### MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE NATIONAL AVIATION UNIVERSITY FACULTY OF ENVIRONMENTAL SAFETY, ENGINEERING AND TECHNOLOGIES DEPARTMENT OF ECOLOGY

# **MASTER THESIS**

# (EXPLANATORY NOTE)

SPECIALTY 101 «ECOLOGY» Training Professional Program "ECOLOGY AND ENVIRONMENTAL PROTECTION"

# Theme: <u>«Assessment of the environmental safety level of the fuel storage</u> <u>facility»</u>

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**KYIV 2020** 

### МІНІСТЕРСТВО ОСВІТИ І НАУКИ УКРАЇНИ НАЦІОНАЛЬНИЙ АВІАЦІЙНИЙ УНІВЕРСИТЕТ ФАКУЛЬТЕТ ЕКОЛОГІЧНОЇ БЕЗПЕКИ, ІНЖЕНЕРІЇ ТА ТЕХНОЛОГІЙ КАФЕДРА ЕКОЛОГІЇ

ДОПУСТИТИ ДО ЗАХИСТУ Завідувач випускової кафедри \_\_\_\_\_\_В.Ф. Фролов «\_\_\_\_\_» \_\_\_\_\_20 р.

# **ДИПЛОМНА РОБОТА**

# (ПОЯСНЮВАЛЬНА ЗАПИСКА)

# ВИПУСКНИКА ОСВІТНЬОГО СТУПЕНЯ МАГІСТРА

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1. Theme: «<u>Assessment of the environmental safety level of the fuel storage facility</u>» approved by the Rector on October 11, 2019, № 2364/ст.

2. Duration of work: from <u>14.10.2019</u> to <u>09.02.2020</u>

3. Output work (project): data on environmentally hazardous objects, basic characteristics of modern oil depots, data on the impact of petroleum products on human health and the environment.

4. Content of explanatory note: (list of issues): list of environmentally hazardous objects, characteristics of modern oil bases, review of sources of oil products entering the environment, review of the impact of oil products on the environment.

5. The list of mandatory graphic (illustrated materials): tables, figures.

# 6. Schedule of thesis fulfillment

№ 3/П	Task	Term	Advisor's signature
1	Receiving of topic assignment, search of the literature and methodology development	18.10.2019 - 20.10.2019	
2	Analytical review of environmentally hazardous objects	21.10.2019 - 10.11.2019	
3	Characteristics of fuel storage facilities	10.11.2019 - 17.11.2019	
4	A review of sources of oil products in the environment and drafting explanatory note for the first preliminart presentation	17.11.2019 - 10.12.2019	
5	First preliminary presentation of the diploma work	16.12.2019	
6	Assessment of the impact of petroleum products on the environment	17.12.2019 - 28.12.2019	
8	Drafting explanatory note for the second preliminart presentation	10.01.2020 - 21.01.2020	
9	Second preliminary presentation of the diploma work	23.01.20220	
10	Formulation of the conclusions and recommendations of the diploma work, editing, consultation with standard's incpector, remarks and recommendations consideration	23.01.2020 - 26.01.2020	
11	Finalizing, signatures receiving, plagiarism verification, preparation to the final protection (presentation)	27.01.2020 - 04.02.2020	
12	Protection (presentation) of the final version of the diploma work at the department	05.02.2020	

# 7. Consultant(s) of certain chapter(s):

Chapter	Consultant	Date, signature	
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> ЗАТВЕРДЖУЮ Завідувач кафедри \_\_\_\_\_Фролов В.Ф. «\_\_\_\_» \_\_\_\_ 20\_\_ р.

#### ЗАВДАННЯ

#### **на виконання дипломної роботи** Мовчан Ірини Вікторівни

1. Тема роботи «Оцінка рівня екологічної безпеки обє'кту зберігання палива» затверджена наказом ректора від «11» жовтня 2019 р. №2364/ст.

2. Термін виконання роботи: з <u>14.10.2019 р.</u> по <u>09.02.2020 р.</u>

3. Вихідні дані роботи: дані про екологічно небезпечні об'єкти, основні характеристики сучасних нафтобаз, дані про впли в нафтопродуктів на здоровя людини та навколишнє середовище.

4. Зміст пояснювальної записки: список екологічно небезпечних об'єктів, характеристика сучасних нафтобаз, огляд джерел потрапляння нафтопродуктів в навколишнє середовище, огляд впливу нафтопродуктів на навколишнє середовище.

5. Перелік обов'язкового графічного (ілюстративного) матеріалу: таблиці, рисунки.

# 6. Календарний план-графік

No	Завдання	Термін	Підпис
3/П		виконання	керівника
1	Отримання завдання, пошук літературних джерел по темі, напрацювання методології роботи	18.10.2019 - 20.10.2019	
2	Аналітичний огляд екологічно небезпечних об'ктів	21.10.2019 - 10.11.2019	
3	Характеристика об'єктів зберігання палива	10.11.2019 - 17.11.2019	
4	Огляд джерел потрапляння нафтопродуктів в навколишнє середовище	17.11.2019 - 10.12.2019	
5	Перше попереднє представлення роботи на кафедрі	16.12.2019	
6	Оцінка впливу нафтопродуктів на навколишнє середовище	17.12.2019 - 28.12.2019	
7	Підготовка до другого попереднього захисту	10.01.2020 - 21.01.2020	
8	Друге попереднє представлення роботи на кафедрі	23.01.2020	
9	Формулювання висновків та рекомендацій, косметичні правки, консультація з нормоконтролером, урахування зауважень	23.01.2020 - 26.01.2020	
10	Дооформлення, отримання підписів, перевірка на плагіат, підготовка до захисту	27.01.2020 - 04.02.2020	
11	Захист готової роботи на кафедрі	05.02.2020	

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#### ABSTRACT

Explanatory note to thesis «Assessment of the environmental safety level of the fuel storage facility»: 78 pages, 4 figures, 7 tables, 10 formulas, 32 references.

Object of research: the impact of petroleum products on the environment.

Subject of research: fuel storage facilities.

Aim of research: to investigate the environmental safety of fuel storage facilities.

Methods of research: analytical method that includes analyzing and generalizing information to determine the environmental safety of fuel storage facilities, and methods for statistical data analysis.

Results, novelty and added value: as a result of assessment of the environmental safety level of the fuel storage facility the proper and effective fuel vapor recovery systems for this fuel storage facility was proposed. Usage of this system will make this fuel storage facility more ecological safety.

FUELS, HYDROCARBONS, LOSSES, EVAPORATION, ECOLOGICAL SAFETY, FUEL STORAGE FACILITIES, VAPOUR RECOVERY SYSTEM

#### ΡΕΦΕΡΑΤ

Пояснювальна записка до дипломної роботи «Оцінка рівня екологічної безпеки обє'кту зберігання палива»: 78 с., 4 рисунків, 7 таблиць, 10 формул, 32 літературних джерела.

Об'єкт дослідження: впливу нафтопродуктів на навколишнє середовище.

Предмет дослідження: об'єкти зберігання палива.

Мета роботи: дослідити рівень екологічної безпеки об'єктів зберігання палива та розробити рекомендації щодо підвищення рівня екологічної безпеки даного об'єкту.

Методи дослідження: аналітичний метод, який включає в себе аналіз і узагальнення інформації для визначення екологічної безпеки об'єктів зберігання палива, методи статистичного аналізу даних.

ПАЛИВО, ВУГЛЕВОДНІ, ВТРАТИ, ВИПАРОВУВАННЯ, ЕКОЛОГІЧНА БЕЗПЕКА, ОБ'КТИ ЗБЕРІГАННЯ ПАЛИВА.

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# LIST OF SYMBOLS, ABBREVIATIONS AND TERMS

RON – research octane number ;

- MON motor octane number;
- MAC maximum allowable concentration;
- VOC volatile organic compounds;
- RVP Reid vapour pressure;
- PAHs polyaromatic hydrocarbons.
- TPHs Total Petroleum Hydrocarbons
- ДСТУ State Standard of Ukraine (Державний Стандарт України).

НПАОП – Normative and Legal Acts on Labor Precaution (Нормативно-правові Акти з Охорони Праці);

#### **INTRODUCTION**

*Relevance of the work.* Nowadays there is an increase in the number of vehicles being used. This, in turn, leads to an increase in the negative impact on the environment. In particular, due to the increasing number of fueling facilities. Therefore, the issue of improving the environmental security of these objects is a pressing issue.

*Aim of the work* - to to investigate the environmental safety of fuel storage facilities. In order to achieve this goal the following *tasks* have been developed:

- 1. To characterize the fuel storage facilities and determine their level of environmental safety;
- 2. To identify the main sources of oil products entering into the environment;
- 3. The analysis of main characteristics of gasoline that determine the level of environmental safety;
- 4. To evaluate the environmental and health effects of petroleum products.

*Object of research* – the impact of petroleum products on the environment.

*Subject of research* – is fuel storage facilities.

*Methods of research* – analytical method that includes analyzing and generalizing information to determine the environmental safety of fuel storage facilities, and methods for statistical data analysis.

*Practical application:* the results of the work can be useful for solving the problem of rational usage of fuel losses from evaporation.

*Scientific novelty*: the results of the work can be used as a justification for the future developments in prevention of fuel losses from evaporation.

*Personal contribution of the graduate*: selection and calculation of the fuel vapour recovery systems.

*Approbation of results*. VIII All-Ukrainian Scientific-Practical Internet Conference «Technogenic and ecological safety of Ukraine: state and prospects of development»

#### **CHAPTER 1**

#### ANALYSIS OF ENVIRONMENTALLY HAZARDOUS OBJECTS

#### 1.1. The concept of environmental safety

Environmental safety has become a high priority issue in the world. Ensuring the safety of an environment is key to productivity and function in a work or research setting.

Environmental safety is the practice of policies and procedures that ensure that a surrounding environment, including work areas, laboratories or facilities, is free of dangers that could cause harm to a person working in those areas. A safe place to work is the key element of environmental safety.

Enhanced Safety, Health and Environment Outcomes Through Improved safety, health and environment outcomes through better design are about eliminating or minimising risks in the preliminary planning stages of a product. Better design provides a foundation for improved outcomes in the development, use and maintenance of a product like plant and equipment or a building. Improved outcomes in design require the many stakeholders who contribute to the design process to critically review its safety, health and environment implications. Therefore, the client, or end user, must be actively involved in the review to ensure that operational requirements and maintenance issues, intrinsically known to the client, are considered by other design stakeholders. For example, safety, health and environment implications inherent in the design of a building project may exist in its construction, use, maintenance and demolition, i.e. its complete lifecycle. Similar implications exist for the design of other products such as plant or equipment, e.g. its manufacture through to decommissioning [1].

### 1.2. List of actual activities and actions to ensure environmental hazards

1. In the field of thermal energy:

- thermal power plants (TPP, TPP);
- equipment for the production of electricity, steam and hot water with a thermal output of 200 kW or more using organic fuel.

2. In the field of hydropower:

- hydroelectric power plants on rivers irrespective of their capacity (including small hydroelectric power plants);
- hydroelectric power plants (HPP).
- 3. In the field of nuclear energy and the nuclear industry:
- nuclear installations;
- facilities designed for radioactive waste management;
- uranium objects.

4. Production in the field of ferrous and non-ferrous metallurgy (using non-ferrous metals, ore, ore or secondary raw materials, metallurgical, chemical or electrolytic processes).

5. Mechanical engineering and metalworking facilities, except for those without chemical processing plants.

6. Extraction of minerals, except for local minerals, extracted by landowners and land users within the limits of land provided to them for economic and household needs.

7. Processing of minerals.

8. Production of building materials (cement, asphalt, glass, heaters, including extruded polystyrene foam).

9. Chemical production (including production of basic chemicals, chemicalbiological, biotechnical, pharmaceutical production, production of plant protection products, growth regulators, mineral fertilizers, polymeric and polymer-containing materials, production and storage of nanomaterials with a capacity of more than 10 tons per year, chemical storage products (basic and cost warehouses, warehouses, bases) regardless of methods and volume of production; enterprises for extraction, production and processing of asbestos, asbestos-containing products ( zbestotsementnoyi production capacity of over 20 thousand. tons per year, friction material - more than 50 tons per year of finished products, other products - more than 200 tons per year).

10. Production, storage, disposal and destruction of ammunition of all kinds, explosives and rocket fuel and other toxic chemicals.

