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Article

Identification Methodology for Chemical Warehouses Dealing with Flammable Substances Capable of Causing Firewater Pollution

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Abstract: Major accidents involving flammable substances can lead to significant environmental damage. The operators of chemical warehouses—in order to prevent and mitigate harmful environmental impacts—based on fire prevention strategies should apply "firewater pollution prevention" (FPP) measures. The identification of affected warehouses already in operation is an important law enforcement task. Therefore, the authors—based on the assessment of firewater run-off scenarios—propose a simple and easy-to-use dangerous establishment identification procedure and methodology based on event tree analysis and indexing preliminary risk analysis approaches. Two independent expert groups validated—in the case of 10 facilities—the index components of the approach. The testing of the applicability of the approach took place in parallel with the analyses of the Hungarian operator's practice. The research results—covering the inspection of 24 facilities—can assist the operators in the effective and unified implementation of FPP measures. In the case of 14 facilities, it was necessary to introduce FPP measures, which highlight the need to improve the law enforcement compliance of identified operators. The investigation results can also contribute to increases in the fire and environmental safety performance of chemical warehouses, which ensures a higher level of environmental protection and people's health near chemical warehouses.

Keywords: major accidents; environmental impact; dangerous establishment; dangerous substances; firewater pollution prevention; risk assessment

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1. Introduction

In the introduction, the authors, after the analyses of the environmental hazards of major accidents involving flammable dangerous substances, will determine the scope of the present research and will then introduce the research problems and research objectives of the present study.

1.1. Environmental Impacts of Major Accidents Involving Dangerous Substances

The occurrence of natural and human-made disasters, as well as major accidents, has become almost a daily practice all over the world [1]. For example, the pesticide warehouse fire that occurred in 1986 in Basel (Switzerland) caused significant cross-border water pollution in Germany, France and the Netherlands [2] (p. 46). Among the international databases [3,4] dealing with the environmental effects of major accidents involving dangerous substances, the Major Accident Reporting System established by the European Commission can be highlighted [5], where the majority of the submitted major accident reports stated a greater or lesser environmental impact among the consequences of major accidents [6]. Internationally accepted case studies [7–9] are also evaluated in detail, including the effects and impacts of environmental scenarios at major accident hazard sites.

Industrial and logistical facilities that produce, process or store dangerous substances, as well as plants processing hazardous waste, can pose a significant accident impact on the surrounding population and environment. Major accidents involving dangerous substances, such as other disaster phenomena, often have serious consequences for the surrounding built environment and for other environmental elements, such as surface and underground waters and soil [10]. In the event of a major accident, an explosion or a large-scale fire resulting from the release of flammable substances could have catastrophic effects, for example, the "red sludge disaster" that occurred in Hungary in 2010 [11]. The impacts can easily reach cross-border waters courses and can even extend beyond the national borders, such as in the case of "Tisza River cyanide and heavy metal pollution" that happened in 2000 [12].

Flammable substances often have, among other things, toxic or environmentally hazardous chemical properties, which, in the case of emergency, could further endanger the environment together with the toxic combustion products propagated during the fire events involving flammable substances. Similarly, a vital environmental safety problem is the polluting effect of firefighting foams used during firefighting intervention operations. These operations require increased utilisation of fire extinguishing water or agents (altogether firewater), as a result of which they are contaminated with the accidentally released dangerous substances and fire combustion products. The environmental pollution impacts of such an accident can be eliminated or minimised by capturing, draining, collecting and storing (together retention) the contaminated firewater. The development of major environmental damage can be prevented by introducing technical, planning, organisational and management measures of the operators of affected facilities in order to prevent firewater pollution [13].

Operators of facilities dealing with dangerous substances—in order to protect against the environmental impact of major accidents involving dangerous substances—must meet a number of safety requirements. Figure 1 shows the connection areas of disaster management (mainly fire prevention), environmental protection and water protection regulations.

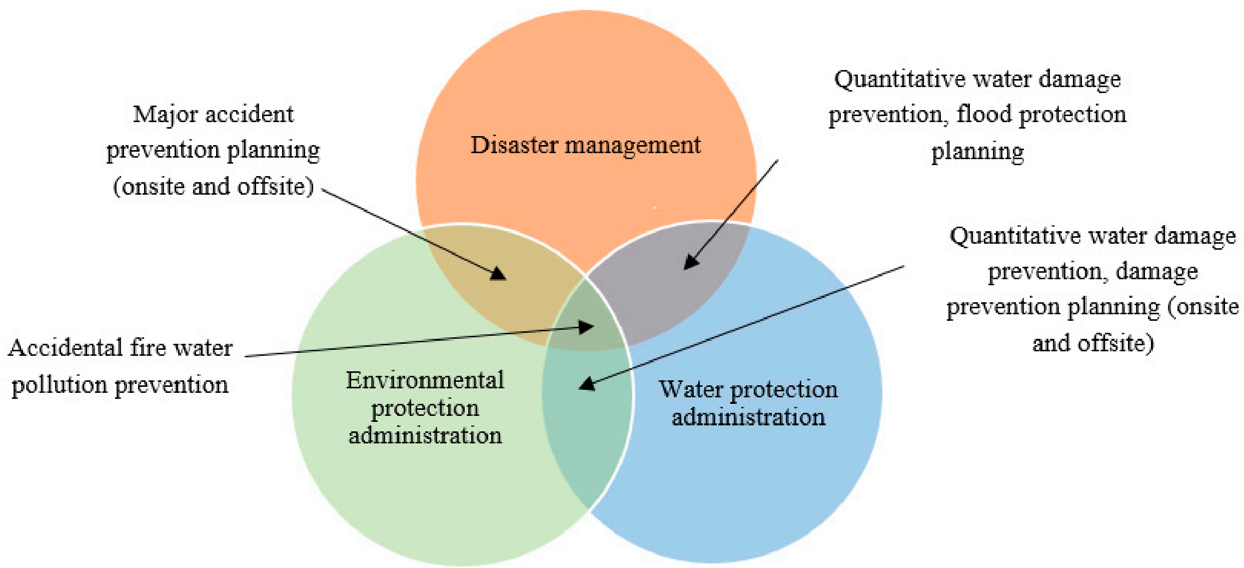

Figure 1. Interconnection of operational safety policies. Source: own research.

In the common intersection territory of three main safety disciplines, the "firewater pollution prevention measures of the operators" are situated.

1.2. Determination and Limitation of the Scope of the Research

It is important to determine the scope of the research. Therefore, it is necessary to identify the group of industrial and logistical facilities in which operators should implement FPP measures prescribed by international and national level legal regulation.

The industrial sites covered by the present research are primarily dangerous establishments identified based on international and European Union (EU) legislation.

These pieces of legislation are the UN Economic Commission for Europe (UN ECE) "Industrial Accidents Convention" [14] and the so-called "Seveso III. Directive", dealing with the prevention of major accidents involving dangerous substances [15]. In accordance with the directive, the affected sites are classified into upper- and lower-tier establishments. The identification procedure for these dangerous activities is based on the quantitative and qualitative properties of the dangerous substances present at these facilities [16]. The Government Decree [17] adopting the European Union's major accident regulations into the Hungarian legal system introduces a third category of establishments, the so-called under-tier establishments, which significantly expanded the range of establishments inspected in Hungary. Establishments are identified based on the chemical safety rules of dangerous substances present on site, which are stipulated in the relevant EU directive, titled "the Regulation on the Classification, Labelling and Packaging of Substances and Mixtures" (CLP directive) [18].

It can be concluded that operators that fall under the scope of the major accident prevention regulations must introduce and implement FPP measures. However, the range of dangerous activities dealing with dangerous substances, dangerous goods or hazardous waste is much wider. Practical experience shows that there is a significant number of facilities dealing with dangerous substances that do not fall under the scope of the major accident regulations but—because of possible major accident hazards with environmental impacts—would still require the extensive application of FPP measures.

In the following, the authors review the most important categories of dangerous facilities. The dangerous activities mostly affected by the FPP regulation are logistics warehouses, where dangerous substances and goods are stored in transport packaging. These facilities fall under the scope of the UN ECE regulation on the Transport of Dangerous Goods by Road [19] (ADR regulation). The operational facilities of railway transportation activities are railway marshalling yards, while in the case of inland waterway transportation, the ports deal with dangerous goods. Preparatory storage facilities for air transportation can also be classified in this circle [20]. Among hazardous waste facilities, plants installed for the disposal and incineration of hazardous waste are considered the most dangerous ones. Industrial, agricultural and commercial facilities that store dangerous substances and dangerous goods—not covered by major accident prevention regulations—can also represent an environmental hazard for surroundings. These sites are, for example, residential landfills, electrical, battery or plastic waste storage and processing facilities, where in the case of fire, combustion products and contaminated firewater could be released into the environment. However, these sites do not store dangerous substances.

