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Actual Issues of Industrial and Environmental Safety of Chemically Hazardous Sites Operating Refrigeration Units

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Abstract. *The purpose of the work is to determine the risk factors of accidents during the operation of refrigeration equipment at chemically hazardous sites. The discusses the factors related to the storage of hazardous chemicals, their fate, and main trends of their distribution after an accidental release. An analytical review of their physicochemical and toxicological properties, which determine the environmental consequences of the release, is carried out. The mechanism of formation of zones of chemical contamination is considered, the roles of the properties of hazardous chemicals and external factors in it are determined. The authors have revealed the difference in approaches to the classification of hazardous chemicals, identified their main properties that determine the vectors in the impact on the environment and the severity of the consequences. The research group has identified a number of physicochemical and toxicological properties of hazardous chemicals that determine the environmental consequences of the release. This will allow researchers in the future to use them as descriptors in determining the contribution to the nature of the consequences of the impact of hazardous chemicals on the environment.*

Keywords: *hazardous chemical, chemically hazardous site, release, zone of chemical contamination, refrigeration unit, ammonia.*

According to the Committee for Industrial Development and Industrial Safety of the Ministry of Investments and Infrastructural Development of the Republic of Kazakhstan, in 2018, 13 chemically hazardous sites (CHS) functioned in the Karaganda region. 6 of them belonged to the food industry and used refrigeration equipment in their technological process for cooling or freezing raw materials or finished products. This equipment uses ammonia as a refrigerant. At the same time, a number of such enterprises are located within the boundaries of urban development, close to places of mass gathering of the population, which poses a potential threat to their safety.

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As we know, the state of matter is the physical form of a substance, which is determined by the definite temperature-pressure ratio.

Gaseous hazardous chemicals (HC) are stored in liquefied or pressurized condition usually and this fact has a direct relation to the phase-dispersed content and quantity of HCs after their atmospheric release [1, 2].

As a rule, the pressurized gases have very high potential of energy and low temperature of boiling. This fact is able to sufficiently rise the probability of a flash and makes these gases more dangerous than liquids and solids. Additionally, gases being in such conditions have flash temperature lower than this value for some flammable liquids. They are able to diffuse easily and very often sensory organs of human being can not reveal them. Reservoirs where they are kept also massive and heavy. Thereby, physical and chemical properties of pressurized gases determine their high level of danger [3-6]. Unfixed reservoirs are able to fall down and injure operators. Furthermore, it could be a reason of damage, leakage or release of the matter being stored. One more reason of the overpressuse within container can be damaged

pressure regulator.

The contact of substances, which have low temperature of boiling, is able to cause chilblain of tissues in the site of contact. Liquefied oxygen and nitrogen are sources of cryogenic hazard, reservoirs with other liquefied gases also become too frozen when these gases being unloaded.

HC have the following classification dependently on their physicochemical properties and conditions where they are kept:

- pressuarized volatile and liquid (compressed and liquefied gases);
- volatile and liquid gases kept in reservoirs in the absence of pressure;
- smocking liquids;
- non-volatile solids and bulky at keeping temperatures up to 40°C;
- volatile solids and bulky at keeping temperatures up to 40°C.

It was established 3 kinds of liquid, flotation of that correlates with the ratio of own density-air density. Heavy gases and gases which have density lower that air have an evident difference in the scenario of release. Thus, being released heavy gases move above the place of release and after then they are directing to the land surface and form a secondary plume that is able to spread for many miles from the place of accident.

It is possible to capture just 3 phases when a plume of a gas with density less than air being dispersing. These are the jet phase, the transition phase, and the passive phase. A transition phase and a complete passive phase follow after a jet phase which appears initially. It is applied a special set of equations to calculate the dimensions of the plume and the content of hazardous chemicals within the plume towards the downwind side. The transition phase begins in relation to a few criteria. The most important of them are maximum distinction between the velocity of plume and the velocity of wind; and the extremal distinction between the density of plume from the density of atmosphere. his transition should be done because we need to avoid intermittentness of spreads and concentrations.

Differencies in the share content of HCs and the duration of release which is depending on several determine the degree of the contamination of the environment and environmental consequences.

Phase condition of hazardous chemicals in concrete meteorological conditions is a basic physical and chemical parameter that forms the dimension of the dangerous zone of the spreading HC. Simultaneously, the participation of HC represented by liquefied gases in industrial failures and HC boiling at low temperatures will pose the greatest danger to the population.

As a result of failures related to liquefied or gaseous hazardous chemicals gases, vapors, non-settling aerosols are produced. They being distributing over a distance of several kilometers. This fact reliably rises the volume of and severity of consequences. The formation of a zone of chemical contamination occurs in this case. It is a territory where the danger of chemical damage to the entire environment, personnel, and population exists.