11. Waste management:

- hazardous (collection, transportation, sorting, storage, treatment, processing, disposal, disposal, disposal and disposal);
- household (treatment, recycling, disposal, disposal and disposal).
- 12. Production of cellulose, paper and cardboard from any raw material.
- 13. New construction, reconstruction, restoration, major repairs:
- railway stations, railways and structures;
- underground, underground underground lines as single complexes, including a depot with a complex of maintenance structures;
- tramways, suspension lines or similar lines used for the carriage of passengers, including a depot with a complex of facilities for the maintenance and repair of rolling stock;
- parks of vehicles (motor transport enterprises with complex of structures for maintenance and repair);
- maintenance stations, which include painting chambers, car washes, as well as those where the repair and testing of diesel car engines and the repair of bodies using methods of chemical surface treatment are carried out;
- Airports and aerodromes with a major runway of 2100 meters or more;
- highways, highways and public highways of national and local importance of all categories with four or more lanes, or the reconstruction and / or extension of existing lanes to four or more, provided that they are continuous 10 kilometers or more;
- sea and river ports, loading and unloading wharves (except ferry wharfs);

- specialized transport terminals;
- deep-sea navigations, including in the natural course of rivers, special canals on land and in shallow waters of the sea;
- trunk pipelines (pipelines for transporting gas, ammonia, oil or chemicals).

14. Manufacture of wood processing (chemical processing of wood, wood-fiber boards, woodworking using synthetic resins, preservation of wood impregnation).

15. New construction, reconstruction, restoration, major repairs:

• water intakes of surface and groundwater for systems of centralized water supply of settlements, industrial enterprises;

- constructions of water preparation of systems of drinking water supply;
- water supply and sewerage networks with a diameter of more than 1000 millimeters;
- sewage pumping systems to isolated underground aquifers;

• systems of reverse water use, drainage, treatment (preparation) and discharge of mine, quarry, drainage water;

- sewage treatment plants, wastewater discharge systems into water bodies;
- reservoirs.

16. Carrying out works on clearing and dredging of the river bed and bottom, their shore consolidation, change and stabilization of the river beds.

17. Carrying out works involving the extraction of sand and gravel, laying of cables, pipelines and other communications on the lands of the water fund.

18. Carrying out works on inter-basin redistribution of river runoff.

19. New construction, reconstruction of the main hydraulic structures of all kinds.

20. In the field of livestock, poultry and fisheries:

• livestock complexes for pig production (5 thousand heads and more), cattle (2 thousand heads and more), fur animals (3 thousand heads and more), poultry (60 thousand laying hens and more, 85 thousand broilers and more);

• meat-packing plants and meat-processing enterprises;

• production in the field (installations) for processing and disposal of animal waste, including poultry, fish farming;

• tanning operations.

21. Manufacture in the field of light industry, which involves dyeing and chemical treatment.

22. Production of carbon black and electrographite.

23. Radio engineering facilities (radio transmissions, radio broadcasting, radar stations).

24. Electrical lines (overhead, cable) and substations of 330 kW or more.

25. Installations for surface treatment of metals, wood, polymeric materials using organic solvents, in particular for finishing, printing, coating, degreasing, waterproofing, calibration, dyeing, cleaning or saturation.

26. Deforestation (except for deforestation) in an area of more than 0.12 hectares.

27. New construction of facilities, economic activity (except for forestry) in the protection zones of the territories and objects of the nature reserve fund, in the territories adjacent to water protection zones, coastal protective strips of water bodies, zones of sanitary protection.

28. Genetic engineering activities, introduction into circulation of genetically modified organisms and products produced with their use (in open and closed systems).

29. Introduction of alien species of fauna and flora.

30. Production of microbiological products.

31. Storage, processing and transportation of hydrocarbon raw materials (natural gas, shale gas, gas dissolved in oil, gas of central basin type, gas (methane) of coal deposits, condensate, oil, bitumen of oil, liquefied gas), also solutions for gas supply to households and industrial enterprises.

32. Refineries (with the exception of crude oil lubricants) and equipment for gasification and liquefaction of coal or oil shale.

33. Gas stations and complexes, as well as gas filling compressor stations, automobile gas filling stations of liquefied gas [2].

#### 1.3 Environmental safety of filling stations and tank farms

The concept of environmental safety of filling stations and tank farms includes properties of petroleum products which effect on humans and natural environment, for example, soil and air contamination by evaporated fuel hydrocarbons.

Soil contamination by petroleum products causes changes in its structure, chemical and microbiological composition, which can lead to the death of plants. Restoration of the productive capacity of contaminated soil is very slow, for example, the yield and quality of agricultural land are restored after 10 years.

When petroleum products enter the water they spread out, forming a film. Small quantities of petroleum products cover huge areas of water, for example, 1 ton of oil covers with a film of  $10 \text{ km}^2$  of water surface. This film violates the conditions of heat exchange of the water basin with the atmosphere, which affects the climate of the planet, causes pollution and death of aquatic vegetation and living organisms.

Most petroleum products easily penetrate the body even through undamaged skin, causing a disturbance in metabolic processes.

To reduce atmospheric pollution by hydrocarbon emissions in areas of filling stations and tank farms, it is necessary to implement measures to reduce losses of petroleum products and pollutants control.

A part of oil pipelines, tank farms, filling stations are reservoirs for receiving, storing and dispensing of petroleum products.

The operation of steel vertical and horizontal tanks should not lead to contamination of the environment (air, surface water, soil) with pollutants above permissible standards, it is shoed on Fig. 1.1.

Among the main pollutants emitted to the environment from the reservoirs are vapors of petroleum products (mainly hydrocarbons) formed due to evaporation during the reception, storage and dispensing of petroleum products.

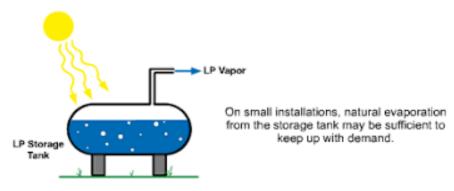


Fig. 1.1. Evaporation from operating horizontal tank

When operating tank farms and filling stations, environmental requirements determined by environmental legislation and existing normative and technical documents on environmental protection must be fulfilled. The production activity of tank farms and filling stations should not lead to pollution of the natural environment (air, surface water, soil) with harmful substances above permissible standards.

The main sources of pollutant emissions at tank farms and filling stations are:

• reservoirs with petroleum products (evaporation of petroleum products – "large and small breaths");

• fuel dispensers (evaporation when filling gasoline tanks of cars);

• objects of treatment facilities (evaporation of petroleum products and discharge of residues (after purification) into the sewage system;

• accidental and unintentional spills of petroleum products on the territory of tank farms and filling stations;

- tightness of technological equipment and communications;
- exhaust emissions of vehicles;
- wastes from cleaning tanks.

• To reduce emissions of pollutants into the environment from pollution sources of filling stations it is recommended:

• to maintain technical condition of reservoirs, their tightness, technological equipment and pipelines;

• to maintain the technical integrity of the breathing valves, timely carry out their maintenance and appropriate adjustments;

• to ensure tightness of drain and measuring devices, manholes, inspection and drainage wells, including during operations of draining petroleum products during their storage;

• to discharge petroleum products from tank trucks only with the use of hermetic quick-release couplings (on a tanker and a tank of a filling station);

• to prevent overflows and spills of petroleum products when filling tanks and refueling motor vehicles;

• to maintain metering and dosing devices and overflow prevention devices[3].

1.3.1. Characteristics of fuel storage facilities

Production, refining, and distribution of petroleum products require many different types and sizes of storage tanks. Small bolted or welded tanks might be ideal for production fields while larger, welded storage tanks are used in distribution terminals and refineries throughout the world. Product operating conditions, storage capacities, and specific design issues can affect the tank selection process.

An oil depot is an industrial facility for the storage of oil and/or petrochemical products and from which these products are usually transported to end users or further storage facilities. An oil depot typically has tankage, either above ground or below ground, and gantries (framework) for the discharge of products into road tankers or other vehicles (such as barges) or pipelines.

Oil depots are usually situated close to oil refineries or in locations where marine tankers containing products can discharge their cargo. Some depots are attached to pipelines from which they draw their supplies and depots can also be fed by rail, by barge and by road tanker.

Most oil depots have road tankers operating from their grounds and these vehicles transport products to petrol stations or other users.

An oil depot is a comparatively unsophisticated facility in that (in most cases) there is no processing or other transformation on site. The products which reach the depot (from a refinery) are in their final form suitable for delivery to customers. In some cases additives may be injected into products in tanks, but there is usually no manufacturing plant on site. Modern depots comprise the same types of tankage, pipelines and gantries as those in the past and although there is a greater degree of automation on site, there have been few significant changes in depot operational activities over time [3].

#### 1.3.2. Classification of oil storage tanks

Oil storage tanks may be present in many locations for different reasons. They function as staging areas to collect crude oils from various production fields and to deliver them into pipelines or tankers.

Oil storage tanks may be present at locations close to refineries. They collect crude oils from the transportation sectors (e.g., oil transmission pipelines, tankers, rail cars, and trucks). Storage tanks are also present immediately after the refinery to store different refined products. The functionality and operating principles of all oil storage tanks are similar. Tanks are built in groups – commonly known as tank farms. They can be as high as 14 m and as wide as 100 m. The tank size depends on batch arrival, demand for refined products, cycle-time, safety-stock, tank-bottom, and safe-fill allowance. Batch arrival is the frequency at which particular crude arrives. Demand for refined products varies seasonally; for example, gasoline demand is typically higher in the summer, whereas heating fuel demand is typically higher in the winter. Cycle-time is the time between delivery of batches of a particular product. Tank-bottom is the volume of oil in the bottom of the tank that cannot be accessed. Safe-fill allowance is the safety factor to keep the tank from overflowing. The roofs of the tanks may be fixed or floating. Fixed roof tanks can be pressurized.

Floating roof tanks are operated at atmospheric pressure. Floating roofs provide minimum void between the surface of oil and the roof and are designed to provide a good

seal between the periphery of the floating roof and the tank shell. This arrangement minimizes oxygen contamination. In certain designs, a combination of fixed roof with internal floating-roof is used, e.g., in areas of heavy snowfall or rain to prevent the accumulation of snow or water on the floating roof [3].

Oil depots are distinguished by:

- by nature of operations transshipment, distribution and prize-winning;
- by delivery method water (sea and river), railway, pipeline, motor transport;
- by the nomenclature of stored petroleum and petroleum products.

• Depending on the total capacity of tanks and containers for storage of oil and petroleum products are divided into 3 categories:

- And more than 100,000 m<sup>3</sup>,
- II from 20000 to 100000 m<sup>3</sup>,
- III up to 20000 m<sup>3</sup>.

Oil bases are also divided by the nature of their operational activities and the conditions of import and export of petroleum products: transshipment oil bases, raw materials and commodity factory oil depots, imported oil depots, distributors and more. There are many mixed-use oil depots that simultaneously perform transshipment, import and distribution operations.

The following basic operations are carried out at oil depots:

1) reception of petroleum products delivered to the base in railway tanks, oil tanks, pipelines, etc .;

2) storage of petroleum products in reservoirs and containers;

3) release of large batches of petroleum products into railway tanks, oil tanks, pipelines;

4) supplying small volumes of petroleum products to small consumers through bottlers and container depots in containers, barrels, cans;

5) heating of freezing and viscous oil products in tanks, railway tanks, oil tanks, pipelines.

In addition, auxiliary operations can be carried out at oil depots: cleaning, lighting and regeneration of oils, production of small containers, etc. On-site petroleum depots, if necessary, make dehydration and desalination of crude oil.

The whole territory of the oil depot is divided into six zones:

- I the area of receipt and release of petroleum products;
- II storage area;
- III operating area;
- IV zone of auxiliary technical structures;
- V administrative and economic zone;
- VI zone of treatment facilities.

The Petroleum Reception and Release Zone includes facilities designed to receive and release large quantities of petroleum products. The structures of this area include moorings, railway cul-de-sacs with pouring trestles, a bilge pump and a laboratory for the analysis of petroleum products.

The storage area includes a tank with measuring instruments for measuring small batches of petroleum products. This area houses a foam storage station to produce the foam required to extinguish burning tanks.

The objects of the first and second zones are interconnected by a network of pipelines that allow to direct oil products from one object to another.

In the operational area, the release of petroleum products in small batches in tanks, containers, barrels, cans. In this zone are placed auto-pallets for releasing petroleum products in tanker trucks, bottling stations for bottling oil in barrels and cans, container warehouses, which are stored in small containers of packaged petroleum products, automobile scales for weighing empty and loaded cars.

The zone of auxiliary technical structures is designed to service the main facilities of the oil depot. It includes the following facilities: a discharge area intended for unloading railway equipment, materials, spare parts and petroleum products that have arrived by rail; warehouses; boiler room for supply of steam power plants, as well as heating of petroleum products and space heating; mechanical workshop; a bonding shop; power plant or transformer substation; water pump with tanks or water tower.

The zone of administrative and economic structures includes an office with a checkpoint, a fire depot, an oil depot security building, a garage.

In the sewage treatment plant there are facilities for sewage treatment and collection of products spilled on the territory of the oil depot. The structures of this zone include sandblasting plant, oil collector, emergency barn, sludge site.