The range of operators to be examined in the present study represents a fairly wide range of economic organisations. In the following, the authors will examine the facilities as a whole as "dangerous activities" as a collective term, and they will limit their scope of investigation to facilities that store dangerous substances. The latter facilities are collectively called "chemical warehouses".

The environment and fire safety level of chemical warehouses are influenced by several recent global factors. Impacts of the latest pandemic, war, natural calamities and other crisis situations influenced the just-in-time supply chain. Therefore, the expansion of buffer storage capacities was observed [21]. Investigation data on the causes and circumstances of chemical warehouse structure fires [22] show that despite stricter fire protection regulations, the number of warehouse fires did not decrease. The storage sizes of warehouse buildings are becoming larger, so the consequences of the subsequent fires are becoming more serious, and consequently, a larger amount of contaminated firewater is produced [23].

The issue of industrial fire protection, among others, raises several fire protection planning and design issues in the case of chemical warehouses. The wide range of scientific problems are related to the so-called "built-in fire protection" issues of chemical warehouse buildings [24]. These problems are significantly linked with the effectiveness of operators' FPP measure implementation, which is determined by the relevant environmental risk assessment procedures and methodologies.

Environment risk assessment procedures are always started with the identification of affected dangerous activities. Absolute and relative ranking approaches are widely used in connection with major accident hazard establishments [25]. Preliminary risk assessment techniques, such as indexing hazard analyses approaches, are widely used in connection with the implementation of fire protection, major accident prevention and environmental safety requirements. However, there is no internationally harmonised, effective and simple procedure for identifying dangerous activities harmful to the environment that has been utilised widely, with the exception of the indexing methodology used by the International Commission for The Protection of the Danube River back in 2001, which resulted in the creation of the Inventory of Potential Accidental Risk Spots in the Danube River Basin [26].

1.3. Introduction of Research Problem and Objectives of the Present Study

The scientific investigation of the processes that cause firewater pollution in the event of major accidents, the analysis of their risks and preparations to prevent possible harmful effects can contribute to the increasing level of fire and environmental safety of the territory and near chemical warehouses.

The FPP issues of chemical warehouses under planning and those already in operation (existing chemical warehouses) must be dealt with separately. According to the motivation of the authors, the effectiveness of the official inspection tool system available to the competent authorities should be increased, which needs to be supported in a scientifically and technically sound manner. The identification of the existing chemical warehouses is the main objective of this article.

The scientific novelty of the present study is the foundation of the technical basis for the identification procedure and methodology of the existing chemical warehouses requiring the introduction of FPP measures, which is a vital prevention task for the operators of chemical warehouses and competent governmental authorities as well.

Considering the above-described scientific problems, the author's research work will primarily cover the following main research objectives:

- Examination of the consequences and impacts of major accident scenarios causing firewater pollution.
- Development of the identification procedure and methodology for the existing chemical warehouses requiring the introduction of FPP measures.
- Assessment of the operator's FPP measures implementation practice of Hungarian chemical warehouses and testing the applicability of the identification procedure and methodology.

The research results should assist the competent authorities responsible for the enforcement of FPP measures in the development of legal regulations and increase the efficiency of law enforcement activities.

2. Literature Review

In order to examine the literature background of the present research topic, the authors will analyse methodological guidelines issued by international organisations and determine national authorities and research institutes. Some analyses of the research work of benchmark authors belonging to the author's research area can also be found here. However, the authors will examine these scientific works in detail in the methodological part of the article, especially with regard to risk analysis procedures and basic requirements.

2.1. In the Field of FPP Policies and Safety Measures

International, EU and Hungarian regulations are implemented by the competent authorities and operators are subject to the major accident prevention regulations. In the introduction section, the authors examined the most important legal regulatory instruments. The effective and uniform implementation of legal regulations requires the development of appropriate authority procedure, legal, technical and methodological guidance documents.

The so-called UN ECE Industrial Accident Convention's "firewater retention guideline" [27] can be considered—at the international level—as a model document representing the best authority and operators' FPP policies and practices. The main purpose of the document is to introduce preventive measures and good law enforcement practices in order to prevent firewater pollution. The scope of the guidance covers storage, processing and production procedures in hazardous activities covered by the Convention, but it can also be extended to activities outside of its scope. The guidance document deals with technical and organisational recommendations for "firewater retention and disposal" affecting the national governments, the competent authorities and the operators.

The set of proposed measures covers fire protection requirements, the planning of firewater retention installations and equipment and the calculation of the amount of required water. Among the international standards, the ISO/TR 26368 standard [28] can be emphasised, which is entitled "Environmental damage limitation from fire-fighting water run-off" and can be used as a technical advice instrument.

The procedural and technical solutions to the scientific problem—in relation to the retention and storage of firewater—are contained in several national guidelines, of which the German [29] and Swiss [30] methodological guidance documents have particular importance. The publications regulate, in detail, the technical design of installation and equipment for collecting contaminated firewater and the order of organisational measures related to their application. These documents also contain a consequence-based facility identification procedure in order to determine the range of the obliged operators.

The contents of the guidelines proposing best industrial practices [31,32] can serve as a good example for the development of the national technical equipment system. Technical recommendations developed by the Hazardous Materials Committee of the Federal Republic of Germany [33] can also be used for the development of technical regulations.

The "Storage of Hazardous Substances" guideline [34] published by the German Chemical Industry Association in 2013 has great importance. The guideline deals, among other things, with the responsibility of chemical warehouse operators, risk analysis, packaging rules, packaging and storage facilities, occupational health and safety rules and technical specifications for chemical warehouse design and the calculation method of the amount of contaminated firewater produced in the event of a chemical accident.

All of the above-mentioned technical guides present the detailed risk analysis procedure and methodology so that the environmental risk caused by chemical warehouses can be determined as accurately as possible.

In addition to international official legal legislation, guidelines and handbooks, a number of scientific publications have been produced on the topic of the fire safety of chemical warehouse logistics and the examination of firewater retention. Unfortunately, only a very limited number of these publications contain relevant technical information useful for the present article. The authors experienced a similar situation concerning the Hungarian research situation as well. The same conclusion was reached by Scholz, M. in his review article dealing with the management of the storage, treatment and recycling of firewater [35]. In his opinion, the scientific investigation of firewater management problems still awaits. Based on his valuable practical experience gained in the United Kingdom, he made suggestions concerning cost-efficient and rapid on-site treatment methods.

In several articles, Sikorova, K. and Bernatik, A. dealt with the investigation of the environmental effects of the industrial accidents at the Seveso establishments and also with the application of the environmental risk assessment procedures and methodologies. In their study [36] concerning an analysis of firewater run-off in Seveso chemical plants, the authors reviewed and evaluated the data related to environmental risks from the Major Accident Reporting System (eMARS) database of the Joint Research Center. Beyond that, the scenarios involving the release of firewater were evaluated through various case studies. An important case study analysis was carried out to identify environmental hazards, consequences and effects. Useful suggestions were also made by the authors for the implementation of risk reduction measures. Reports on major accidents involving dangerous substances contain many descriptions of events related to environmental damage, the experiences of which are elaborated upon in the articles of Meel, A. et al. [37] and Ansaldi, S.M. et al. [38]. It should also be highlighted that the European Network for the Implementation and Enforcement of European Law is an important mechanism within the framework of which case studies of major accidents with environmental impact are considered to be analysed [39]. Specific accident reports are also of great importance, such as the report on the recovery of the environmental consequences of the major accident at the fuel storage plant in Buncefield (United Kingdom) in 2005 [40].

Hybska, H. and co-authors dealt with the examination of the toxic effects of the firewater in detail and concluded that if environmental contamination can no longer be prevented, the spread of contaminated firewater must at least be reduced [41]. Vanessa, C. Erazo-Chamorro, et al., in their article, assess the information about security risk factors and necessary safety requirements for a safe workplace [42]. In relation to Hungary, the examined topic came to the attention of the competent authorities after the firewater retention guidelines of the Convention were issued [43].

2.2. In the Field of Risk Assessment of Major Accidents Involving Dangerous Substances

The operability and resilience of the local security system of the industrial operator can be ensured by introducing prevention and preparedness measures. The application of these measures aims to eliminate or reduce the main consequences and impacts of major accident events, such as explosions, fire and the spread of toxic substances. However, the primary step for the application of all these measures is the risk analysis of dangerous technologies.

