurrence of accidents having in mind the significant number of causes which influence the nature of hazard. Risk assessment at the exposure to certain hazardous substances requires an analytical approach in identifying potential hazards and consequences of their harmful events, especially for human health. Although qualitative methods had a significant contribution to risk assessment in the past, not diminishing their importance, it should be mentioned that in the past few years the main point of risk assessment has moved towards quantitative methods, see Figure 4 [6].

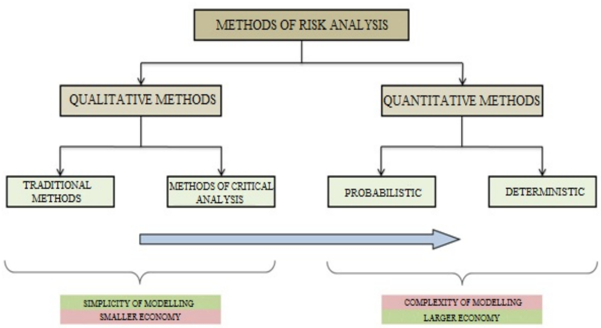

Figure 4. *Methods of risk assessment*

Risk assessment should also encompass special methods of knowledge by which we could discover structural, functional, causal and genetic dependencies, mutual conditionality, identicality or similarity of more appearances (chemical accidents, hazardous matters, chemical injuries, damages of material goods, etc.).

In this field, there is a larger number of generally accepted methods: "What If" Study, Checklist Study, Job Safety Analysis, Safety Function Analysis, Hazard and Operability Study (HAZOP), Event Tree Analysis, Fault Tree Analysis, etc. [12].

There are actual methodologies for the assessment of ecological risk in a technical-technological accident, such as: REHRA Rapid Environmental and Health Risk Assessment, US EPA ecological risk assessment methodology, APELL methodology - Awareness and preparedness for emergencies at the local level, EIA methodology of environmental impact assessment, Methodologies within standards - ISO 31000:2009 and ISO 31010:2009, LCA methodology of life cycle assessment, etc.

CONCLUSION

Due to the increased awareness about the consequences of possible chemical accidents, and a hazard to people and the environment, there has been a rise in the awareness of the need for their assessment and management. The companies which operate within the systems with hazardous substances are usually of a closed type, and they strictly keep information about all the accidents and those that were almost prevented, because they are an indicator of the state within such a system.

In those circumstances, the risk assessment comes down to the expert analysis performed by employees who use conventional techniques and methods. The risk assessment carried out in such a way is not reliable enough, because it is more quantitative and it mostly depends on the experience of the assessor.

This approach is not possible for a wider circle of researchers, therefore, the risk assessment within the system of hazardous substances exists in the frame of traditional methods. Contemporary business environments go beyond these and develop preconditions in which risk of an accident is increased, despite all investments in the modernization of plants that operate with hazardous substances. Certain processes in industry are characterized as hazardous, and the risk is perceived in terms of the usage of hazardous and harmful substances in such systems. The most common cause of the occurrence of chemical accidents are errors arising from human factors and poor and outdated technology which is still being used.

This is the point at which the need for the assessment and management of such risk arises. The main goal of risk management from a chemical accident is to achieve system safety and protect people, property, and the environment. The foundation for successful risk management is to perform risk assessment and analysis so that all the risks would be identified on time and all the consequences recognized.

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BIOGRAPHY of the first author

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METODOLOGIJA PROCENE HEMIJSKOG UDESA

Danijela Stojadinović, Amelija Đorđević, Jasmina Radosavljević

Rezime: *Osnovni izvor opasnosti u hemijskoj industriji su postrojenja sa opasnim supstancama. Opasne supstance su one supstance koje mogu izazvati štetne pojave kod eksponiranog čoveka, životinja i/ili životnu sredinu, pri neodgovarajućem postupanju sa njima, u procesu proizvodnje, manipulacije, njihovog skladištenja, transporta, upotrebe, hazarda ili udesa. U radu je data definicija hemijskog udesa, opisane su faze udesa kao i njihove zone pri formiranju rizika nastalog usled hemijskog akcidenta. Procena i upravljanje rizicima koji su uslovljeni hemijskim udesnim događajima predstavlja složen proces, koji zahteva sistemski pristup prilikom identifikacije, kontrole i redukcije rizika.*

Ključne reči: opasne supstance, hemijski udesi, rizik, procena rizika.