Size of particles and features of spreading in the atmosphere are the most significant characteristics that indicate atmospheric spreading of HC. So, gases and vapours have size of particles up to 0.001 μm. As well as non-settling aerosol, such as fog and smoke, which are from 0.001 to 30 μm in size, they are belonged to non-settling admixtures. Settling admixtures are presented by settling aerosols, such as drizzle and large smoke particles from 30 to 500 μm in size, and air suspensions (drip-liquid fractions) with the size more than 500 μm.

In turn, the zone of chemical contamination consists of 3 main zones: a heart of chemical contamination, a zone of distribution of contaminated air with dangerous concentrations of hazardous chemicals (with non-settling hazardous chemicals), a zone of contamination of the territory (in the presence of settling admixtures). The outer boundaries of the zone of chemical contamination are limited by the threshold value of the toxic dose of hazardous chemicals during inhalation exposure to humans.

The method applied to keep hazardous chemicals on chemically hazardous sites impacts the character of the development of an emergency. The HCs could be kept in pressuarized condition in containers (pressuse 16-18 kg/cm^2); liquefied gases are stored in isothermal storage facilities within tanks with additional cooling where a pressure is close to atmospheric; compressed gases are kept at the temperature of environment and pressure ranging from 0.7 to 30 kg/cm^2; liquids are kept in sealed volumes at atmospheric pressure and temperature of environment.

The destruction of the body of a reservoir filled with pressurized hazardous chemicals is able to cause their leakage into the pallet or atmospheric release. This process can be happening for such a long period of time. Conditionally in this case, it is possible to establish 3 stages in such vaporisation process:

- dynamical stage characterized by intensive evaporation of HC;
- the period of unstable evaporation of HC;
- the period of stationary evaporation.

Initially, when the pressurized liquified gas has been leaving a reservoir, the formation of aerosol occurs. Primarily, it looks like a heavy plume that can reach a height of 20 m and after that moves to the ground due to gravitation. Contours of the aerosol plume are strict just after release. 2-3 minutes later it is diluted by air and contours disappear. It is very difficult to establish its disposition using only meteorological data because in this case the formation and direction where the plume being moving are strongly uncertain. The plume usually is 1 km or more in diameter

When the tanks of an isothermal storage are depressurized, followed by the spill of a large amount of hazardous chemicals into the pallet (embankment),

periods of first non-stationary and then stationary evaporation are characteristic. The number of HC being penetrated into the primary plume is no more than 5 percent. Such a situation provides the formation of the secondary plume.

A primary plume doesn't appear when the damage of reservoirs filled with liquids that have high boiling temperatures if these reservoirs weren't previously overheated. The evaporation of a liquid has a stationary character, while the temperature of atmospheric air and the density of hazardous chemicals.

In the Republic of Kazakhstan the monitoring of chemically hazardous sites is carried out in accordance to *Standard of the Republic of Kazakhstan 22.1.10-2010 Safety in Emergencies. Monitoring of Chemically Hazardous Sites. General Requirements.* According to this standard, during the monitoring it is necessary to take into account a number parameters of hazardous chemicals:

1) Physicochemical properties, such as their temperature of boiling or melting. relative density by air, ability to solute in water and other solvents, danger of fire and explosion, ability to be oxidized etc.;

2) Toxic properties of HC include class of hazard in accordance with *National Standard 12.1.005.*

The detection and evaluation of the hazard of HC starts from studying their physical and chemical properties. Scientists are close in the opinion that that the most important of them are title of a chemical, its application, the nature of its danger, and common requirements to prevention and and activities in the case of release, including instructions, safety signs, methods of fire extinguishing.

In the necessity, it is required for evaluation of hazard the data about the chemical formula, content of a pure substance, aggregate condition, smell, taste, look, and concentration.

The established groups of physical, chemical, and ecotoxicological parameters of HC as soon as some parameters that characterize occupational and industrial safety at an enterprise, and the vulnerability of environment we used as descriptors for environmental risk assessment in our original methodology [7]. Let's consider these parameters in part of «Balyk» LLP.

«Balyk» LLP is situated in the center of Karaganda city. The storage of chilled, frozen, perishable products is the main activity of this enterprise. Its technological process is carried out in industrial refrigerators, where ammonia is used as a refrigerant. According to Figure, the nearest environmental objects are Fedorovskoye reservoir and Bukpa river.

The total length of pipelines through which ammonia is supplied is about 15 km. This enterprise has been operating since 1960, however, all equipment is in a technically sound condition, all necessary repairs are carried out in accordance with the established terms, which makes it possible to ensure trouble-free operation of the enterprise. The depreciation rate of fixed assets does not exceed 0.01, the replacement rate of fixed assets is more than 0.95.