Risk-based quantitative risk analysis procedures and methods that can be used for hazardous activities have recently been developed. The benchmark methodological publications in the field of major accident risk analysis are published by the Netherlands Organisation for Applied Scientific Research (TNO). The main book of the research area is the Guide to Quantitative Risk Analysis (CPR 18 Guide) [44], which contains the technical description of the quantitative risk analysis procedure and the related technical methodology. This publication contains a description of the series of major accident events to be examined from the perspective of the present research topic, as well as the application of related risk analysis procedures and methods.

The PGS 15 guide on Risk Analysis Methodology for CPR-15 Establishments [45] is used for the quantitative risk analysis to be carried out in chemical warehouses. An equally important basic work on the subject of risk analysis of processing industry technologies is the three-volume book of P. F. Lees titled Loss Prevention in the Process Industries [46], which deals with loss prevention in the manufacturing industry—including facility identification techniques—and should also be highlighted.

In the study of Török, Z. and Ozunu, A., the analysis procedures of the risks caused by the sites for the storage of dangerous substances of the Seveso type were reviewed in the form of case studies. The results presented in the study serve as a useful scientific basis for reducing the consequences of major accidents [47].

Further detailed technical information on the application of procedural and methodological aspects can be obtained from the work of authors of risk assessment articles relevant to the present research topic [48,49]. Delvosalle, C. and his co-authors performed a significant study on developing the results of the Accidental Risk Assessment Methodology for Industries (ARAMIS) project. In the relevant publication by the authors [50], information on the procedures and methodology related to the identification of accident scenarios, the fault tree and the event tree risk assessment methods are described. Duim, N.J. also deals with the possibilities of using safety barrier diagrams, who in article [51], discusses the applicability of the method for the improvement of safety management systems. Technical support for the risk analysis of transport accidents can be obtained from the paper of Landucci, G. et al., which is based on the example of the Viareggio LPG accident [52].

The aim of the present article is to develop a simple (easy-to-use) methodology and procedure appropriate for the external safety situation in Hungary, which is supported by the major accident prevention manual [53], developed by Szakál B. and his co-authors. From a methodological point of view, the dangerous establishment's identification procedure concerning the chemical monitoring systems installed in Hungary in the vicinity of so-called Seveso establishments could serve as a supporting study as well [54].

Furthermore, various procedures and methodologies [55,56] were used to analyse dangerous technologies in the processing industry, which serve as the basis for the research conducted in the framework of this publication.

3. Materials and Methods

In the introduction section, the authors have already concluded that the main question is in which cases chemical warehouses must necessarily apply FPP measures. To resolve this question, the authors have developed an easy-to-apply indexing methodology, taking into account the relevant local circumstances. In this section, the authors will first deal with the presentation of the environmental pollution consequences and impacts of dangerous substances released into the environment; then they will assess the consequence assessment procedures of firewater run-off scenarios and, finally, they will propose an identification procedure for the existing chemical warehouses obliged to introduce FPP measures.

3.1. Environmental Pollution Consequences and Impacts of Dangerous Substances Released into the Environment

The majority of major accidents are caused by the release of dangerous substances into the environment. The consequences and harmful impacts of major accidents involving dangerous substances can be the following:

- Toxic effects caused by the release of toxic, dangerous substances.
- The fire following the release of flammable substances and a subsequent release of contaminated firewater.
- The effect of the toxic combustion products produced during the fire, which can have both air and water pollution environmental impacts.

In this case, dangerous substances harmful to the environment can run off into the vicinity of chemical warehouses [57]. The major accident scenarios primarily depend on the properties of the dangerous substances and the composition of their mixtures.

Once the dangerous substances or the contaminated firewater are released into the surrounding environment, the accident scenario can ultimately lead to air, soil and water pollution impacts. Firewater run-off scenarios of major accidents present a major threat to aquatic environments and depend on the pollution sources, including the properties of dangerous substances; the firewater protection concept, including the firewater retention and storage design of the facility; characteristics of pollution pathways to sensitive environment; and finally, the location and features of endangered receptors of the surrounding environment.

The firewater run-off risk posed by chemical warehouses can generally be carried out in two stages. In the first one, a simple screening risk analysis (preliminary risk analyses) can be used to identify the facilities, where a detailed environmental risk analysis can be carried out in the second stage of the analyses. The related guidelines are presented in Section 2.1. In addition, an environmental risk analysis software named PROTEUS 8.13 developed in the Netherlands, can be used to assess risks related to surface water pollution [58].

The geological conditions are also important aspects to take into account in the vicinity of chemical warehouses, which are primarily linked with the extent of soil and underground water pollution and are characterised by the water permeability of the soils. The water permeability of soils is characterised by the rate of water seepage [59], which—in accordance with the formula of Darcy H.—can be calculated as follows:

$$v = \frac{Q}{A \times t} = \frac{\Delta H}{\Delta L} \times K_S \quad (1)$$

where: v¯ water seepage,

Q—amount of percolating water,
ΔH—hydraulic pressure difference,
A—cross-section of the soil column,
t—the time,
ΔL—length of soil column,
K_S—the leakage factor.

The environmental significance of the K_S value (Formula (1)) is that it can be used to model the dynamics of the spatial spread of point-based soil pollution. According to this, a layer of clay can be considered practically waterproof.

In line with Mados, L.'s tests on the water permeability of different soils, it can be concluded that the water permeability of loose sandy soils is high (sand: 0.58 mm/min), for silts with a tighter structure, it is medium (loam: 0.32–0.46 mm/min), while in the case of soils with a bound structure (clay: 0.27 mm/min), it is considered low [60].

Figure 2 schematically shows the consequences and impact of major accidents involving dangerous substances released into the environment.

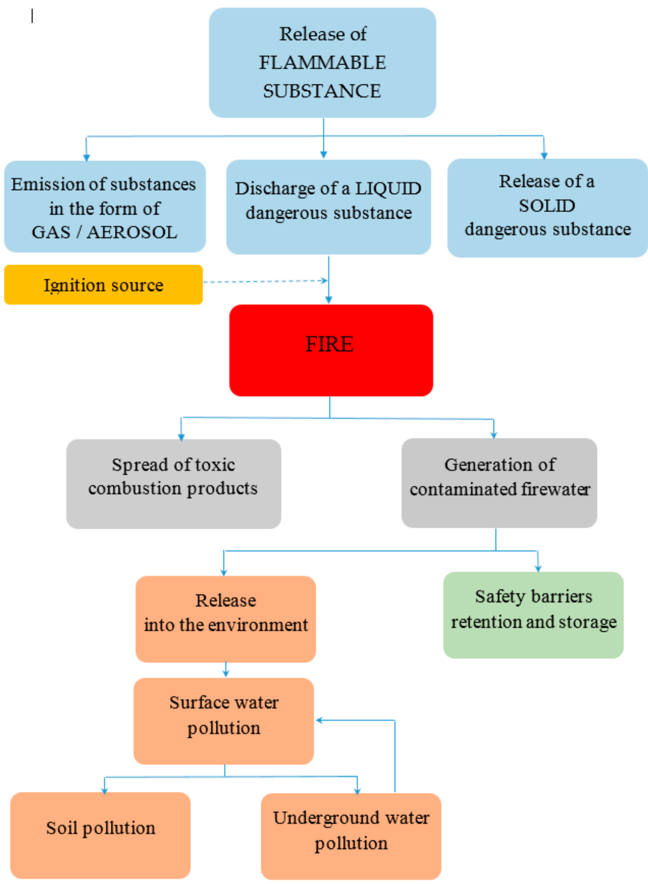

Figure 2. Environmental pollution consequences and impacts of dangerous substances released into the environment. Source: own research.

The impacts of pollution consequences can be eliminated or reduced with the help of technical, control and management measures, named "safety barriers", by the chemical warehouse operators. The operator's measures can be preventive, responsive and restorative in nature, and they can be introduced before, during and after a major accident occurs.

The analysis of the major accident scenarios is carried out by risk and consequence analyses software tools. The competent Hungarian authorities, for example, use the risk and consequence assessment software named "Phast Safety 6.4" of Det Norske Veritas [61].

3.2. Consequence Assessment of Firewater Run-Off Scenarios

In the following, the authors will examine the possible consequences of contaminated firewater run-off scenarios, for which purpose they will use the event tree analysis method. Event tree analysis is a qualitative or quantitative analysis technique that can be used to identify the possible outcomes of the initial event and, if necessary, their probability of occurrence. The analysis procedure is an inductive method, the basic question of which is: "what happens if?" [62]. The analysis procedure basically consists of two main steps:

1. A detailed understanding of the operation of the tested system, including safety barriers, as well as their breakdown into technological elements.
2. Investigation of the possible failures of technological elements and analysis of the consequences of these failures.