All objects of the oil depot (boiler, pumping, trestles) are interconnected by industrial communications, which include electricity, water, steam, etc.[4]

#### 1.4. Conclusions to Chapter 1

Petroleum and chemical products are primary resources in our life and considered one of the most important basic building blocks for sustainable development. The growing demand of hazardous chemicals has brought a significant increase in risk to human and its environment .The results of a historical analysis have shown that 17% of major accidents in the chemical industries were during storage processes.

The possible hazards are a function of both the inherent nature and the involved quantity of the chemical. Therefore, it is important to conduct a profound and adequate hazard analysis of the oil storage facility to figure out the potential scenarios having damage to life and property as well as provides a clear picture for the decision makers to be satisfied with the safety levels in the storage tank farm.

#### **CHAPTER 2**

#### SOURCES OF ENVIRONMENTAL POLLUTION BY PETROLEUM PRODUCTS

## 2.1. Gasoline. Its properties and characteristics

Gasoline is a mixture of volatile, flammable liquid hydrocarbons derived from petroleum and used as fuel for internal-combustion engines. It is also used as a solvent for oils and fats. Originally a by-product of the petroleum industry (kerosene being the principal product), gasoline became the preferred automobile fuel because of its high energy of combustion and capacity to mix readily with air in a carburetor [5].

Gasoline is a refined product of petroleum consisting of a mixture of hydrocarbons, additives, and blending agents [6]. The composition of gasolines varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. Gasoline is a complex mixture of hundreds of different hydrocarbons. Most are saturated and contain 4 to 12 carbon atoms per molecule [5]. The typical composition of gasoline hydrocarbons (% volume) is as follows: 4-8% alkanes; 2-5% alkenes; 25-40% isoalkanes; 3-7% cycloalkanes; 1-4% cycloalkenes; and 20-50% total aromatics (0.5-2.5% benzene). Additives and blending agents are added to the hydrocarbon mixture to improve the performance and stability of gasoline. These compounds include anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes. At the end of the production process, finished gasoline typically contains more than 150 separate compounds although as many as 1,000 compounds have been identified in some blends [6].

Gasoline was at first produced by distillation, simply separating the volatile, more valuable fractions of crude petroleum. Later processes, designed to raise the yield of gasoline from crude oil, split large molecules into smaller ones by processes known as cracking. Thermal cracking, employing heat and high pressures, was introduced in 1913 but was replaced after 1937 by catalytic cracking, the application

of catalysts that facilitate chemical reactions producing more gasoline. Other methods used to improve the quality of gasoline and increase its supply include polymerization, converting gaseous olefins, such as propylene and butylene, into larger molecules in the gasoline range; alkylation, a process combining an olefin and a paraffin such as isobutane; isomerization, the conversion of straight-chain hydrocarbons to branched-chain hydrocarbons; and reforming, using either heat or a catalyst to rearrange the molecular structure [5].

The main characteristics of motor gasoline are: octane number, volatility, density, and hydrocarbon composition [7].

2.1.1 Gasoline physical and chemical properties

Information regarding the physical and chemical properties for the gasoline mixture is located in Table 1.1 [6].

Table 1.1

No	Property	Information	
1	2	3	
1	Molecular weight	108	
2	Color	Colorless to pale brown or pink	
3	Physical state	Liquid	
4	Melting point	No data	
	Boiling point	Initially, 39°C	
		After 10% distilled, 60°C	
5		After 50% distilled, 110°C	
		After 90% distilled, 170°C	
		Final boiling point, 204°C	
6	Density	$0.7-0.8 \text{ g/cm}^3$	
7	Odor	Gasoline odor	
8	Odor threshold	0/025 ppm <sup>2</sup>	

Gasoline physical and chemical properties

9	Solubility: Water at 20°C Organic solvent(s)	Insoluble Absolute alcohol, ether, chloroform, benzene	
10	Vapor pressure at 60°C at 56°C at 51°C at 47°C at 41°C	465 mmHg 518 mmHg 593 mmHg 698 mmHg 773 mmHg	
11	Henry's law constant: at 20°C	$4.8*10^{-4}-3.3 \text{ m}^{3}/\text{mol}^{d}$	
12	Autoignition temperature	280-486°C	
13	Flashpoint	-46°C	
14	Flammability limits	1.4-7.4%	
15	Conversion factors	No data	
16	Explosive limits	1.3-6.0%	

From the moment of manufacture at the plant and before combustion in the engine, a number of factors are affected by the fuel. The quality of fuels varies under the influence of these factors, depending on their composition. The ability of the fuel to maintain its original properties is called stability. In the processes of transportation, storage and application, the properties of fuels can change due to physical or chemical processes. Therefore, we can distinguish physical and chemical stability.

The concept "physical stability" includes the propensity to change the properties of fuels with their partial evaporation. The fuel is distinguished by its propensity to losses from evaporation: the more easily boiling fraction in the fuel, the lower the temperature of the start of boiling fuel and the higher the pressure of its saturated vapor, the more its propensity to losses from evaporation.

So, based on the foregoing, we can conclude that physical stability of gasoline is characterized by gasoline quality indicators such as hydrocarbon composition and evaporability.

#### 2.1.2. Gasoline octane number

The antiknock characteristics of a gasoline – its ability to resist knocking, which indicates that the combustion of fuel vapor in the cylinder is taking place too rapidly for efficiency – is expressed in octane number [5].

This tendency is especially prevalent in smaller, high-compression engines. Preignition causes the piston to work against the movement of the crankshaft, and results in the knocking or pinging sound associated with this problem. Engine knock can lead to a loss of power and, if not rectified, eventually may cause damage to the engine. Eliminating engine knock is often accomplished by burning fuels with a high octane value.

The octane number for a gasoline is determined by comparing its antiknock performance against a reference fuel with a known octane number. Because of its high antiknock value, iso-octane ( $C_8H_{18}$ ) is assigned an octane number of 100. Normal heptane ( $C_7H_{16}$ ), which has poor antiknock characteristics, is given an octane number of 0. The octane number of a test gasoline is then the percent of iso-octane in the blend. In a test engine, the antiknock performance of a gasoline component with an unknown octane rating can be compared to the performance of various reference blends of iso-octane and normal heptane to determine its octane value. A blending component determined to have an octane rating of 90, for example, will behave similarly to iso-octane/normal heptane test mixture that has an iso-octane concentration of 90 percent.

As important as the overall octane rating of the gasoline is the allocation of highoctane components over the range of hydrocarbon fractions. Achieving smooth starting and operating performance requires an even distribution of octane across the entire range of hydrocarbon fractions. A motor fuel with most of its antiknock characteristics confined to the heavier gasoline fractions, for example, may exhibit poor knock resistance under certain driving conditions, such as during rapid acceleration.

The octane rating of gasoline sold to motorists is based on the average of the research octane number (RON) and the motor octane number (MON) and is symbolized as (R+M)/2. The RON is s measure of the performance of a gasoline under laboratory conditions while the MON measures a gasoline's performance under relatively harsh operating conditions, such as when a vehicle is towing a heavy load [8].

#### 2.1.3. Gasoline volatility

Volatility refers to a fuel's tendency to vaporize under certain conditions of temperature and pressure. The petroleum industry measures gasoline volatility in pounds per square inch (psi) of Reid Vapor Pressure (RVP). The RVP of a fuel is the surface pressure required to prevent vaporization at 60 degrees Fahrenheit under atmospheric pressure. The object for refiners is to produce gasolines that will vaporize readily in the combustion chamber during cold engine starts but are not so volatile that they will vaporize in the fuel system when engine is warm.

At high temperatures and high altitudes, some gasolines can vaporize in the fuel system, leading to a condition known as vapor lock. When vapor forms in the fuel line, the gasoline pump is no longer able to draw fuel and the engine stalls. The engine will not restart until the vaporized gasoline in the fuel line condenses. This condition is particularly prevalent in older cars.

The appropriate RVP for a motor fuel will change with geographic location, altitude, and season. Gasoline sold in the northern regions tends to have higher RVPs than gasolines sold in the southern parts. In addition, adjustments to volatility are made for altitude. To compensate for the lower air pressures in the mountainous regions, refiners will blend gasolines with comparatively low RVPs for these areas. Volatility also varies with the season. During the summer months, when vapor lock is more of a problem, RVPs generally will be lower than during the winter months, when cold starting is more of a consideration.

Adjusting the volatility of a gasoline can be accomplished in many ways, but varying the content of normal butane, which has a RVP of about 52 psi, is the most effective way. However, normal butane, with an octane number of about 92, is relatively high in octane, so varying its content can result in a lower octane rating. Therefore, high-octane, low-volatility substitutes, such as the ether blending components methyl-tertiary butyl ether (MTBE) and ethyl-tertiary butyl ether (ETBE), have been developed that can reduce gasoline volatility without sacrificing gasoline antiknock performance [8].

#### 2.2. Sources of gasoline evaporative losses

The greatest share of all kinds of losses during transportation, storage and use falls to evaporation. Such losses are very typical of hydrocarbons which easily evaporate.

Gasoline is a mixture of volatile organic compounds (VOC), mostly hydrocarbons that can freely evaporate at ambient temperatures. Retail gasoline outlets contribute to overall VOC emissions through fuel-related activities carried out on a daily basis. Gasoline contains compounds such as benzene, toluene, and ethylbenze, some of which have adverse impacts on human health [9].

Exposure to volatile organic compounds (VOC) can bring a variety of harmful health effects, including asthma, headaches and, in some cases, an increased risk of cancer.

VOCs are important air pollutants in the urban atmosphere. Some of the VOCs are toxic, potentially carcinogenic and mutagenic at concentrations levels found in the urban environment (Edgerton et al. 1989). Exposure to VOCs is of concern as it may result in significant risk to human health. Atmospheric reactions of VOCs lead to secondary pollutants, which is turn cause the deterioration of air quality and damage to Corps and vegetation [10].

Evaporative losses from retail gasoline outlets can be classified into two categories. The first category includes those attributed to the processes and equipment used by the retail outlet to supply the gasoline. The second category includes losses attributed to vehicles being filled (vehicle tank refuelling loss).

Following this classification, the sources of gasoline evaporative losses from retail outlets can be detailed as follows:

• losses from standard operations of a retail gasoline outlet (storage tank losses, residual losses);

• losses from the refuelling of vehicles.

2.2.1. Losses from standard operations of a retail gasoline outlet

2.2.1.1. Storage tank losses

Working loss in gasoline storage tanks is due to the combined effects of gasoline delivery to the storage tanks (the filling of storage tanks) and the emptying operation (the pumping of gasoline from storage tanks to the dispensers/gas pumps). During the filling of storage tanks, fuel vapours are released to the atmosphere due to the increased liquid level in the tank pushing up and reducing the vapour space in the tank. This space is also called outage space or headspace.

The vapour is consequently compressed in the tank, forcing the air-vapour mixture out through a vent pipe. If the tank is equipped with a pressure/vacuum valve on its vent pipe, vapours are released only when the pressure inside the tank exceeds the valve relief pressure. In the absence of such valves, any increase of tank pressure above atmospheric levels will release the vapours through the open vent pipe. The absence of such pressure/vacuum (P/V) valves on the storage tank vents of retail gasoline outlets was traditionally based on the consensus that P/V valves may freeze during the winter season, risking the implosion of storage tanks.

In some cases, tanker truck drivers who deliver gasoline to retail gasoline outlets are required to attach a second hose to the storage tank while refilling it to capture part of the air-vapour mixture that would have otherwise escaped from the vent pipe. This is called vapour balancing. The effectiveness of this particular "second-hose" vapour recovery method (that is, vapour balancing) in the absence of a P/V valve on the vent pipe of a tank is uncertain. Although some reports claim 90% recovery, these reports have mostly assumed the presence of a P/V valve or some sort of an orifice restriction during gasoline tanker truck deliveries.

Two methods are commonly used in filling storage tanks in retail gasoline outlets: splash filling and submerged filling. Significant liquid turbulence and vapour/liquid contact occur during a splash filling operation, resulting in high levels of vapour generation and subsequently high evaporative losses through the vent pipe. In submerged filling, the drop tube extends close to the base of the storage tank with fresh fuel being dispensed below the original liquid surface level. Liquid turbulence is thus controlled, resulting in much lower vapour generation and less evaporative losses than in the case of splash filling method.

#### 2.2.1.2. Residual losses

Operations and activities that involve opening the lids of gasoline storage tanks trigger the release of gasoline vapours to the atmosphere. Gasoline vapours accumulate in the headspace above the liquid gasoline level of tanks. This activity, though a minor contributor, is nonetheless an extra source of evaporative losses in retail gasoline outlets. Lids of gasoline tanks are regularly opened by the operators of the outlet to check the level of gasoline and for the presence of water in the tanks. Storage tank lids are also regularly opened by the gasoline delivery personnel during their filling operations.