In the cold season, an AB 100 compressor with a capacity of 275 m^3/h is used to supply ammonia; in the warm season, an AU 200 compressor with a capacity of 550 m^3/h is used. Storage of ammonia at this chemically hazardous site is carried out in 3 tanks. Two of them have a volume of 3.5 m3 and one – 2.5 m3. Automatic shut-off valves are installed at ammonia loading points, tanks and pipelines. This chemically hazardous site is equipped with the full range of ammonia localization means.

All the staff of this chemically hazardous site regularly and in a timely manner undergo training in the rules for the safe operation of technological equipment, actions in the event of a chemical accident. The technological process at the enterprise is carried out in 3 shifts. The revision of the instructions aimed at the safe operation of the facility is carried out at least once every 3 years. All necessary documentation is present in full. The technological process is equipped with means of automatic control and monitoring. The quality of maintenance and repair work is good.

To assess the vulnerability of the environment in the event of an accident at this HOO, two objects closest to it and at the same time equidistant (1.4 km) from it were selected: the Fedorovskoye reservoir located on the outskirts of the residential area and the Bukpa river flowing in the city center.

The research of the vulnerability of the environment was carried out on the basis of geological and hydrogeological data plotted on the map of the study area and described in detail in the reports of «Kaznedra» specialists. To determine the depth of the ground to the surface of groundwater and the degree of water permeability of the ground (filtration coefficient), the results of drilling geological exploration wells located at the shortest distance to the studied chemically hazardous site, obtained by «Kaznedra» specialists, were used.

So, according to the information obtained during the drilling of well No. 3677, we took the depth of groundwater of 3.8 m, the filtration coefficient of 0.5 m/day. On the basis of GPS data, the slope from the studied chemically hazardous site towards the Fedorovskoye reservoir and the Bukpa river was determined. These reservoirs have a cultural and household purpose.

Thus, the information obtained makes it possible to fully determine the parameters that determine the hazard coefficient of a chemically hazardous site and the environmental vulnerability coefficient. The combination of these coefficients determines the level of environmental risk for the researched environmental objects, showing its absence in our example. The leading factors in this case are the high volatility of ammonia and the remoteness of the investigated water bodies from the chemically hazardous site.

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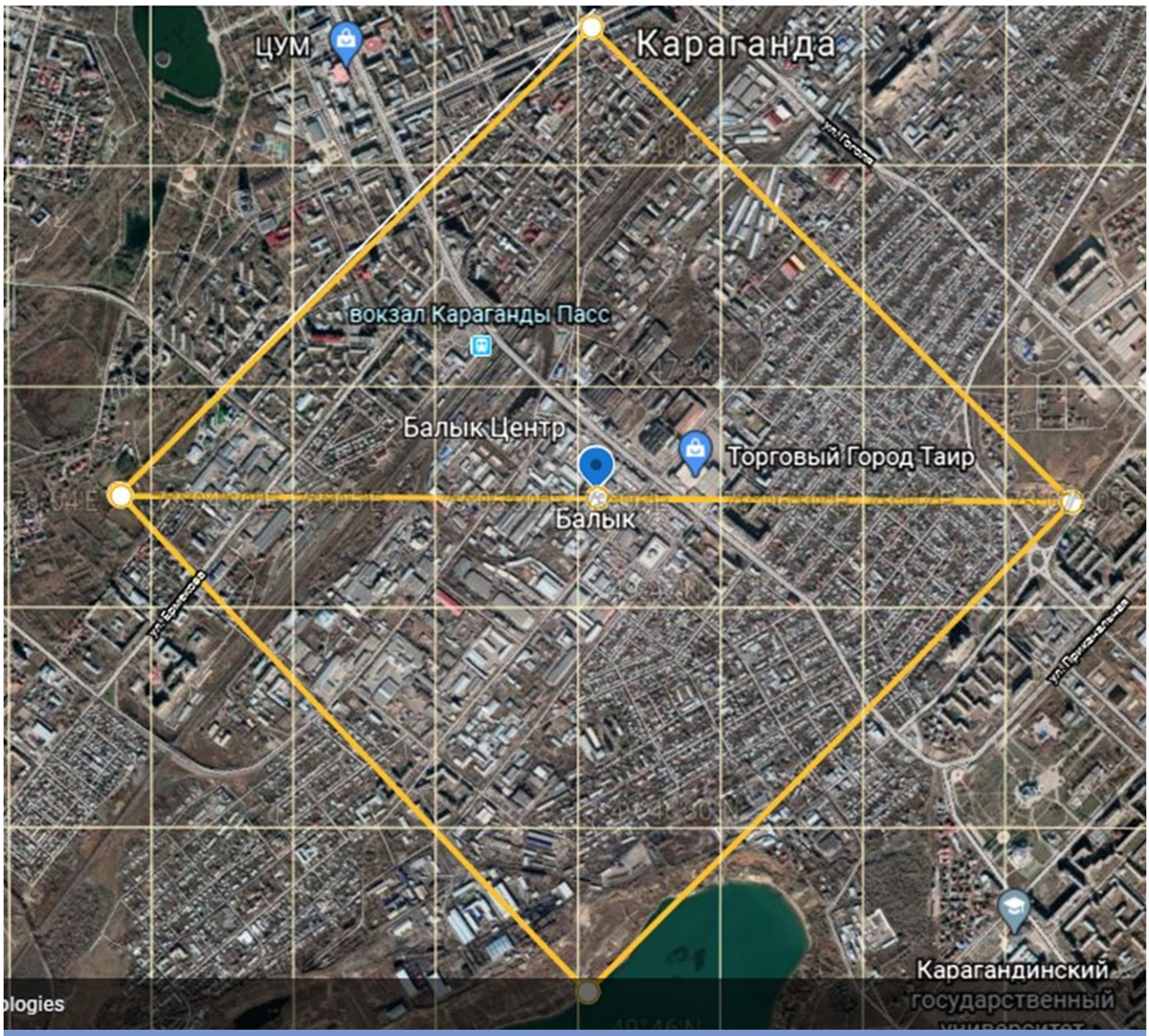