The event tree analysis can be used perfectly in the planning phase of a chemical warehouse, given that the consequences after the initial event can be identified so that the safety barriers can already be determined at the planning phase of the chemical warehouse. In order for the technical safety design to be complete, it must be assumed—regardless of the probability—that all identified major accident scenarios can occur. The research of the authors does not require a detailed event tree analysis, as the determination of the probability values is indifferent in this case. By performing the event tree analysis, the author's primary goal is to determine what could happen if the contaminated firewater is released into the environment.

The possible outputs of the firewater run-off scenarios can be divided into three main categories:

1. On the occasion of a "local event", no actual catastrophic impact or permanent damage to the state of the environment should be expected.
2. In the case of an output with a "major environment impact", a catastrophic effect may develop, or permanent damage to the state of the environment may occur. However, there is no need to count on an impact beyond the national borders.
3. In the event of an output with an "extreme impact", a catastrophic effect may develop, and there may also be permanent damage to the state of the environment, which may also cause an impact beyond national borders.

Major accident events can, therefore, be examined based on three types of event trees, which are detailed in the following.

3.2.1. Event Tree Related to Contaminated Firewater Generated Inside the Building

Figure 3 shows that if the firewater is generated inside the building, it can seep through the industrial floor, and if there is no waterproof layer, it can infiltrate into the ground. Depending on the type of soil, the contaminated firewater can enter the groundwater, through which it can even appear in the surface watercourse.

3.2.2. Event Tree for Firewater Run-Off Outside the Territory of the Building

This event tree can be used if the firewater originates outside the building (open space storage) or spills out of the storage building (Figure 4). In the case of the absence of protection locks, including localisation points and buffer storage installation, the firewater can move from the paved surface through the surface water drainage system. After that, the contaminated firewater can reach an off-site receiver (typically a surface water ditch), from where it can enter into the surface watercourse. Depending on the type of soil, the contaminated firewater can enter into the groundwater, through which it can even appear on the surface watercourse.

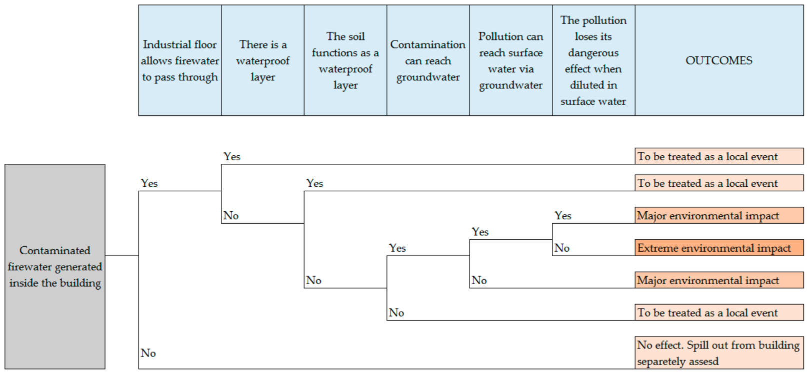

Figure 3. Structure of an event tree in the case of contaminated firewater generated within the territory of the building. Source: own research.

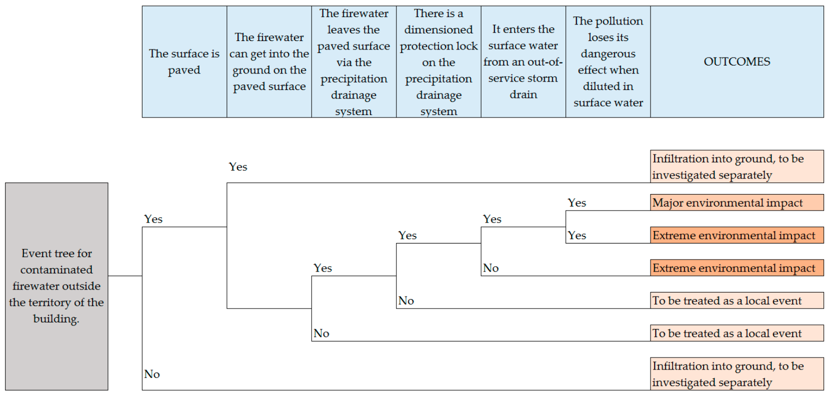

Figure 4. Structure of an event tree in the case of contaminated firewater spills out of the building. Source: own research.

3.2.3. Event Tree for Contaminated Firewater Falling on the Ground Outside of the Building

Depending on the type of soil, contaminated firewater can enter into the groundwater, through which it can even appear in surface watercourses (Figure 5).

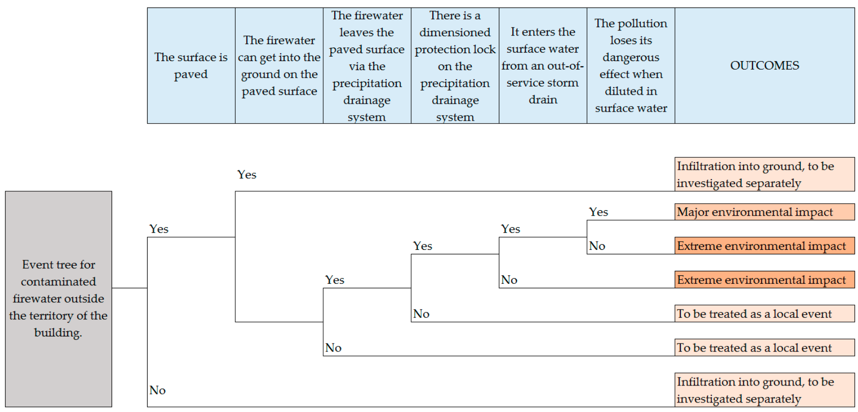

Figure 5. Structure of an event tree in the case of firewater spilled onto the ground surface outside of the building. Source: own research.

3.3. Development of Identification Procedure for Existing Chemical Warehouses

The authors of this article propose a dangerous facility identification procedure and methodology that can be used by the authorities responsible for the implementation of the PFF policy. The purpose of the preliminary risk analysis procedure is to identify existing chemical warehouses capable of firewater pollution and then oblige them to take PFF measures, including detailed risk assessment. It also includes the methodological criteria system for the risk analysis performed at the selected sites.

The firewater retention authority obligations need to be considered within the framework of the construction permit or environment permit procedures. The latter objective can be examined by the competent authority during the environmental impact assessment procedure, which is regulated in the territory of Hungary by the European Union directive for environmental impact assessment [63].

3.3.1. Determination of Index Components and Validation of their Values and Ranges

The authors have developed a relative ranking methodology to identify the existing potentially affected chemical warehouses. The index components that form the basis of the approach were determined based on the results of the event tree analysis. In Section 3.2, the authors—covering all important details—examined an event tree analysis procedure to present the possible outcomes that could lead to serious environmental pollution.

The authors selected the most important hazard factors from the point of view of FPP as the main components of the indexing procedure, which were as follows:

1. Amount and type of stored dangerous substances.
2. Fire prevention device of the chemical warehouse.
3. Firewater retention device installed inside the storage building.
4. Firewater retention device installed outside of the storage building.
5. Sensitivity of the pathways and receiving environment.

The authors' methodology can be applied in accordance with Formula (2):

$$K = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \quad (2)$$

where K is the summary index necessary to issuing the competent authority's obligation to introduce and apply FPP measures.

In order to validate the applicability of the defined values and ranges of the index components—in the framework of investigation—two independent expert groups were invited by the authors. These expert groups participated in environment protection, fire prevention and major accident prevention.

The groups of experts performed the identification procedure for the same 10 chemical warehouses participating in the present investigation. They used the available safety documentation (safety reports and internal emergency plans), construction and design documentation and on-site inspection data from the facilities.

The composition and working procedure of the validation expert group were similar to those used for the purposes of internationally accepted process safety risk assessment procedures referenced earlier in Section 2.2. The order of assessment also takes into account the internationally accepted approaches [64].

Detailed technical criteria for determining index components K_1, K_2, K_3, K_4 and K_5 involved in the procedure are presented in the following sections.

3.3.2. K_1 Index Component—Amount and Type of Stored Dangerous Substances

Index component K_1 takes into account the amount and type of dangerous substances stored in the chemical warehouses. The value of the index component can vary between 1 and 10.