Monitoring also involves inserting a wooden dipstick into the storage tanks to measure the gasoline liquid levels and to check for the presence of water. The measurement of gasoline level and water monitoring in storage tanks is carried out on a regular basis. The measurement of gasoline level is conducted by both the operator of the retail outlet and the gasoline delivery personnel, independently. It involves the immersion of a graduated wooden stick into the liquid inside the tanks to determine the level of gasoline. In addition, operators use the wooden stick to check for the presence of water at the base of the tank by

placing a special paste at the tip of the stick and observing any change in the colour of the paste.

A residual loss is any uncontrolled leak/spill that occurs from dispensers. Part of this residual loss is from nozzle spills. Since absorbents are mainly used by retail gasoline operators to clean up after this particular type of spill, it is assumed that the amount of such spills is correlated with the quantity of absorbents used.

#### 2.2.2. Losses from the refuelling of vehicles

Refuelling emissions occur when vapour from the headspace of a vehicle fuel tank is displaced by the liquid gasoline that is dispensed into the fuel tank. The volume of displaced vapour during the refuelling operations is equal to the volume of gasoline dispensed into the vehicle fuel tank, plus the entrapped droplets of liquid fuel as a result of splashing and turbulence during filling which are subsequently released as vapour. The quantity of displaced vapours depends on the temperature of gasoline in the vehicle fuel tank, temperature of dispensed gasoline, gasoline Reid vapour pressure (RVP), and the dispensed volume of gasoline. The volume of vapour released during refuelling also depends on the vapour recovery method used [9].

#### 2.3. Liquid fuel spills

Liquid fuel spills at the nozzle have received less attention than liquid releases due to LUSTs. These fuel spills occur when the dispensing nozzle is moved from the dispensing station to the vehicle tank and vice versa, when the automatic shutoff valve fails, due to spitback from the vehicle tank after the shutoff has been activated, and when the customer tops off the tank.

Spilled fuel may move downward in liquid or vapor phase and potentially reach the groundwater table. The physical mechanisms that govern subsurface movement of spilled fuel are the same as for fuel released due to LUST, except that spilled fuel must first

penetrate relatively impermeable pavement underneath fuel-dispensing stations. Gasoline and diesel will not penetrate the groundwater table as a liquid, because they have densities lower than that of water. Released fuel may also evaporate within the sediment, and a portion of it will move downward as a vapor and potentially reach the groundwater table. Whether the fuel reaches groundwater in liquid or vapor form, the fuel will then partition into groundwater and become a dissolved chemical that is carried away by molecular diffusion and groundwater flow and associated hydrodynamic dispersion. Therefore, the spills can contaminate downstream drinking water wells. Biodegradation can decrease contaminant concentrations significantly; however, its efficiency depends on many factors including the chemical composition of the fuel and the presence of suitable microbial species that can metabolize a given contaminant, bioavailability, and electron acceptor availability.

Partitioning of the contaminant into other phases will cause retarded transport of the contaminant within groundwater. For instance, hydrophobic contaminants such as benzene tend to sorb to the sediment. For this reason, large-scale contamination of aquifers and associated adverse health effects due to the ingestion of contaminated drinking water from these aquifers are often considered a lesser concern for hydrophobic contaminants.

Laboratory experiments and modeling have shown that gasoline from small-volume spills can infiltrate into the concrete that usually covers the ground underneath gasoline dispensing stations—despite the low permeability of concrete and the high vapor pressure of gasoline. It is unlikely that liquid fuel fully penetrates a concrete slab to contaminate the underlying natural subsurface due to the low permeability of concrete, although preferential pathways for fluid flow such as cracks and faulty joints between concrete slabs can allow for such liquid penetration. It has been hypothesized that evaporation of infiltrated gasoline and subsequent downward migration of the vapor through the concrete may lead to contamination of underlying sediment and groundwater.

Runoff water that flows over pavement can also get contaminated with hydrocarbons spilled onto the pavement, and such contamination has specifically been linked to filling stations. If a spill occurs while runoff occurs, the hydrocarbon can be expected to float on top of the water sheet, because gasoline, diesel oil, and lubricants are typically less dense than water (light non-aqueous phase liquids or LNAPLs). While runoff water is not directly ingested, it is funneled into the stormwater drainage system, and may be released to natural water bodies, often without treatment. Whereas volatilization decreases contaminant levels in the stormwater within hours depending on the exact environmental conditions, and biodegradation will further decrease levels, significantly contaminated stormwater might be released to natural water bodies if they are close by. Finally, fuel spilled at marine gas stations may directly enter natural water bodies [11].

#### 2.4. Contamination of water bodies with oil and petroleum products

Oil and petroleum products are the most common pollutants in the oceans. According to the international organization IMCO, the general the amount of oil and petroleum products that annually enter the waters of the World Ocean reaches 10 million tons. The greatest loss of oil associated with its displacement 11 from extraction sites. Emergency situations, draining tankers overboard flushing and ballast water - all this causes the permanent presence of contamination fields on routes of sea routes. Large quantities of oil come from the sea along rivers, with domestic and rain runoff. The amount of pollution from this source is 2.0 million tons / year. With industrial effluents, 0.5 million tons of oil are produced annually. Getting into the marine environment, the oil first flows in the form of a film, forming layers of different power. You can determine the color of the film thickness (Table 2.1):

Table 2.1

Appearance	Thickness, µm	Amount of oil, 1 / km2
Silver Glare	0.76	88
Traces of color	0,152	176

#### Determination of the amount of oil by color and thickness

Brightly colored divorces	0.303	352
Paint Painted	1,016	1170
Dark colored	2,032	2310
Barely noticeable	0.038	44

The oil film changes the composition of the spectrum and the intensity of light penetration into the water. The transmission of light by thin films of crude oil ranges from 11-10% (280 nm) to 60-70% (400 nm). The film with a thickness of 30-40 microns completely absorbs infrared radiation. When mixed with water, oil creates an emulsion of two types: direct "oil in water" and reverse - "water in oil". Straight emulsions composed of droplets of oil with a diameter of up to 0.5 microns are less stable and characteristic of oils containing surfactants. When the volatile fractions are removed, the oil forms viscous inverted emulsions that can be stored at surface, carry current, eject ashore and settle to the bottom.

Significant quantities of petroleum products are supplied to surface water bodies (rivers and reservoirs) with insufficiently treated industrial sewage, as well as sparse runoff. According to the Ministry of Ecology and Natural Resources of Ukraine together with wastewater to surface water 405.2 tons of oil were dumped in 2012.

The ability of water bodies to self-purify is often not enough to bring the quality of natural waters to a state that meets the standards, so there is the need to develop methods for reducing the content of petroleum products directly in water bodies.

Sources of hydrocarbons into water bodies can be divided into:

1) anthropogenic (income from economic activity):

- primary (revenues with insufficiently treated wastewater, with diffuse runoff resulting from accidents);
- Secondary (atmospheric rainfall, "outflow" from the bottom deposits);

2) natural (the natural content of hydrocarbons in water).

Significant quantities of petroleum products are supplied to surface water bodies from sewage of enterprises of oil-producing, refining, chemical, metallurgical and other

industries. A feature of industrial discharges is their local character, which sometimes leads to high concentrations oil and petroleum products in a limited area of the water area.

But in addition to organized and dispersed runoff, an integral parttoday there are industrial and transport accidents.

The occurrence of emergencies and emergencies related to environmental pollution at potentially hazardous sites may be conditioned as dangerous natural phenomena (geological, meteorological, hydrological), and the reasons for technogenic character (violation of technology and rules of operation of objects, design and construction errors, etc.). Environmental disasters can also be caused by a set of other factors.[12]

#### 2.5. Conclusion to Chapter 2

Environmental pollution by oil and petroleum products occurs as a result of their losses during storage in reservoir parks. According to this the most important task during the operation of reservoir parks is to maintain the quality and quantity of the product stored.

This requires the maximum sealing of all drainage, filling and storage processes. The majority of evaporation losses are in the tanks. All losses of oil and oil products are classified into the following types:

Quantitative losses occur as a result of leaks, spills, incomplete drainage of transport tanks and tanks. Quantitative losses are made possible by the leakage of the walls and bottoms of the tank, malfunction of the shut-off valve, non-observance of the technology of operations and other reasons.

The losses include the incomplete discharge of petroleum products, especially viscous originating through structural defects in transport capacities (insufficient inclination of the bottom of the container - to the drain pipe), oil sticking and film formation on the walls of the tank, which requires extra time for drainage.[12]

#### **CHAPTER 3**

# ENVIRONMENTAL AND HEALTH EFFECTS OF PETROLEUM PRODUCTS RELEASE DURING FUEL STORAGE

#### 3.1. Harmful chemicals of fuel

Fuels have historically contained significant fractions of harmful chemicals, some of which have been documented as contributing to morbidity and mortality in exposed persons. Crude oil, from which fuels have historically been refined, already contains toxic chemicals such as benzene. Fuel additives including anti-knocking agents and oxygenates have historically also been a health concern. Fuel composition has changed over time, primarily due to environmental and health concerns. Fuel composition also depends on geographic location and fuel type (e.g., conventional versus reformulated gasoline). In the 1920s, lead was added to gasoline as an anti-knocking agent to replace added benzene because of its carcinogenicity. Due to the massive release of lead to the environment and its neurotoxicity, lead was replaced in the 1970s by less toxic anti-knocking agents including methyl tert-butyl ether (MTBE). To reduce formation of ground-level ozone and associated adverse respiratory health effects, cleaner burning of fuel was sought in the 1990s by adding oxygenates to gasoline. This was accomplished by increasing the concentrations of MTBE, which acts as an oxygenate. However, MTBE accidentally released to the subsurface contaminated downstream drinking water wells relatively quickly, moving almost with the speed of groundwater, because MTBE is hydrophilic and poorly biodegradable. MTBE was later on identified as a potential human carcinogen.

In current gasoline formulations, benzene, toluene, ethylbenzene, and xylene (BTEX) and particularly benzene are the most studied chemicals and are currently believed to be of greatest health concern. In many countries, lead and MTBE are no longer used. Benzene levels in gasoline are currently much lower in most countries (e.g., on average 0.62 % by

volume in the USA), though the chronic health effects of benzene and other BTEX chemicals at relevant exposure levels are not well understood.[11]

#### 3.2. Environmental effects

Gasoline is a mixture of relatively volatile hydrocarbons, including normal and branched chain alkanes, cycloalkanes, alkenes, and aromatics, that vary widely in their physical and chemical properties. Liquid gasoline generally contains alkanes, aromatics, and alkenes (IARC 1989). Gasoline is formulated to meet certain product performance specifications. Each batch of gasoline is likely to have a unique chemical composition as a result of the variable composition of the petroleum starting materials and the specific types of processing methods used in the formulation of different seasonal and performance grades of the product. Upon release to the environment, gasoline is not transported as a mixture; rather, the various components of the mixture selectively partition to the atmosphere, soil, or water according to their individual physical/chemical properties. Therefore, gasoline itself is unlikely to be found in different environmental media.

The volatile fractions of gasoline are released to the atmosphere during every phase of the product formulation, handling, and marketing chain, including purchase by the consumer during refueling of gasoline-powered vehicles. These fractions generally consist of short-chain aliphatic hydrocarbons, alkenes, and aromatics (Air Force 1989; CRCS 1985; NESCAUM 1989).

Gasoline is released to the atmosphere as hydrocarbon vapors from processing and use as a fuel, and to surface water, groundwater, and soil.

The volatile hydrocarbon fraction of gasoline, which consists primarily of short-chain  $(C_4-C_5)$  alkanes and alkenes and some aromatics, partitions to the atmosphere where photochemical oxidation is the main removal process. Much of what is released to surface waters and surface soils is lost by volatilization to the atmosphere. Releases to subsurface soils may leach through the unsaturated zone and contaminate groundwater. Aromatics constitute most of the water soluble fraction of gasoline. Biodegradation of gasoline

hydrocarbons by a diverse group of microorganisms is an important removal process in surface waters, soil, and groundwater. Bioconcentration and sorption of gasoline hydrocarbons to soils and sediments may be important only for higher molecular weight hydrocarbons that are resistant to biodegradation.

Gasoline vapors are released to the air during refueling of gasoline-powered vehicles, bulk transfer of gasoline at distribution terminals, leaks from storage containers and loading equipment, and during removal and maintenance of underground storage tanks. Volatile hydrocarbons in gasoline spilled on soil or surface water will rapidly evaporate, contributing to air contamination.

Releases of small amounts of gasoline vapors have been shown to occur at service stations during refueling of vehicles. Most of the release comes from displacement of hydrocarbon vapors during filling of the vehicle or the underground storage tank. Some release will also occur from spills and line leaks.

Releases of gasoline vapors during bulk transfer operations occur primarily via displacement of hydrocarbon vapors from the tanker by the liquid gasoline. Other sources of release include leaks in fill lines and spills. The amount released during transfer operations will vary with the method used. Loading operations employing vapor recovery systems do not release as much vapor as those not utilizing them.