Location of the researched chemically hazardous site and environmental objects

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Тоңазытқыш қондырғыларын пайдаланатын химиялық қауіпті объектілердің өнеркәсіптік және экологиялық қауіпсіздігінің өзекті мәселелері

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Аңдатпа. *Жұмыстың мақсаты химиялық қауіпті объектілерде тоңазытқыш жабдықтарды пайдалану кезінде авариялық жағдайлардың қауіп факторларын анықтау болып табылады. Химиялық қауіпті заттарды сақтауға қатысты факторлар, олардың тағдыры және апаттық шығарудан кейінгі таралу сипаты қарастырылған. Шығарындылардың экологиялық салдарын анықтайтын олардың физика-химиялық және токсикологиялық қасиеттеріне аналитикалық шолу жүргізілді. Химиялық зақымдану аймақтарының пайда болу механизмі қарастырылып, авариялық химиялық қауіпті заттардың қасиеттері мен ондағы сыртқы факторлардың рөлі анықталды. Авторлар авариялық химиялық қауіпті заттарды жіктеуге тәсілдердің айырмашылығын анықтады, олардың қоршаған ортаға әсер ету сипаты мен салдардың ауырлығын анықтайтын негізгі қасиеттерін анықтады. Зерттеу тобы шығарындылардың экологиялық салдарын анықтайтын авариялық химиялық қауіпті заттардың бірқатар физика-химиялық және токсикологиялық қасиеттерін анықтады. Бұл оларды қоршаған ортаға авариялық химиялық қауіпті заттардың әсер ету салдарының сипатына үлесін анықтау кезінде дескриптор ретінде одан әрі пайдалануға мүмкіндік береді.*

Кілт сөздер: *авариялық химиялық қауіпті зат, химиялық қауіпті объект, шығарындылар, химиялық жұқтыру аумағы, тоңазытқыш қондырғы, аммиак.*

Актуальные вопросы промышленной и экологической безопасности химически опасных объектов, эксплуатирующих холодильные установки

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Аннотация. *Целью работы является определение факторов риска аварийных ситуаций при эксплуатации холодильного оборудования на химически опасных объектах. Рассмотрены факторы, относящиеся к хранению аварийно химически опасных веществ, их судьба и характер распространения после аварийного выброса. Проведен аналитический обзор их физико-химических и токсикологических свойств, определяющих экологические последствия выброса. Рассмотрен механизм образования зон химического заражения, определены роли свойств аварийно химически опасных веществ и внешних факторов в нём. Авторами выявлена разница в подходах к классификации аварийно химически опасных веществ, выделены их основные свойства, определяющие характер воздействия на окружающую среду и тяжесть последствий. Исследовательской группой был определен ряд физико-химических и токсикологических свойств аварийно химически опасных веществ, определяющих экологические последствия выброса. Это позволит в дальнейшем использовать их в качестве дескрипторов при определении вклада в характер последствий воздействия аварийно химически опасных веществ на окружающую среду.*

Ключевые слова: *аварийно химически опасное вещество, химически опасный объект, выброс, зона химического заражения, холодильная установка, аммиак.*

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