According to the provisions of the CLP directive, the physical danger caused by dangerous substances is determined by the essential properties of the substances or mixture of substances. The dangerous substances can be assigned to a hazard class on the basis of their potential harmful effects, the criteria of which are determined by the hazard categories as a standardised description. In line with the CLP regulation, four main categories are defined for the classification of chemical substances: physical, health, environmental and other hazards. Several hazard categories belong to each hazard class.

Index component K_1 is linked with the hazardous characteristics of dangerous substances stored on the territory of a chemical warehouse. The determination procedure of index component value K_1 is based on the following logical algorithm shown in Figure 6.

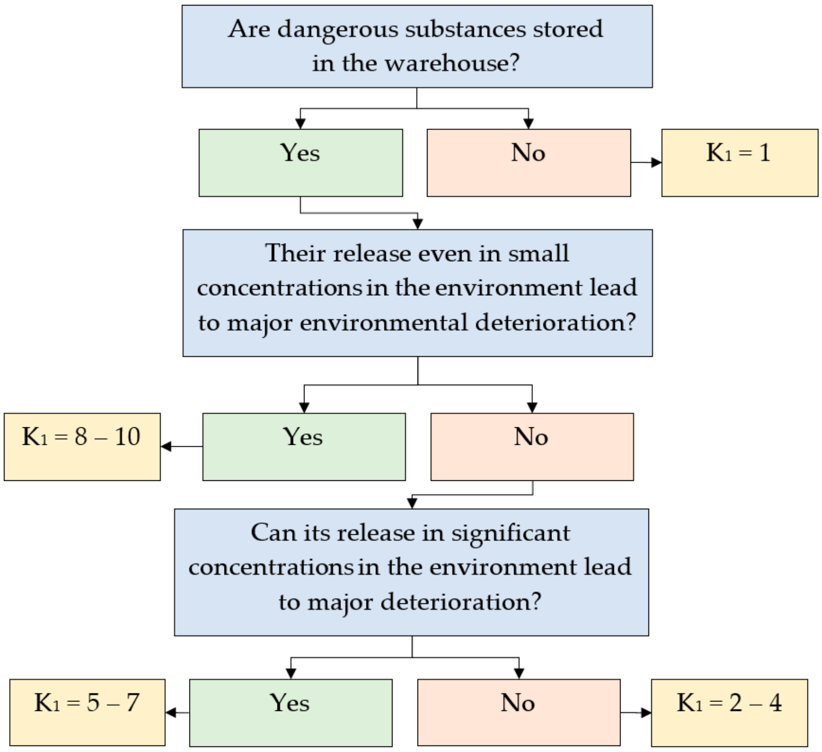

Figure 6. Determination of index component value K_1. Source: own research.

The value of index component K_1 is 1 if it is assumed that no dangerous substances are stored in the chemical warehouse. In this case, the generation of contaminated firewater cannot be ruled out, but due to the low level of pollution, the probability of serious environmental pollution is negligible.

The index component value is between 2 and 4 if it is assumed that the storage of dangerous substances is carried out in the chemical warehouse. The probability of creating a risk of serious environmental pollution is negligible because either it has no direct effect on the environmental elements or the concentration of the dangerous substances component in the mixture is low.

The index component value is between 5 and 7 if it can be assumed that dangerous substances stored in chemical warehouses could cause serious environmental pollution if released. In this case, the dangerous substances are released in high concentration without changing the essential properties of the dangerous substances; otherwise, the diluting effect of the firewater is ignored.

The index component value is 8 to 10 if it can be assumed that dangerous substances are stored in the chemical warehouse. The possibility of serious environmental pollution exists despite the diluting effect of the firewater.

For example, it can be listed as: "hazardous to the aquatic environment, acute category 1; Chronic category 1, 2" or "acute toxicity category 1, 2". However, concentrated acids and alkalis should be included in this category of dangerous substances as well, as many aquatic organisms are extremely sensitive to PH changes.

3.3.3. K_2 Index Component—Fire Protection Device of Chemical Warehouse

The K_2 index component is used to characterise the fire protection device applied in the event of a fire. The index component value can vary between 1 and 10. In relation to the chemical warehouse, the "fire prevention strategy" must be established, and the implemented protection infrastructure must be assessed.

The logical algorithm of determining the K_2 index component is detailed in Figure 7.

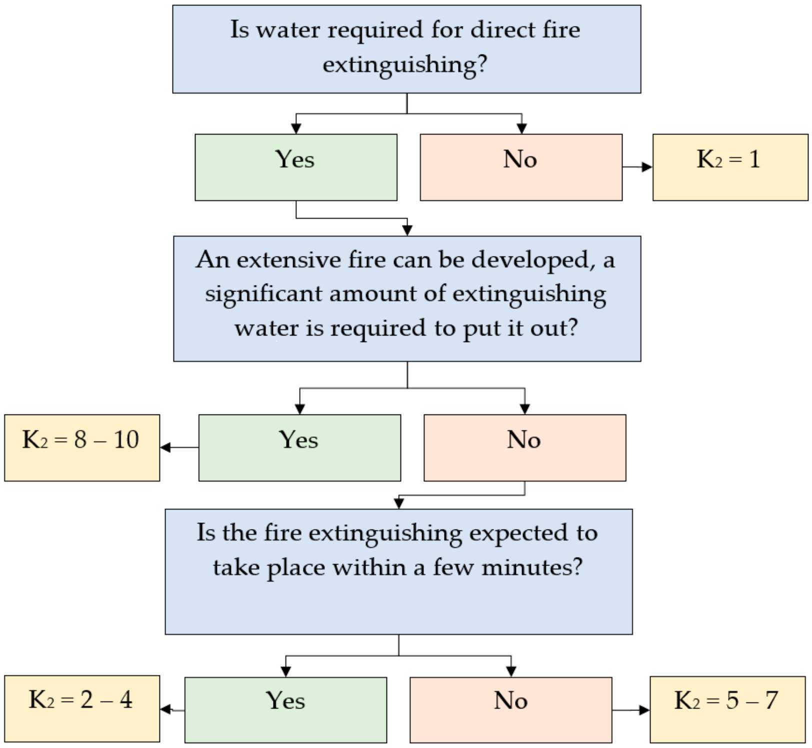

Figure 7. Determination of the value of index component K_2. Source: own research.

The index component value is 1 if water is not used directly during the fire extinguishing procedure. This could be the case, for example, if the facility is equipped with automatic gas extinguishing system.

The index component value ranges from 2 to 4 if the fire is put out within a few minutes after its origination and the occurrence of an extensive fire and a large amount of contaminated firewater is unlikely. This value can be applied to the K_2 index component in the case where an automatic fire alarm and fire extinguishing system was installed in the warehouse building.

The index component value is between 5 and 7 if the fire is not extinguished within a few minutes after its occurrence, but at the same time, the occurrence of an extensive fire—and thus the generation of a large amount of contaminated firewater—is unlikely. A value of 5 to 7 can be applied to this index component if the facility is equipped with an automatic fire alarm system and permanent trained personnel are present at the site who can start to extinguish the fire or prevent the fire from spreading until the governmental fire brigade arrives.

The index component value is 8–10 if the fire extinguishing procedure is carried out over a long period of time. Thus, there is a possibility of the development of an extensive fire and the generation of a large amount of contaminated firewater.

A value of 8 to 10 can be applied to the K_2 index component if there is no automatic fire extinguishing system in the chemical warehouse, no permanent trained personnel is hired and no fire alarm system is in operation. In that case, the governmental fire brigade will start extinguishing the already extensive fire.

3.3.4. K_3 Index Component—Firewater Retention Device Installed Inside of Storage Building

Index component K_3 is used to characterise the firewater retention device working as a safety barrier that can prevent contaminated firewater from escaping from the building. Its value can vary between 1 and 10. The built-in safety barriers that prevent or inhibit the spread of contaminated firewater must be assessed. Its value can be determined in line with the flowchart, according to Figure 8.