Gasoline hydrocarbons volatilized to the atmosphere quickly undergo photochemical oxidation. The hydrocarbons are oxidized by reaction with molecular oxygen (which attacks the ring structure of aromatics), ozone (which reacts rapidly with alkenes but slowly with aromatics), and hydroxyl and nitrate radicals (which initiate side-chain oxidation reactions). Alkanes, isoalkanes, and cycloalkanes have half-lives on the order of 1-10 days, whereas alkenes, cycloalkenes, and substituted benzenes have half-lives of less than 1 day (EPA 1979a). Photochemical oxidation products include aldehydes, hydroxy compounds, nitro compounds, and peroxyacyl nitrates.

Gasoline also can migrate to groundwater from the soil and air. Of the hydrocarbon components of gasoline, only xylenes, trisubstituted benzenes, and naphthalenes have been reported to undergo photolysis and photooxidation in aqueous solution. Alkanes, benzenes, and monosubstituted benzenes have been found to be resistant to photolytic breakdown in aqueous systems. The rate of reaction of trisubstituted benzenes and naphthalenes is competitive with that of volatilization from surface waters (Air Force 1981). Many of the hydrocarbon components of gasoline have been found to undergo biodegradation in surface waters and sediment. Microorganisms in marine and estuarine environments, including bacteria, yeasts, and filamentous fungi, are capable of degrading petroleum and petroleum products, including gasoline. Degradation of gasoline hydrocarbons in surface waters is expected to be rapid under conditions favorable to microbial activity; however, it may be slow or limited under unfavorable conditions, such as low pH, low temperature, low oxygen levels, or high salinity, or where populations of degrading microbes are low (Air Force 1989).

After volatilization, biodegradation and photooxidation are the most important removal mechanisms for gasoline hydrocarbons released to surface soils (Air Force 1989). Photooxidation in surface soils is less important than in surface water environments since infiltration of the liquid product into the soil will limit exposure to solar radiation.

Biodegradation of gasoline hydrocarbons in soil by a diverse group of microorganisms has been reported by numerous investigators. Bacteria and fungi appear to be the most important hydrocarbon-utilizing microbes in soils. n-Alkanes, n-alkylaromatics, and aromatics of carbon chain length  $C_{10}$ - $C_{22}$  are the most readily degradable hydrocarbons. n-Alkanes, alkylaromatics, and aromatics above  $C_{22}$  are generally not available for metabolism by soil microbes because of their limited water solubility and solid physical state. Higher molecular weight hydrocarbons sorbed to soil particulates are also generally unavailable for metabolism by microorganisms. Hydrocarbons in the  $C_5$ - $C_9$  range are biodegradable only at low concentrations since at higher concentrations they exhibit membrane-solvent toxicity to soil microbes and are generally removed by volatilization. Hydrocarbons with condensed ring structures, such as polyaromatic hydrocarbons (PAHs), and cycloalkanes are relatively resistant to biodegradation. Isoalkanes and 1,3,5-trimethylbenzene have also been reported to be resistant to biodegradation. Some of the intermediate products of metabolism (e.g., alcohols, aldehydes, and monocarboxylic acids)

are more water soluble or strongly sorbed than the parent hydrocarbons. The rate of biodegradation is highly dependent upon the amount of the hydrocarbon substrate and a number of site-specific environmental factors, including temperature, oxygen content, moisture content, nutrient content, salinity, and pH. Degradation of hydrocarbons by soil microbes appears to be almost exclusively an aerobic process. The initial steps in microbial metabolism require oxygen; reference to biodegradation under anaerobic conditions is limited [14].

## 3.2.1. Environmental Effects of Oil Contaminated Soil

The current pace of industrial development and the growing energy needs of mankind have led to an annual increase in oil production around the world, so in recent decades, issues related to the impact of oil and petrochemical production on the environmental situation in various regions have intensified.

As a result, large areas of high productivity are being removed from agricultural use of black earth, soil in the areas of oil fields and along oil pipelines, groundwater and surface water are polluted with petroleum products and related toxic substances, which transforms fertile land into ecologically critical ecosystems [19].

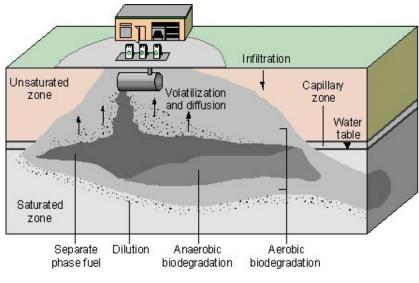


Fig.3.1. Leaking underground storage tanks

Petroleum is a complex mixture of organic compounds: alkanes (paraffinic or acyclic saturated hydrocarbons), some cycloalkanes (naphthenes) and aromatic hydrocarbons of different molecular weights, as well as oxygen, sulfur and nitrogen compounds. Hydrocarbons (48%), carbon monoxide (32%), solids (20%) are characteristic pollutants formed in the process of oil production.

One of the recipients of oil pollution is soil. Soil contamination is closely linked to amplification negative impact of harmful substances on vegetation and wildlife. In the process of developing oil and gas soil is contaminated with oil, petroleum products, various chemicals and highly mineralized wastewater. The contamination of the soil with petroleum products disturbs it ability to self-purify.

Oil pollution leads to significant changes in the physical and chemical properties of soils. In particular, due to the destruction

Soil structures and dispersion of soil particles reduces the water permeability of soils, violates the filtration regime of soils. In contaminated soils, the ratio of carbon to nitrogen at the expense of carbon is increasing sharply. This impairs the soil's nitrogen regime and disrupts the plant's root nutrition.

Remediation of disturbed and contaminated lands in oil fields is one of the most important tasks for achieving equilibrium of disturbed agricultural landscapes. They require reclamation and return to agricultural production. With the help of modern agrotechnical, phytomeliorative and microbiological technologies, there is a real possibility of returning disturbed and polluted lands to normal natural existence in a short time.

During the development and operation of oil and gas fields, soil contamination and vegetation preservation can be prevented as a result of the following measures: development and implementation of effective methods and means of separating sludge from drilling sewage and its removal to specially designated places; decrease in usage volumes washing solutions due to reuse of drilling sewage, improvement of technology and technology of their purification; introduction of new ways of moving rigs (use of pneumatic devices, etc.); development and introduction of systems for the collection

and processing of oil gas and gas condensate. As mentioned below Petroleum hydrocarbons contaminated soil is a concern for a number of reasons (Fig. 3.1).

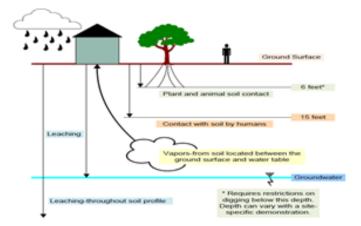


Fig. 3.2. Soil points of compliance for various exposure pathways.

At present, there are several groups of methods for the purification of soil from oil pollution: mechanical, physical and chemical (extraction, sorption), biological and complex. The use of one or another group of methods depends on the thinking of the region of development, the nature and degree of pollution. Let's look at the most modern technologies of cleaning and restoration of oil-contaminated soils.

1. Mechanical methods. They consist of collecting oil from the soil surface by mechanical means to eliminate oil pollution. Soil is cleaned by cutting off the oil-contaminated layer and replacing it with imported soil. Contaminated soil is stored in designated areas.

2. Physicochemical methods based on the use of physicochemical properties of substances (reagent neutralization of oil-contaminated soils, steam extraction, restoration of territories with the help of humic sorbent, washing of oil-contaminated soil, use of activated peat, purification by solid peat, purification by solid peat.

3. Biological methods are based on the intensification of the processes of soil selfpurification by introducing special biological preparations, representing in a certain way selected groups of microorganisms (bacteria and fungi).

4. Complex methods are a set of means for improving the condition of soils and elimination of oil pollution, consisting in the application of mechanical, physical, chemical

and biological methods of purification in combination with agricultural and amelioration works[20].

### 3.2.2. Characteristics of atmospheric pollution by petroleum products

Each year, according to various estimates, 50 - 90 million tons of hydrocarbons are emitted into the planet's atmosphere. Most of these emissions are from refineries and oil and gas industries. The specific losses of hydrocarbon due to their evaporation at the refineries of different countries of the world are 1.1 - 1.5 kg per 1 ton of product.

Significant pollution of atmospheric air by vapors of petroleum products occurs when filling and emptying the reservoirs of oil storage tanks with so-called "breathing" reservoirs. From the moment of production to the direct use of petroleum products are subjected to more than 20 transshipments, with 75% of losses occur from evaporation and only 25% - from accidents and leaks. The bulk of "breathing" tanks is concentrated in oilfields, oil pumping stations, and in oil refineries. The share of reservoir parks accounts for approximately 70% of all petroleum product losses at refineries[21].

Atmospheric oil and oil vapor pollution is also caused by the pouring of road and rail tanks on the overpasses and the refueling of vehicles at gas stations. The specific losses of petroleum products during the filling of railway tanks are several times greater than the losses from tanks. According to estimated data, gas stations of Russia emit more than 140 thousand tons of hydrocarbon vapors during the year, gas stations in Germany - 145 thousand tons, England - 120 thousand tons.

Losses of hydrocarbons at "big breaths" are caused by compression of the steamair mixture in the gas space) of the reservoir to the entrants to it with liquid oil. When the pressure in the DP reaches a certain limit value, a part of the steam-air mixture is released into the atmosphere through a special "breathing" valve. Losses from "big breaths" are determined by a number of factors: the volume, temperature and gas saturation of the oil pumped into the tank, the concentration of oil vapor in the steam-air mixture, the pressure in the gas space. The vapor content of the DP increases as the tank is filled, but the bulk of the hydrocarbon vapor accumulates in the DP during the storage period of the oil in the tank. Average annual losses from "big breaths" make about 0,14% of the volume of the saved oil product[20].

## 3.3. Influence of oil pollution on living organisms

3.3.1. Impact of petroleum products on aquatic ecosystems

The presence of petroleum products in the water body leads to the suppression of the aquatic life due to the general deterioration of water quality (changes in pH, color, appearance of a specific taste and odor). These changes are due to the presence in the aquatic environment of both petroleum products and products of their chemical and biochemical oxidation, the toxicity of which often exceeds the toxicity of the original petroleum products [22].

Hydrocarbons found in a water body interact with the ecosystem: on the one hand, oil affects the biota as a toxicant, and on the other hand, hydrobionts affect the oil, carrying out the process of its transformation.

It is known that the environmental hazard of petroleum products depends on the process of redistribution of fractions, which occurs over time, due to evaporation, dissolution, chemical and biochemical oxidation, emulsification, sorption, temperature and other factors. The main result of the redistribution of fractions is change the ratio between water-soluble and insoluble components of oil in an aqueous ecosystems[23].

The water-soluble fraction of petroleum contains predominantly light aliphatic and mononuclear aromatic hydrocarbons, the ratio of which changes very rapidly (in the first hours) toward the predominance of the latter.

The degree of toxicity and the cumulative effect of petroleum and petroleum products are directly dependent on their solubility in water. Since the most soluble are aromatic hydrocarbons, the most toxic in the series are aromatic hydrocarbons[21].

The addition of additional double or triple bonds also increases the solubility and therefore the toxicity of the hydrocarbons. Petroleum and petroleum products have some toxic effect on phytoplankton.

The negative impact of petroleum products, especially film products, at concentrations of 0.001 - 10 mg / dm3 affects the development of higher aquatic vegetation (macrophytes). The toxic effects of petroleum and petroleum products on zooplankton were noted at a concentration of 0.001 ml / dm3. At the concentration of petroleum products, at the level of 0.1 mg / dm, zooplankton dies.

For aquatic organisms, oil and petroleum products are highly toxic substances and belong to the group of nerve poisons.

Hydrocarbon oils are mainly detrimental to the early stages of the development of hydrobionts and do not lead to the rapid and mass extinction of adult organisms. For caviar, fledgling fish and crustaceans, the concentration is detrimental oil is only 0.1 - 0.01 mg / dm, whereas in adults such concentration does not have a toxic effect.

The narcotic effect caused by hydrobionts oil and petroleum products, is associated with a soluble component, and irreversible toxic action - with heavy fractions that cause disturbance of gas and water exchanges, processes, filtration, damaging the outer shell, penetrating inside the body, penetrating inside the body, .

The risk of oil contamination for hydrobionts is exacerbated by the combined presence in the aquatic environment of heavy metals, pesticides, and temperature factors, since synergistic effects are observed with different combinations of oil with these xenobiotics[24].

The peculiarity of petroleum hydrocarbons is their ability to move freely from the digestive tract into the bloodstream and be introduced into adipose tissue, which creates the danger of transporting petroleum hydrocarbons in the general trophic bonds of hydrobiocenoses and penetration of these substances into the human body.

The maximum permissible concentration of petroleum products (in the dissolved and emulsified state) for water of water objects of economic drinking and cultural use is equal to 0.3 mg / dm3, for fishery water bodies - 0.05 mg / dm3[25].

#### 3.3.2. Effects of petroleum on animals and plants

Oil has an external effect on birds, food, egg contamination in cubes, and so on. External oil pollution destroys plumage, entangles feathers, causes eye irritation. The death is the result of cold water, the birds are drowning. Birds that spend most of their lives on the water are most vulnerable to spills of oil on the surface of reservoirs. Birds swallow oil when they feather beak, drink, consume contaminated food and breathe vapor. Oil swallowing is rarely a cause direct death of birds, but leads to extinction from starvation, disease, predators. Birds' eggs are very sensitive to the effects of oil. A small amount of some types of oil may be sufficient for death during the incubation period.

Oil spills can have both rapid and long-lasting effects on birds. Oil evaporation, food shortages, and cleanup measures can reduce the use of the affected area. The deaths and reductions caused by oil spills are easier to detect locally or in colonies than in the region or whole scale.

Marine mammals, which are primarily distinguished by the presence of fur (sea otters, polar bears, seals, newborn fur seals) often die from oil spills. Oil-contaminated fur begins to become entangled and loses its ability to retain heat and water. Adult seals and cetaceans (whales, guinea pigs and dolphins) are distinguished by the presence of a fat layer, which is affected by oil, increasing heat consumption. In addition, oil can cause skin, eye irritation and impede normal swimming ability.

The large amount of oil that has entered the body, can lead to the death of the polar bear. However, seals and cetaceans are more durable and quick to digest. Oil released into the body can cause gastrointestinal bleeding, kidney failure, liver intoxication, blood pressure disorders.

Steam from oil evaporation leads to organ problems breathing in mammals near or in close proximity to major oil spills.

Sea otters and seals are particularly vulnerable to oil spills due to the density of accommodation, the constant stay in the water and the impact on the thermal insulation of fur[26].

Fish are exposed to oil spills in water when contaminated food and water are consumed, as well as when they come into contact with oil during movement of caviar. The death of fish, excluding rejuvenation, usually occurs with major oil spills. Therefore, a large number of adult fish in large reservoirs of oil will not die.

However, crude oil and petroleum products have a variety of toxic effects on different species of fish. A concentration of 0.5 ppm or less of oil in water can lead to the death of trout. Almost lethal effect of oil on the heart, changes breathing, increases liver, slows growth, destroys fins, leads to various biological and cellular changes, influences behavior.

Oil and petroleum products affect aquatic fauna in several directions:

- the surface film of oil delays the diffusion of gases from the atmosphere into water and disrupts the gas exchange of the reservoir, creating oxygen deficiency;
- oily substances, covering the surface of the gills with a thin film, disrupt gas exchange and lead to asphyxia of fish;
- water-soluble compounds easily enter the body of fish;
- at a concentration of oil of 0.1 mg / 1 the meat of fish acquires an indispensable "oil" smell and taste;
- The bottom sediments of the oil undermine the water base of the reservoirs and absorb oxygen from the water.

Plants, because of their limited mobility, are also good objects for monitoring the impact of environmental pollution. Published data on the effects of oil spills include the deaths of trees, seagrass, most algae, severe long-term destruction of salt marshes of swamps and freshwater; increase or decrease of biomass and activity for photosynthesis of phytoplankton colonies; changing the microbiology of colonies and increasing the number of germs [27].

The impact of oil spills on major native plant species may last from several weeks to 5 years, depending on type of oil; the circumstances of the spill and the species affected. Work on the mechanical cleaning of contaminated sites may increase the recovery period by 25% -50%.

It takes 10-15 years for complete restoration of the forest. Plants in the water column of large volume return to their original (to oil spill) state faster than is the case with plants in smaller reservoirs [27].

## 3.3.3. Impact of petroleum products on human health

The toxicity of the petroleum products and gases released from them is determined mainly by the combination of hydrocarbons that are part of them (aromatic hydrocarbons, phenols, etc.). Heavy gasoline is more toxic than light gasoline, and the toxicity of a mixture of hydrocarbons is higher than the toxicity of its individual components.

The toxicity of petroleum products in the processing of sulfuric oils significantly increases. The most harmful to the human body is a combination of hydrocarbon and hydrogen sulfide. In this case, toxicity is detected faster than when isolated.

All hydrocarbons affect the cardiovascular system and blood levels (decrease in hemoglobin and erythrocyte content), liver damage and endocrine glands are also possible. The peculiarities of the action of oil vapor and its products are related to its composition. Oil, poor in aromatic hydrocarbons, in its action approaches the gasoline fractions. Liquid oil has a great effect on the skin, causing dermatitis and eczema.

When gasoline vapor enters the respiratory tract or as a result of absorption into the bloodstream from the gastrointestinal tract, there is a partial dissolution of the body's fats and lipids. Not only does gasoline affect the central nervous system, but it can also cause acute and chronic poisoning, sometimes with fatal.

All types of gasoline have a pronounced effect on the cardiovascular system. Receptor irritation causes excitation in the corrigal brain, which involves the process of suppression of the organs of vision and hearing. In acute gas poisoning, the condition resembles alcohol intoxication. It is coming at a concentration of gasoline vapor in the air 0.005-0.01 mg / m3. At a concentration of 0.5 mg / m3, death occurs almost instantaneously. Frequent repeated gas poisoning develops nervous disorders, although with repeated actions of small amounts, addiction may occur (decreased sensitivity)[28].

The overall effect of gas is similar to that of gasoline, although the irritant effect of its vapors on the mucous membranes is much stronger. In toxic concentrations, gas vapors are close to gasoline vapors, but they also affect the skin like oil, lubricating oils, causing dermatitis and eczema.

Boundary hydrocarbons are the most inert chemistry, but they are still toxicants. With the increase in the number of carbon atoms, the force of the narcotic action increases, but its own effect is weakened by the insoluble solubility in water and blood. Characteristic instability of reactions of the central nervous system arising under the influence of steam hydrocarbons. This is manifested not only at high but also at low (pie) concentrations.

Organic mercaptans RSH are highly toxic compounds. They are formed by thermal action on the sulfur contained in the oil. Mercaptans are found in the air of oil and gas refineries at lower concentrations than hydrogen sulfide. Mercaptans have a pronounced specific odor, which is why they can be detected in the air even at a concentration of  $2 \cdot 10-9 \text{ mg} / \text{m3}[25]$ .

#### 3.5. Conclusion to Chapter 3

As it was mentioned above, hydrocarbons released due to evaporation losses effect both humans and natural environment. The main sources of hydrocarbons release are standard operations of a retail gasoline outlets and tank farms and also vehicles refueling. Gasoline vapours contain significant fractions of harmful chemicals such as benzene, toluene, ethylbenzene, and xylene. These chemicals are believed to be of the great concern for human health. At the same time, vapours significantly contribute to environmental contamination and especially to atmospheric pollution.

## CHAPTER 4 SELECTION AND CALCULATION OF THE FUEL VAPOUR RECOVERY SYSTEMS

## 4.1 Adsorption of gas impurities

Adsorption is called the process of selective absorption of a gas, vapor, or solution component by the porous surface of a solid (adsorbent). Adsorption is used to purify gases with a low content of gaseous or vaporous contaminants to obtain very low volume concentrations. Adsorption is used to capture the ventilation emissions of sulfur compounds, hydrocarbons, chlorine, nitrogen oxides, organic solvent vapors, etc.

Adsorption processes are selective and reversible. Each absorber has the ability to absorb only certain substances and not absorb others. The absorbed substance can always be separated from the absorber by desorption.

Unlike absorption methods, adsorption allows gas to be purified at elevated temperatures[15].

The target absorbed component in the purified gas is called an adsorbent, the same component in the adsorbed state, ie the absorbed substance in the adsorbent is adsorbate.

The ability of surface particles (ions, atoms, or molecules) of condensed bodies to attract and retain gas molecules is caused by excess energy on the surface (compared to the average energy of particles in the bulk of the body) and is inherent in all solids and liquids. In practice, it is advantageous to use substances with a developed specific (per unit volume) surface as adsorbents.

The amount of adsorbate retained on a single surface area of the phase separation is ultimately determined by the strength of the interaction between the molecules of the adsorbed substance and the particles located in the surface layers of the adsorbent.

The nature of the interaction of the adsorbate with the surface distinguish between physical and chemical adsorption.

Physical adsorption is conditioned by the forces of intermolecular interaction (dispersion, orientation and induction effects). The intermolecular forces are weak, so only a small deformation of the adsorbed particles occurs during physical adsorption. This type of adsorption is a purely physical process with an activation energy of the order of 4 ... 12 kJ / mol. During physical adsorption, the molecules of gases and vapors are absorbed by the van der Waals forces, and by chemosorption, chemical forces. In physical adsorption, the interaction of molecules with the surface of the adsorbent is determined by relatively weak forces (dispersion, induction, orientation). Physical adsorption is characterized by high speed, low bond strength between adsorbent surface and adsorbent, low heat of adsorption (up to 60 kJ / mol)[16].

However, the possibilities of the adsorption process are far from being exhausted. In some cases, it can be used to create a new generation of treatment systems that meet not only sanitary standards, but also economic requirements. For example, adsorption can be applied in a two-stage purification scheme for pre-concentration of highly diluted organic pollutants, which are then supplied to thermo-neutralization. Thus, concentrations of pollutants in ventilation emissions can be increased tenfold.

Adsorption can take place in a stationary (moving) layer, a fluidized bed (fluidized) adsorbent.

The mechanism of the adsorption process. Adsorption phenomena develop at the boundary of a solid or liquid phase with another liquid phase or gas[17].

#### 4.2. Characteristics of adsorbents

Qualitative indicators of the process of adsorption treatment of waste gases largely depend on the properties of the adsorbents. The adsorbents are of high porosity and have a large specific surface area. Thus, in the most common adsorbents it can reach 1000 m 2 / g. Industrial adsorbents are made of solid porous materials and used in crushed, granular or powder form.

The adsorbent should have a high sorption capacity, that is, the ability to absorb a large amount of adsorbent at its low concentration in the gas environment, which depends on the specific surface area and the physical and chemical properties of the surface particles. The adsorption capacity of the adsorbent depends on its nature. It increases with increasing surface area, porosity, with decreasing pore size of adsorbent, and with increasing concentration of adsorbent in carrier gas and system pressure. As the temperature and humidity increase, the adsorption capacity of the adsorbents decreases. Good adsorbents can withstand hundreds and thousands of adsorption cycles - desorption without significant loss of activity.

The adsorbent should have a high selectivity (selectivity) relative to the adsorbed component, have sufficient mechanical strength. To keep the aerodynamic resistance of the layer low, the density of the adsorbent should be small, and the shape of the particles streamlined and create a high porosity of the bulk. The adsorbent for the process of physical sorption should be chemically inert with respect to the components of the purified gas environment, and for chemical sorption (chemisorption) - to interact with the pollutant molecules in a chemical reaction. To reduce the cost of desorption of trapped components, the retention capacity of the adsorbent should not be too high, that is, it must have the ability to regenerate. Adsorbents should be of low cost and be made of available materials.

The pores in solids are classified by macropores with a radius of more than 1000 ... 2000 A; transient (mesopores) with a radius of 15 to 1000 A; micropores - up to 15 A.

Macropores with pore sizes greater than 1000 ... 2000 A are transport channels for bringing adsorbed molecules to meso- and micropores. In macro- and mesopores, a layer-by-layer mechanism of adsorption is observed; in micropores, the size of which is equal to the size of adsorbed molecules, adsorption has the character of bulk filling. Therefore, for microporous adsorbents, the pore volume, not the surface of the adsorbent, is crucial in the adsorption.

Large pore adsorbent adsorbs substances with large size molecules and at high pressures. Medium-porous adsorbent adsorbs more effectively at medium pressures, and fine-porous adsorbents at low pressures.

The specific volume of micropores in adsorbents reaches  $0.2 \dots 0.6 \text{ cm } 3 / \text{g}$ , and the specific surface area - up to 500 m 2 / g and more, so micropores play a major role in the separation of gas mixtures, especially in the purification of gases from low concentrations of impurities. Other things being equal, the amount of adsorbed substance (adsorbate) will increase as the adsorption surface increases.

Highly developed porosity, substances with a very high porosity, spongy structure or in the state of the finest grinding have a highly developed surface. From practically used adsorbents (adsorbents) the leading place belongs to various types of activated carbon (wood, bone, etc.), whose surface can exceed 1000 m 2 / g. Good adsorbents are also silicic acid gel (silica gel), alumina, kaolin, some aluminosilicates (alumogels), zeolites and other substances that differ in the nature of the material and, as a consequence, in their adsorption properties, granule size, density, etc.

Activated carbon is a porous carbon adsorbent. Several brands of activated carbon, differing in size of micropores, are used. Activated carbon of the respective brand is used for adsorption of various components (gases, volatile solvents, etc.) having different properties. The size of the granules of activated carbon is  $1.0 \dots 6.0$  mm, the bulk density is  $380 \dots 600$  kg / m 3.