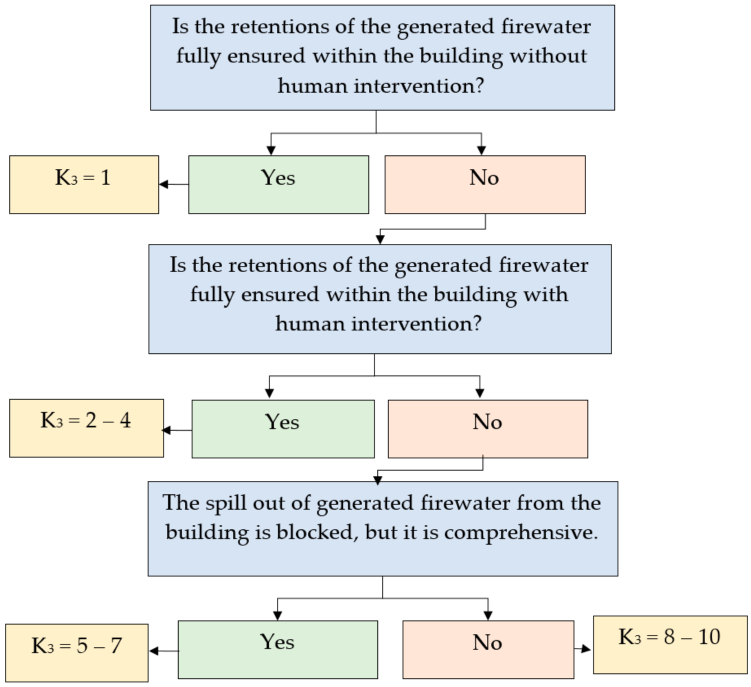

Figure 8. Determination of the value of index component K_3. Source: own research.

The value of the index component K_3 is 1 if the contaminated firewater is captured within the territory of the facility without human intervention. This means that the storage facility also functions as a firewater retention basin.

The index component value ranges from 2 to 4 if the facility does not fully function as a firewater retention facility. However, a shut-off device has been installed that enables a full-scale damage recovery operation, which requires human operation.

The value of the K_3 index component is between 5 and 7 if the warehouse does not fully function as a retention facility and the contaminated firewater can escape outside the building, but the facility is able to capture a significant amount of firewater.

The value of the K_3 index component is 8–10 if there is no retention equipment or device installed to prevent the release of contaminated firewater from the building. Even if there is such an equipment or device, a significant proportion of the firewater can spill out of the building.

When determining the index component K_3, the authors did not consider the possibility of the infiltration of firewater through the building floor. According to the experience of the authors, the floors of chemical warehouses are usually made with a waterproof, acid- and alkali-resistant coating, so infiltration in these occasions is usually negligible.

3.3.5. K_4 Index Component—Firewater Retention Devise Installed Outside of the Storage Building

Index component K_4 is used to take into account the retention device, such as safety barriers, used outside of the building to prevent and inhibit the further spread of the firewater run-off. The value of the index component can range from 1 to 10.

The value of K_4 can be determined by the procedure shown in Figure 9.

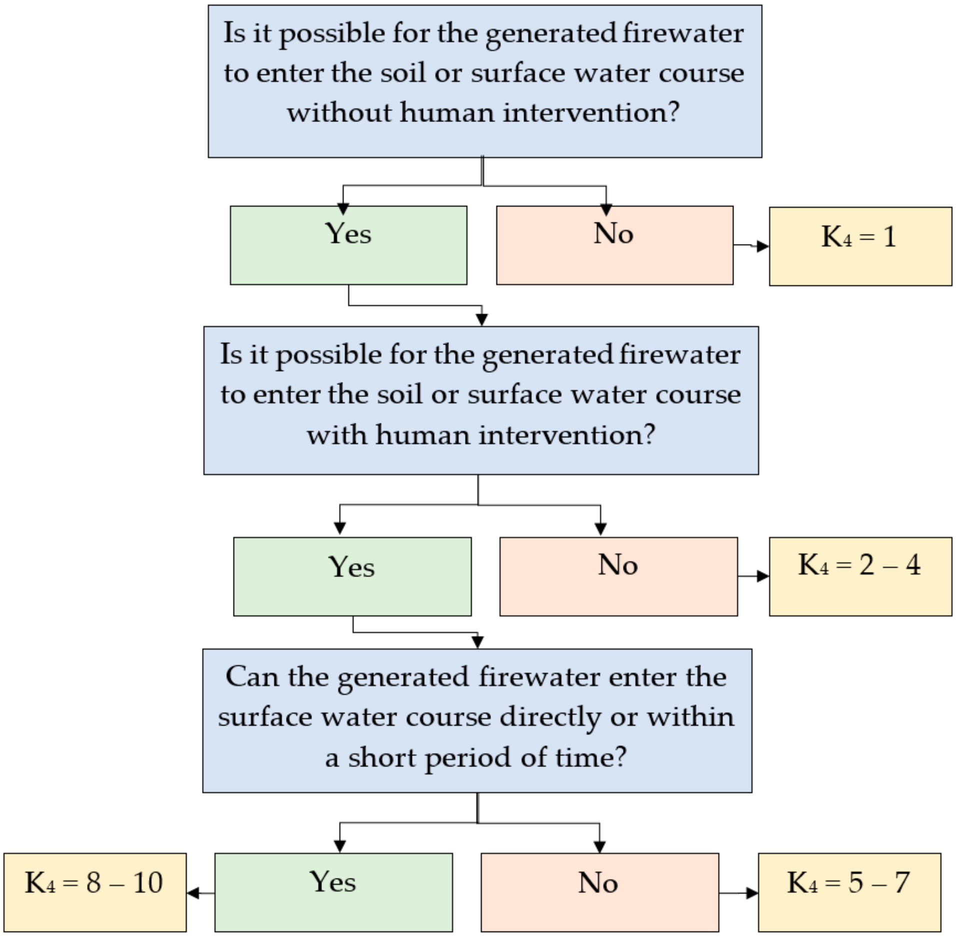

Figure 9. Determination of the value of index component K_4. Source: own research.

The value of index component K_4 is 1 if a closed system has been established for the drainage and collection of the firewater run-off. In this way, the prevention of the infiltration of firewater into the ground and entering the surface watercourse was achieved without human intervention.

The value of the index component is between 2 and 4 if the system for draining and collecting system fulfils its function only with the help of human intervention. The value is between 5 and 7 if the retention device prevents only the spread of contaminated firewater on the surface and its entry into the surface watercourse, but there is a risk of the pollutant's infiltration into the ground and spreading in it. The value is 8–10 if there is no retention device installed or if it cannot be used to prevent the surface spread of contaminated firewater. In this case, there is a risk of direct entry of the firewater into the surface watercourse.

3.3.6. K_5 Index Component—Sensitivity of the Pathways and Receiving Environment

Index component K_5 is used to examine the features of the surrounding area. It is necessary to assess, on the one hand, the extent to which the territorial conditions—such as the type of soil—can prevent the spread of polluted firewater. On the other hand, it is also necessary to assess the location of the environmentally sensitive territories—public surface water abstraction points, vulnerable habitats, sensitive groundwater and aquifers must also be taken into account. The procedure for evaluating the K_5 index component is presented in detail in Figure 10.

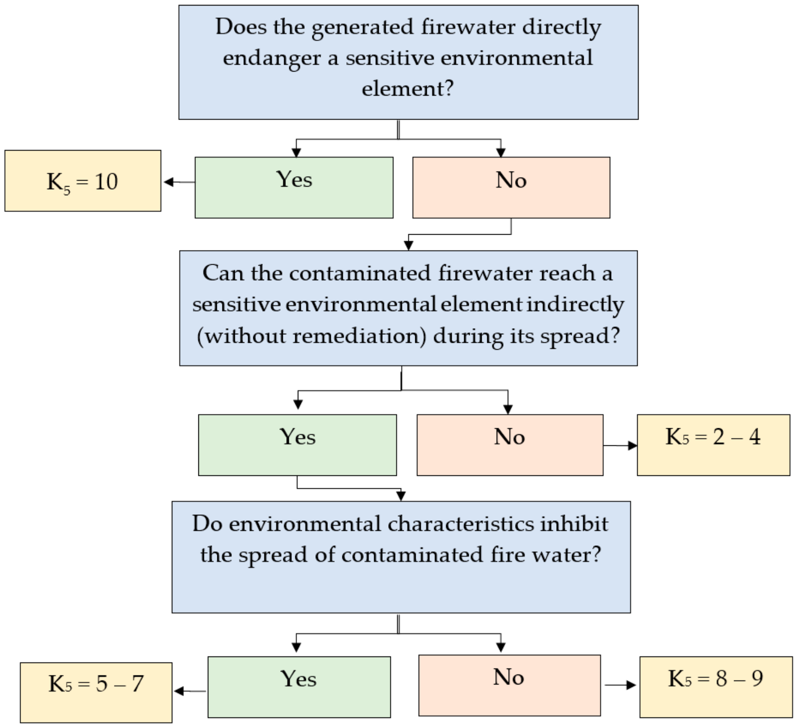

Figure 10. Determination of the value of index component K_5. Source: own research.

The authors excluded the value $K_5 = 1$ because, in the case of a firewater pollution event, environmental damage will certainly occur. Therefore, the smallest value can be 2.

The value of the index component varies between 2 and 4 if the spread of the contaminated firewater is eliminated by geological conditions. For example, if the water permeability of the soil is less than 0.3 mm/min, the released firewater cannot enter the surface watercourse directly, and there are no environmentally sensitive territories near the facility. The index component $K_5 = 2$ can be used, for example, if there is no surface water flow nearby and the soil is demonstrably clayey. Before construction, a geological survey of the area has to be prepared. This vital information is available for the purposes of risk assessment.

The value is between 5 and 7 if the spread of the polluted firewater is eliminated by geological conditions, the water permeability of the soil is more than 0.3 mm/min, the released firewater cannot enter the surface watercourse directly and there are no environmentally sensitive territories in the vicinity of the site. The later index component can be used if the soil of the surrounding territory is demonstrably clayey or loamy in composition.

The value is between 8 and 9 if the spread of the contaminated firewater is not eliminated significantly by geological conditions, the released firewater can enter the surface watercourse directly and there are environmentally sensitive territories in the vicinity of the site. The index component $K_5 = 8–9$ must also be used for sandy soil conditions. The value is 10 if the polluted firewater can directly enter the surface watercourse and other environmentally sensitive territories.

3.3.7. Definition of the Summary Evaluation Criteria for the Identification Procedure

The indexing procedure described earlier is performed by using the already presented Formula (2). The maximum value of the summary index K can be 5 values of 10, i.e., 100,000.

In order to determine the summary evaluation criterion, the authors established the minimum "social acceptability level" with the following logical system of boundary conditions:

- The authors assume that the contaminated firewater directly enters the surface water course, in which case $K_5 = 10$.
- On this occasion, the maximum protection criterion must be met in order to retain the contaminated firewater inside the building or discharge outside of the building. In this case, at least one of the component values of K_3 or K_4 should be 1.
- Furthermore, If $K_2 = 4$, then significant environmental pollution does not occur, and, in that case, any dangerous substances can be present in the area of the chemical storage facility; that is, $K_1 = 10$.

The calculated K summary index: $K = K_1 \times K_2 \times K_3 \times K_4 \times K_5 = 10 \times 4 \times 1 \times 10 \times 10 = 4000$. This means that if the original value of K exceeds 4000 in relation to the examined chemical warehouse, in this case, an environmental protection obligation must be imposed in order to preserve the state of the environment.

3.4. Inspection of the Enforcement Level of FPP Measures for Existing Chemical Warehouses

In order to examine the applicability of the chemical warehouse's identification procedure developed by the authors, it was necessary to inspect the safety documentation of the assessed chemical warehouses for the purpose of the determination of the value of the index components. The value of the index components can be determined by sending out a preliminary questionnaire in which the operator of the chemical warehouses declares the existence of FPP measures and the effectiveness of their application. For this purpose, questionnaires capable of checking the entire legal application situation are already available, of which the authors find the one used in Germany to be the most professionally sound [65].

In this study, the authors used a simple but effective inspection method of checking the safety, design and contraction documentation of the operators of chemical warehouses, which can be supplemented with an on-site inspection visit.

4. Results and Discussion

In this part of the article, based on the methodological research detailed in Section 3, the authors first assess and discuss the operator's FPP measures implementation practice for existing Hungarian chemical warehouses and then test the applicability of the identification procedure and methodology proposed by the authors. The authors present their experience with the validation of the approach and its applicability limits as well.

4.1. Assessment of the Operator's FPP Measures Implementation Practice for Existing Chemical Warehouses in Hungary

The scientific analysis of the legal and technical solutions related to firewater pollution caused by dangerous activities—such as chemical warehouses—has not been completely performed yet in Hungary.

The authors' investigation covered the safety documentation of a total of 24 chemical warehouses that are under the scope of the Hungarian major accident prevention regulations. In Hungary, an upper-tier establishment prepares a safety report, and a lower-tier establishment prepares a safety analysis. In accordance with the Hungarian national legislation, the so-called below-tier establishments should submit a major damage prevention plan to the competent authority during the licensing procedure.

In accordance with the results of the survey, 54% of the inspected chemical warehouses were upper- and lower-tier establishments covered by the Seveso III Directive. The implementation of FPP measures must be required for those operators that fall under the scope of the major accident prevention regulations. However, it can also state that the range of sites of dangerous activities is wider. The authors found that 46% of the plants are below the Seveso threshold levels, and in line with Hungarian legislation, these dangerous establishments must be treated separately. Similar safety problems can be encountered in connection with transportation facilities dealing with dangerous substances and goods [66].

Figure 11 provides detailed information on the hazardous classification of dangerous substances stored in the examined chemical warehouses.

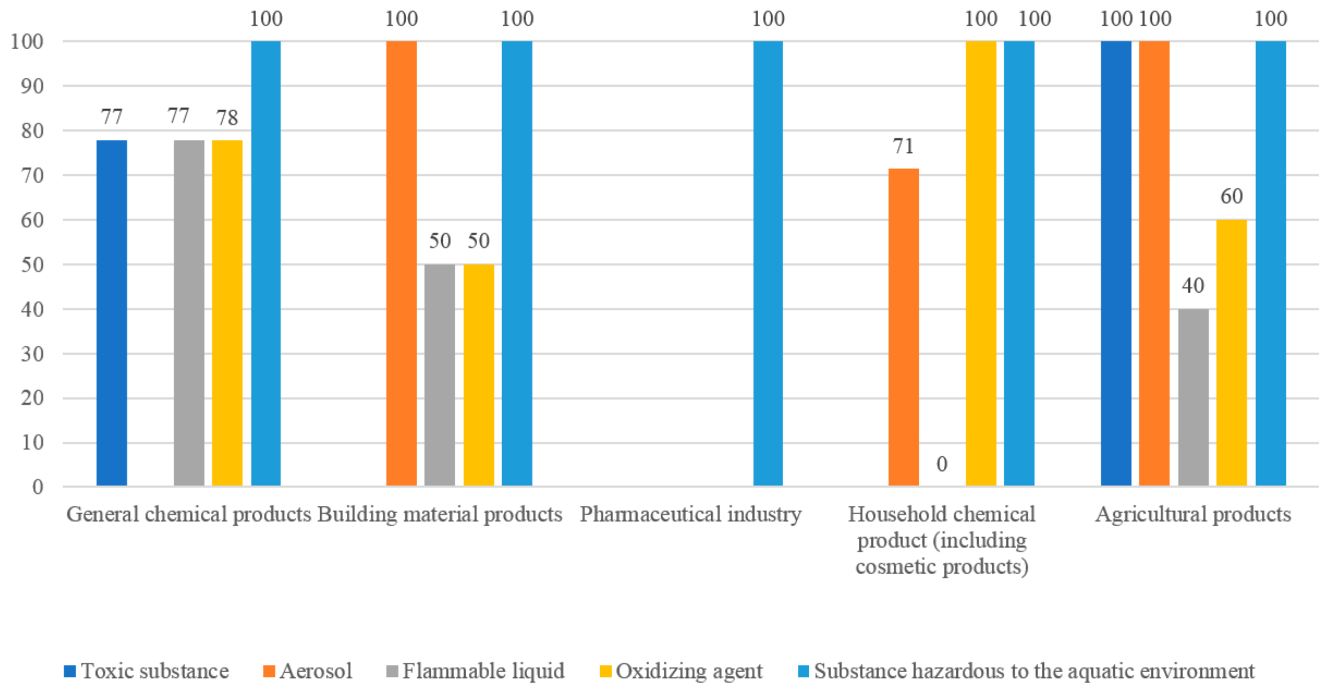

Figure 11. Hazardous classification of dangerous substances. Source: own research.

Based on the author's evaluation of the dangerous substances stored in the chemical warehouses, the following conclusions can be made:

- In 38% of the examined chemical warehouses, general chemical products are typically stored in liquid or solid state. The IBC (intermediate bulk container) is typically the largest packaging unit in storage facilities, but products can also be stored in barrels, cans, bags and smaller packages.
- Liquid, solid products and aerosols are stored in the chemical warehouses of household chemical products, including cosmetic products, in 29% of the examined chemical warehouses. It is typical for storage that the size of the packaging units usually does not exceed 10 litres.
- Liquid or solid products are stored in agricultural product chemical warehouses, which is 21% of the examined chemical warehouses. The largest packaging unit is the big-bag packaging, but the entire spectrum of packaging equipment from IBC to smaller packaging units can be found in these chemical warehouses.
- The storage of building material products (8% of all warehouses) is mainly present in liquid, solid and aerosol form. The largest packaging unit is typically the IBC, but similar to other chemical warehouses, the entire spectrum of packaging devices can be used during storage.
- In the case of pharmaceutical product's chemical warehouses (4% of all warehouses), the main objective was the examination of the chemical warehouses storing the finished product.