Silica gel is a synthetic mineral adsorbent. Silica gels are hydrated amorphous silica (Al i O 2 nH 2 O). The specific surface area of silica gel is 400 ... 770 m 2 / kg. It is mainly used for moisture absorption because it is able to hold up to 50% moisture by weight of the adsorbent. Its advantages in comparison with activated carbon are non-combustibility, low regeneration temperature (100 ... 200 ° C), low cost in mass production, relatively high mechanical strength. The industry produces a number of brands of silica gel, differing in the shape and size of the grains (0.2 ... 7.0 mm - lumpy and granular), bulk density 400 ... 900 kg / m 3. Silica gel has a high adsorption capacity. It is often used to drain gas and absorb vapors, such as methyl alcohol from a gas stream

Activated carbon is a versatile adsorbent that works satisfactorily in humid environments. It satisfies most other requirements and is therefore widely used. One of the major disadvantages of activated carbon is the chemical instability to oxygen, especially at elevated temperatures. [18].

## 4.3. Principles of recovery of steam fuels in tank

In the case of storage of light petroleum products in tanks distinguish two main types of losses - from "small breaths" and from "big breaths".

Losses from "small breaths" are called losses in case of fixed storage of fuels, caused by daily average temperature changes.

Losses from "big breaths" are those losses that occur when filling the tank from which steam-air mixture is displaced. When feeding steam to the tank to the tank, the mixture is compressed to a critical pressure Pk, which corresponds to the pressure of the respiratory valve, then in case of further increase of this pressure there is an exhalation.

The losses from "small breaths" in the reservoirs depend on the volume of gas space. The smaller the volume of gas space and the larger Pk, the less will be the loss of "small breaths". Losses from "small breaths" can be greatly reduced by removing the steam-air mixture displaced from the reservoir through the pipeline (gas strapping) into a special gas picker - gas gauge.

Loss of petroleum products from evaporation causes not only financial losses caused by the loss of fuels, but also significant damage to the natural environment. Technological, organizational and technical measures have been developed in Ukraine and abroad to reduce the pollution of the ambient air of fuel filling enterprises by emissions of toxic substances in Ukraine and abroad. One of the main measures to reduce atmospheric air pollution by steam of petroleum products of tank farms is the return to the tank of a steamair mixture emitted during "big breaths". This process is called steam recovery.

One of the effective ways to reduce emissions of toxic substances into the atmosphere is the use of gas tighting reservoirs fuel filling complexes. For this purpose,

the gas spaces of groups of fuel tanks connect gas pipelines to a single gas-equalizing system. The condition for the effectiveness of such a system is:

$$p_{\Gamma} > p_2 > p_{\kappa},$$

where  $p_r$  – minimum hydrostatic pressure of the column of the liquid during a shower;  $p_2$  – pressure in the gas equilibrium system at the end of the drain;  $p_{\kappa}$  – excess pressure, in which the respiratory valve operates.

The pressure at the end of the discharge is determined from the equation:

$$\frac{p_1}{p_2} = \frac{V_1}{V_2} \to p_2 = \frac{p_1 \cdot V_2}{V_1},$$
(1)

where  $p_1$  – pressure in the gas equilibrium system to the discharge of petroleum products;  $V_1$  – the gas volume of the group of tanks connected to the gas equalization system, to the drain;  $p_2$  – pressure in the gas-smoothing system after the discharge of oil products;  $V_2$  – the gas volume of the group of tanks connected to the gas equilibrium system after the discharge.

The scheme of the binding of vertical vertical tanks equipped with a gas equalizing system with a gas-tanks reservoir and a system for recovering light fractions of petroleum products during the filling of tank-vehicles, railway tanks and fuel delivery to aircrafts is shown in Fig. 1.1

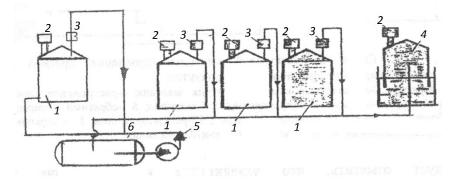


Fig. 4.1 Gas-equilibrium system with gas collector: *1* - reservoir; *2* - respiratory valve; *3* - fire extinguisher;

4 - gas collector; 5 - pump; 6 - collector of petroleum products

Currently, fueling enterprises are also widely used as an adsorption method for the recovery of vapors of petroleum products. In this case, a pair of petroleum products from the upper part of the reservoir enters the adsorber where they are absorbed by a solid absorber, and in the process of desorption, oil can be isolated in liquid form.

In this laboratory work it is proposed to calculate the adsorber of periodic action with a stationary layer of an adsorbent to capture gas vapors from the steam-gas mix of the tank park.

### 4.4. Calculation of the fuel vapour recovery systems

1. Calculate the equilibrium concentration of gasoline in the solid phase X, mol / g by the following equation:

$$X = \frac{W_{01}}{\upsilon} \exp\left[\frac{-B_1 T^2}{\beta^2} \left(\lg \frac{P_s}{P}\right)^2\right] + \frac{W_{02}}{\upsilon} \exp\left[\frac{-B_2 T^2}{\beta^2} \left(\lg \frac{P_s}{P}\right)^2\right],$$
(4.1)

where *X*- equilibrium concentration in the solid phase;  $W_{01}, B_1, W_{02}, B_2$ - constants characterizing adsorbent;  $W_{01} = 0,19 \text{ cm}^3/\text{r}$ ;  $B_1 = 0,74 \cdot 10^{-6} K^{-2}$ ;  $W_{02} = 1,8 \cdot 10^{-1} \text{ cm}^3/\text{r}$   $B_2 = 3,42 \cdot 10^{-6} K^{-2}$ ;  $\beta$ coefficient,  $\beta = 0,4$ ;  $\upsilon$ - molar volume of absorbed component, cm<sup>3</sup>/mole;  $P_S = 12800$  Pa pressure of a saturated vapor of gasoline; P - partial pressure of gasoline vapor in a gas mixture; T - gasoline temperature K.

2. Calculate the velocity of the vapor mixture of gasoline entering the adsorber, m/s:

$$\omega = \sqrt{\frac{0.0167\rho_{\text{max}}d_eg}{\rho_y}}, \qquad (4.2)$$

Where  $_{d_e} = _{2,0\cdot 10^{-3}}M$ ;  $_{\rho_{\text{Hac.}}} = 550 \text{ kg/m}^3$  (for activated charcoal AP-3); air temperature at the temperature 20 °C  $_{\rho_y} = _{1,2}\kappa\Gamma/M^3$ ; g – acceleration of force weight, m<sup>2</sup>/sec.

3. The effective operating speed of the gas in the adsorber is 25% lower than the permissible value.

4. Розрахувати діаметр адсорбера *d*, м:

$$d = \sqrt{\frac{4V}{\pi\omega}},\tag{4.3}$$

where V – Productivity of adsorber, m<sup>3</sup>/sec;  $\omega$  – vapor-gas flow velocity, m/sec.

5. The height of the layer of activated carbon in the apparatus to ensure sufficient time of the adsorber take 0.7 m (in vertical adsorbers VTR, the height of the layer of adsorbent is 0.5 ... 1.2 m), and the total height of the cylindrical part - 1.7 m.

6. At the closest value of the diameter and height of the apparatus in the catalog (given by the teacher) to pick up the adsorber.

де V – продуктивність адсорбера, м<sup>3</sup>/с;  $\omega$  – швидкість парогазового потоку, м/с.

7. Calculate the mass transfer rate  $D_v m^2/s$ , using the formula:

$$D_{y} = D_{y_{0}} \frac{P_{0}}{P} \left(\frac{T}{T_{0}}\right)^{\frac{3}{2}},$$
(4.4)

where  $D_{y0}$  - diffusion coefficient 0,133 cm<sup>2</sup>/sec at t = 0 °C i P = 98,1 kPa;  $P_0$  and P - accordingly, pressure under normal conditions and under the condition of ambient temperature, Pa;  $T_0$  and T - respectively, the temperature under normal conditions and the ambient temperature, K.

8. Calculate the Prandtl criterion by the formula:

$$Pr' = \frac{\mu_y}{(\rho_y D_y)},$$
(4.5)

where  $\mu_{y} = 1,8 \cdot 10^{-5} \Pi a \cdot c$  – the viscosity of the gas phase (air) at ambient temperature;  $\rho_{y}$  – vapor-gas phase density at ambient temperature, m<sup>3</sup>/sec.

9. Calculate the Reynolds criterion by the formula:

$$\operatorname{Re} = \frac{\omega d_{y} \rho_{y}}{\mu_{y}}.$$
 (4.6)

10. Calculate the mass transfer coefficient in the gas phase by the equation:

Nu'= 0,355 Re<sup>0.641</sup> (Pr')<sup>0.334</sup>/<sub>$$\varepsilon$$</sub>, (4.7)

where  $\varepsilon$  – transparency of the layer of adsorbent, equal to 0.01.

де є – прозорість шару адсорбенту, дорівнює 0,01.

11. Calculate the coefficient of external mass return (vapor return of gasoline by steam-air mixture) in m/sec by the equation:

$$\beta_y = \frac{10,03 \, D_y}{d},\tag{4.8}$$

12. Calculate the mass transfer coefficient in adsorbent (coefficient of mass transfer of gas vapor in adsorbent), m/sec by the equation

$$\beta_{\chi} = \frac{10 D_{\phi_{\text{max}}}}{d (1-\varepsilon)} \cdot \frac{\rho_{\text{max}} X C_{\text{mp}}}{C_{\text{m}}}, \qquad (4.9)$$

where  $D_{\phi\kappa}$  – actual diffusion coefficient (taken from the passport of the technical characteristics of the adsorbent), cm<sup>2</sup>/sec;  $\rho_{\text{Hac.}}$  – density of the bulk layer of the adsorbent, (taken from the passport of the technical characteristics of the adsorbent;  $C_{\pi}$  – initial concentration of gas vapor in air, kg/m<sup>3</sup>;  $C_{\pi p}$  – Propellant concentration of gas vapor in adsorbent,%.

13. Calculate the total mass transfer ratio, m/sec:

$$K_{y} = \frac{1}{\left(\frac{1}{\beta_{y}} + \frac{1}{\beta_{x}}\right)}.$$
(4.10)

The required data for calculation is given in Table 4.1.

 $(1 \circ)$ 

Table 4.1.

Variant	<i>V</i> ,	$C_{\pi p,}$	$C_{\Pi_{-}}10^{3},$	Τ,	<i>P</i> ,
	m <sup>3</sup> /year	%	kg/m <sup>3</sup>	°C	MPa
1	6500	5	2	20	0,1013
2	6600	6	2,1	22	0,098
3	6700	5	2,2	24	0,098
4	6800	6	2,3	26	0,1013
5	6900	7	2,4	28	0,098

## Data for calculation

## Table 4.2.

# Results of calculations for Activated carbon

ω,	<i>d</i> , m	Nu	$\beta x$ ,	βy,	К <sub>у</sub> ,
m/s			m/sec	m/sec	m/sec
0,387	2,43	1016,39	1,229	0,561	1,03
0,387	2,44	1499,52	1,068	0,624	0,394
0,387	2,47	804,11	1,115	0,722	0,437
0,387	2,49	1159,27	1,013	0,813	0,451
0,387	2,51	691,52	0,983	0,875	0,982

Table 4.3.

# Results of calculations for Silica gel

ω,	<i>d,</i> m	Nu	$\beta x$ ,	βy,	К <sub>у</sub> ,
m/s			m/sec	m/sec	m/sec
0,252	3,01	1016,39	1,115	0,453	0,322

0,252	3,03	1499,52	1,075	0,503	0,342
0,252	3,06	804,11	0,930	0,583	0,358
0,252	3,08	1159,27	0,898	0,657	0,379
0,252	3,11	691,52	0,839	0,706	0,383

# CHAPTER 5 LABOR PRECAUTION

## 5.1. Organization of the working place of petrochemical expert

As it was mentioned, working place of a petrochemical expert is composed of laboratory of homogeneous catalysis and additives for petroleum products where expert has work with the next devices: gasoline purge unit, chromatograph device and computer for processing and results analysis.

Requirements for premises and equipment of fuel depots laboratory are listed below:

• Fuel depots laboratories must be located in buildings not lower than II degree of fire resistance and have floors of non-combustible materials that do not absorb liquids.

• The gas network of the laboratory should be common gas shut-off valve in all rooms of the laboratory except in addition, overlapping cranes must be installed on each branches from the common gas network, outside the working the premises, in an easily accessible location, indicated by a pointer.

• Tables and exhaust cabinets intended for work with fire and explosive substances must have protective bands and be covered with non-combusting material, and for work with acids, alkalis and other inorganic and organic chemically active materials - substances resistant to their influence.

• Pliability with the fire-prevention regime and equipping premises of chemical laboratories with primary means of fire-fighting.

• All electrical equipment, a power tool with a voltage over 36 V, as well as equipment and mechanisms that can be energized, are reliably grounded.