The evaluation results of the authors on the implementation of the operator's FPP measures practice are summarised in the following:

1. The FPP obligations of the chemical warehouses existing and under planning must be dealt with separately. Theoretically, the best solution is to introduce FPP measures during the design and construction activities of the storage facilities, but the author's experience does not show this operator practice. A total of 34% of the examined chemical warehouses were originally built for the storage of conventional products, not for storing and handling flammable, dangerous substances. Due to various market demands, the function of the warehouse during the operation of these facilities

changes, and consequently, the storage of dangerous substances or dangerous goods also begins.

2. In line with Annex 1 (point 21.) of the European Union directive on environmental impact assessment, the assessment should be performed if the storage capacity of the storage is site more than 200,000 t of total chemical products and in accordance with Annex 3 for the storage capacity of over 30,000 m^3. In the case of the present study, the total storage capacity condition was met in four cases of 200,000 tons and in two cases of 30,000 m^3. At the same time, an environmental impact assessment was carried out for only one chemical warehouse since the function of the chemical warehouse did not yet extend to the storage of dangerous substances during the installation period of the chemical warehouses. The storage function was changed only during operation activities.

It can be concluded that the environmental effects of major accidents involving dangerous substances, especially the effects of contaminated firewater, have not been fully assessed, applying environmental protection regulations.

1. Looking at the technical design of the chemical warehouses, it can be established that they comply with the fire prevention legal obligations. A fire alarm system was installed in 92%, and an automatic fire extinguishing system was installed in 37.5% of the chemical warehouses. There was automatic gas extinguishing in one chemical warehouse, automatic foam extinguishing in two chemical warehouses and water sprinkler fire extinguishing systems in the other chemical warehouses in operation.
2. In each of the examined chemical warehouses, an industrial floor was installed, and the appropriate waterproofing was ensured. Therefore, in the case of contaminated firewater being generated and remaining inside the facility, a significant amount of seepage should not be expected. A total of 21% of the chemical warehouses were designed as scaled-up retention basins.
3. During the environmental hazard analysis procedure, none of the investigated chemical warehouses identified the possibility of the generation of contaminated firewater scenarios. At the same time, the operators, implementing major accident prevention regulations, introduced FPP measures in their safety documentation.
4. It can also be stated that the contaminated firewater cannot enter the surface watercourse directly from any of the investigated chemical warehouses since the sectioning of the precipitation drainage system has been solved. At the same time, the exclusion of contaminated firewater from entering the soil and the minimisation of released pollutants can be realised only in the case of one chemical warehouse.
5. It can also be concluded that the safety level of some of the facilities (41.7%) meets the requirements of international standards and guidelines, as these facilities were designed and built recently based on these safety instructions.
6. In the case of existing chemical warehouses, it is difficult to enforce FPP measures from the authorities' point of view. In the case of existing chemical warehouses, either the range of products to be stored must be limited with a subsequent obligation of a competent authority, or technical measures must be taken to limit the run-off of contaminated firewater.

4.2. Auditing, Testing and Discussing the Applicability of Identification Procedure and Methodology

In this section, the authors first summarise their research results related to the validation of the approach and then present their research experiences related to the application of the developed procedure and methodology.

4.2.1. Results of the Validation of Evaluation Criteria

In accordance with the validation procedure defined in Section 3.3.1, the invited working groups made calculations in the case of ten chemical warehouses. Based on the results, in the case of six warehouses, the K value was greater than 4000, i.e., the necessity of FPP measures is justified. In relation to four warehouses, the K value was less than 4000, so on these occasions, no action was necessary.

In relation to the index components, subjectivity prevailed to a minimum, providing an opportunity to take into account the professional opinion of the expert groups, and the working groups reached the same result as the authors.

4.2.2. Testing and Discussing the Applicability of the Identification Procedure and Methodology

The authors present their calculation results on two important sample examples from their investigations.

- Example 1.

The result of the safety documentation assessment and a subsequent calculation for the inspected chemical warehouse was as follows:

- K_1 = 10, the value was determined by the fact that the examined chemical warehouse falls under the scope of the Seveso III Directive's regulation on the prevention of major accidents; thus, hazardous substances are present in the given chemical warehouse based on their quantitative and qualitative properties.
- K_2 = 4, based on the safety documentation, it was determined that the chemical warehouse has a built-in automatic water extinguishing system.
- K_3 = 6, the examined storage building does not fully function as a fire retention boundary; the contaminated extinguishing water from it can reach the area outside the building, although to a limited extent.
- K_4 = 10, there was no firewater retention system designed and installed outside the chemical warehouse building territory to eliminate the further flow of contaminated firewater.
- K_5 = 8, the spread of the polluted firewater is not significantly hindered by the soil conditions because it is a sandy soil. The entry of polluted firewater into the surface watercourse and the endangering of sensitive environmental habitats, such as drinking water base, exist due to the soil conditions.

The calculated summary index K is as follows:

$$K = K_1 \times K_2 \times K_3 \times K_4 \times K_5 = 10 \times 4 \times 6 \times 10 \times 8 = 19{,}200.$$

The value of the calculated result means that it is necessary to introduce FPP measures to minimise the impact of possible environmental pollution.

- Example 2.

The calculation result of the authors is in line with the early result of the competent authority's inspection procedure, as the competent authority obliged the operator of the chemical warehouse to design safety barriers in order to prepare for the elimination of the possible environmental impact of the contaminated firewater scenarios.

The operator of the chemical warehouse implemented the competent authority's obligation and created the properly sized localisation points outside of the building of the chemical warehouse, which can be used to retain the firewater in a safe manner within the territory of the site.

This means that the previous component value K_4 = 10 has been reduced to K_4 = 2.

The result of the calculation for the first chemical warehouse was as follows:

$$K = K_1 \times K_2 \times K_3 \times K_4 \times K_5 = 10 \times 4 \times 6 \times 2 \times 8 = 3840$$

The value of the calculated K summary index is less than 4000, from which the conclusion can be drawn that introducing further FPP measures is no longer justified.

Summarizing the results of the calculations, the following main conclusions are highlighted:

- It has been proven that the index components can represent the degree of firewater run-off risk caused by the affected chemical warehouse sites. Of course, the preliminary risk analysis technique proposed by the authors can be followed by the application of detailed and more sophisticated risk analyses, but only for a preselected group of operators.
- The application of the site identification process and methodology can be extended to all hazardous activities, but they require the definition of additional special risk assessment components.

4.3. Limitation of the Applicability of Identification Procedure and Methodology

Regarding the issue of the limitation of the applicability of the proposed approach, the following main conclusions can be made:

- The procedure and methodology proposed by the authors can be applied at sites serving as the chemical storage facility of dangerous substances and goods; most of the sites are regulated by major accident prevention regulations.
- The applicability of the approach can also be extended to dangerous establishments producing or processing dangerous substances, where the identification procedure can be carried out at their own chemical warehouse installations operating inside of these facilities.
- The modified approach can be applicable to facilities that use special storage procedures, such as waste disposal sites, inter- and multimodal terminals and other facilities for storing and handling electronic, battery, plastic or household waste. In the latter case, the already discussed (Section 2.1) more complex and punctual calculation procedures and methods can be used.

5. Conclusions

In line with the research results introduced in Section 4 of this article, the following final general conclusions can be drawn up:

1. One of the main conclusions of this publication is that there are significant differences in the design of chemical warehouses, both in terms of built-in modern fire prevention and firewater retention systems, in the implementation of FPP measures.
2. The scientific examination and systematisation of the processes that cause firewater pollution in major accident events can technically lay the foundation for the legal, organisational and institutional system to be established in the case of dangerous activities, such as existing chemical warehouses capable of endangering the surrounding environment.
3. The authors—using the event tree hazard analyses method—investigated the possible environmental pollution effects of the contaminated firewater that may be released in the event of a major accident, and then they proposed an identification procedure and methodology—based on the indexing method—for existing chemical warehouses involved in the implementation of the FPP measures.
4. In accordance with the calculation test and an assessment of the implementation level of FPP measures carried out among the Hungarian chemical warehouse operators, the applicability of the proposed facility identification procedure and methodology was proven. The inspected operators agreed with the results and conclusions of the authors, and in many cases, FPP measures had to be introduced based on the results of the present study. The limitation of the applicability of the approach is described in the discussion part of the article.
5. In the opinion of the authors, safety problems related to commercial and logistics warehouses dealing with dangerous goods, such as inter- and multimodal terminals, may be a future research task.

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