• The level of noise in chemical laboratories should not exceed the norms (60 dBA), established by the State sanitary norms of industrial noise, ultrasound and infrasound

• The microclimate in the working area of the chemical laboratories must meet the requirements of the State Sanitary norms of the microclimate of industrial premises.

The premises of the laboratory shall be kept at all times cleanliness, spilled liquids - get cleaned immediately. Washrooms for washing laboratory glassware from underneath flammable and combustible liquids must be separated from work premises with non-combustible partitions with separate exit outside (into the corridor) and have local exhaust ventilation[28].

## 5.2. Analysis of hazard factors at the working place

Consider the hazardous and harmful production factors that affect a person according to the classification that is given in Interstate standard Classification" and STATE SANITARY STANDARDS AND RULES "Hygienic classification of labor on the indicators of harmfulness and danger factors of the production environment, the severity and intensity of the labor process". The workplace is placed in chemical laboratory. According the following dangerous and harmful production factors affect the worker.

Chemical production refers to industries that pose an increased potential risk of occupational poisoning and diseases. The reason is that many people in the process are exposed to chemicals that have certain toxic properties.

Under the action of toxic substances that can be attached different things you have: acute poisoning; chronic poisoning. Acute defects are no greater than ever before in the case of large major malicious cases, and leave behind the well-used causes that typically use the organization of businesses with discipline. Removing such causes does not require much capital expenditure.

Chronic products are destroyed in the study of long-term admission to a variety of working leather areas. In the end, you can train scientists who need to use different developments. Achieving harmless concentrations of toxic substances in faithful working premises, as a rule, offer with complete manufacture or replacement of technological processes, equipment, construction, structures. These activities require large capital people.

In any sense, the nature of this disappears industrial deviation is manifested as a result of physical psychological activity - toxicity. Toxicity is the authenticity of the use of skin properties for life. Toxic substances (released) - are those things that penetrate their people in different ways, come into contact with their tissues, informing them of normal operation.

Danger of deviation from: 1)physico-chemical properties of substances; 2)reliability in biological impact; 3)dispersion (reduced ability, duration, maturity, aggregate state); 4)existence time; 5)concentration.

Human susceptibility to exposure to toxic substances increases: 1) as a result of increased body temperature; 2) in the presence of overweight (obesity, edema). The toxicity of industrial poisons is characterized by the maximum permissible concentration (MPC) values.

By toxic effects on the human body and by external signs of poisoning toxic poisons are classified and conditionally are divided into 9 groups as follows: 1) nerve (hydrocarbons, alcohols, hydrogen sulfide, lead tetraethyl), which cause disorder nervous system functions, muscle cramps, paralysis; 2) irritants (chlorine, ammonia, sulfur dioxide, nitric oxide), which irritate the upper and deep respiratory tract; 3) burning and irritants (inorganic acids, alkalis), which affect the skin with the formation of abscesses, ulcers; 4) enzymatic (hydrocyanic acid and its salts, arsenic and its compounds, mercury salts), which disrupt the structure of enzymes, destroy them; 5) blood (carbon monoxide, aromatic resins, lead and its inorganic salts), which interact with blood hemoglobin; 6) liver (chlorinated hydrocarbons, phosphorus, selenium), which cause structural changes in liver tissues; 7) mutagenic (ethylene oxide, lead compounds, mercury) affecting the cell's genetic makeup; 8) allergens (some nickel compounds) that cause changes in human reactivity; 9) carcinogens (coal tar, benz (a) pyrene), which cause the formation of malignant tumors[29].

#### 5.2.1. The microclimate and ventilation

Microclimate is a complex of meteorological conditions in the working places: number of air ions, temperature, relative humidity, air exchange, air movement rate, the presence of pleasant odors (aromatherapy), the content of particulate matter (dust) in the air, etc. The microclimate, in fact, has a direct impact on man. If it is good, then a person feels a sense of comfort, and the body does not spend the power to adapt to external conditions. For example, a good microclimate eliminates heat, in which the human body would have to activate the mechanisms of thermoregulation.Microclimate is highly important for working premises, as workers spend much of their time in them and require comfortable conditions to be the most productive[30].

For the case of our laboratory, in warm seasons all microclimatic values are contained within permissible values, as general exchange ventilation system is installed in the premises in accordance with the state building standards and the room has access to the natural air and cooling sources through two windows.

The situation with the heating in cold season is more complicated, as the general heating system and radiators were installed in accordance with older standards and are significantly outdated causing temperature drop up to five degrees below permissible level.

Regulation If the temperature is lower than comfortable, then a heater will be required. And if the batteries, on the contrary, fuel too much, then you will need a thermostat, which can significantly reduce the temperature in the room. In the summertime, you can cool down the room with air conditioning. By the way, the conditioner with the heating function will replace the heater in winter.

## 5.2.2. Chemical hazards and safety

Risk of chemical exposure of workers is possible exclusively in the laboratory condition during conduction of experimental acting. Regulation in the field of chemical safety in labor precaution is provided by the The Law of Ukraine "On Ensuring Sanitary and Epidemic Well-Being of the Population", Hygiene standard "List of substances, products, production processes, household and natural factors carcinogenic to humans", approved by the order of the Ministry of Health of Ukraine of January 13, 2006, Hygienic standard "List of industrial allergens".

According to MPC classification, laboratory work of expert may be deemed harmful of the IV category due to the possible contact with cancerogenic substance as gasoline.

Table 5.1.

№	Name of ibstances	MPC mg/3	Class of danger	Aggregate state	Peculiarities of nfluence on human
1	Gasoline	100	IV	Vapor	Cancerogen

MPC of harmful substances in the air of the working area (gasoline)

Still, in case of adherence to the set of working place chemical safety rules, the working conditions may be comply with the requirements. Those include: good ventilation system, exhaust cabinets, avoidance of close work with dangerous chemicals or work with the special protective equipment (e.g. masks and respirators) and clothing items (e.g. rubber gloves and boots)[31].

## 5.3. Fire safety

The category of the laboratory room is B "Explosive fire hazard" in accordance with State Standard ДСТУ Б B.1.1-36:2016 «Definition of Category of Premises, Buildings and External Facilities According to Explosion and Fire Hazard». According to this it's a rooms which contain flammable dust and / or fibers, flammable liquids with a flash point higher than 28 ° C, combustible liquids in such quantities that they can form explosive dust, steam-air mixtures, in the case of which a projected excessive explosion pressure in the room develops that exceeds 5 kPa.

Compliance with the fire-prevention regime and equipping the premises of chemical laboratories with primary means of fire-fighting is carried out in accordance with the requirements of NAPB A.01.001-2004 and the Model Standards for the use of fire extinguishers, approved by the order of the Ministry of Emergencies and Affairs of Population Protection from the Consequences of the Chernobyl Disaster of April 2, 2004 No. 151. For the localization and liquidation of fires in their initial stage of development it is necessary to use fire extinguishers in accordance with the requirements of DSTU 3675-98 "Fire Engineering. Fire extinguishers are portable. General Technical Requirements and Test Methods "(hereinafter - DSTU 3675-98) and DSTU 3734-98 (GOST 30612-99)" Fire Engineering. Fire extinguishers are mobile. General technical requirements "(hereinafter - DSTU 3734-98), as well as internal fire water pipelines, coverings of non-combustible heat-insulating material, sand and other primary means of fire-fighting.

Exploitation of fire extinguishers shall be carried out in accordance with the requirements of the Rules of operation of fire extinguishers approved by the order of the Ministry of Ukraine on Emergencies and Protection of the Population from the Consequences of the Chornobyl Catastrophe of April 2, 2004 No. 152, registered with the Ministry of Justice of Ukraine on April 29, 2004, No. 555/9154 (NAPB B.01.008-2004), and their maintenance - in accordance with the requirements of DSTU 4297: 2004 "Fire Engineering. Maintenance of fire extinguishers. General technical requirements "[32].

# 5.4. Organizational and technical measures of harmful and dangerous factors mitigation

Workplace safety is a system of organizational measures and technical means, which prevent the working of hazardous industrial factors, and each organization and

enterprise to follow these measures to ensure safe working conditions, which are divided into the following varieties.

Chemical laboratories belong to category B - fire hazardous production. According to the Rules of arrangement of electrical installations, the premises of chemical laboratories belong to the class B-16, since work with even flammable and explosive substances is carried out in the hoods or under the exhaust umbrellas, without the use of open flames and open heating devices.

Chemical laboratories should be located in separate buildings, in special annexes to a production building or at the upper floors of the production building, isolated from other premises. The degree of fire resistance of buildings must be at least three. The walls and ceilings of the chemical laboratory are stained with paints that prevent the adsorption of toxic substances and allow them to be cleaned, washed or degassed. The floors and surfaces of desktops are recommended to be made of non-combustible or combustible anti-corrosion materials. Desktops should be supplied with cold and hot water, gas, direct and alternating current, compressed air.

Each chemical laboratory should be provided possibility of disconnection of gas, water and electricity supply. Cranes and cut-outs are installed outside of work areas in easily accessible locations.

All premises of the chemical laboratory must be equipped with common exhaust and exhaust ventilation, extraction cabinets, and, if necessary, local suction pumps from work stands. In every laboratory there is a list of substances that must be handled in the hoods. When working with acids and alkalis, the premises should be equipped with special hydrants (faucets, fountains, hoses) for prolonged washing of the affected areas of skin or eyes with a jet of water.

When working with glassware and glassware to protect your hands from cuts when cutting, the destruction of glass you must use a towel, with the mechanical and thermal treatment of glassware - safety goggles or safety guards. Thin-walled chemical flasks and glasses cannot be heated on open fire without special nets made of asbestos.

If the work in glass apparatus is carried out at elevated pressure and temperature or under vacuum, which creates a danger of breaking the glass, then the installation must be enclosed with a protective screen made of organic glass, a metal casing, and some, especially dangerous, devices must be protected by a metal mesh that prevents the glass from breaking.

Containers with substances that cause chemical burns, such as acids and alkalis, should be carried in half in special baskets or carts. Solid alkalis should only be taken with laboratory forceps or hands in rubber gloves; when crushing large pieces use dense material (belting). Work should be carried out using personal protective equipment.

Pouring and packaging of caustic liquids should be done with rubber pears, a syringe or special siphons. These liquids cannot be sucked into the pipette by mouth, as this can lead to burns of the oral cavity and poisoning. Concentrated acids and alkalis, as well as potent smoking agents (reagents) can only be stored and transfused under draft in a fume hood.

Special care should be taken when breeding sulfuric acid. Avoid splashing acid pour acid into the water, not the other way around. In case of lesions of caustic substances, it is necessary to quickly wash away the residues of these substances with a jet of water under pressure from special hydrants or fountains, and then consult a doctor.

Flammable and flammable liquids should be stored in thick-walled glass jars or containers with ground screws. Such containers should be stored in metal boxes (cabinets) that are lined inside asbestos and have a sand layer at the bottom. The total supply of flammable and flammable liquids in laboratories should not exceed the daily requirement.

When handling these substances, it is necessary to use a mechanical ventilation hood, it is forbidden to use any sources of open flame. Spent combustible liquids and reaction products are collected in a container specially designed for this purpose and hermetically sealed, and then regenerated or destroyed. Do not allow flammable and combustible liquids to enter drains[30].

#### 5.5. Conclusions to Chapter 5

Therefore, after the completion of labor precaution chapter of diploma, we can conclude that the working place of the petrochemical expert is in sufficient satisfactory condition, though some adjustments are necessary.

After the analysis of workplace conditions certain minor drawbacks of occupational safety system were detected on the part of microclimate provision during cold seasons and insufficiently good equipment and protective clothing for the worker. Considering mainly non-profit character of work as well as big and costly scale of full-on repairs of the whole building, I would suggest the following solutions:

• Purchase new protective clothing for the worker. renovate technical equipment of working places

• Use organizational measures to come with microclimate flaws during cold seasons: cover gaps and cracks in windows and doors with styrofoam and tape; introduce increased breaks working mode and use local heating devices allowed by standards.

Hopefully, those relatively simple and cheap measures will allow adjustment of the situation. As for other factors and fire safety the considered working place was complacent with legislation and current standards and standards.

#### CONCLUSIONS

Petroleum and chemical products are primary resources in our life and considered one of the most important basic building blocks for sustainable development. The growing demand of hazardous chemicals has brought a significant increase in risk to human and its environment .The results of a historical analysis have shown that 17% of major accidents in the chemical industries were during storage processes.

The possible hazards are a function of both the inherent nature and the involved quantity of the chemical. Therefore, it is important to conduct a profound and adequate hazard analysis of the oil storage facility to figure out the potential scenarios having damage to life and property as well as provides a clear picture for the decision makers to be satisfied with the safety levels in the storage tank farm.

Environmental pollution by oil and petroleum products occurs as a result of their losses during storage in reservoir parks. According to this the most important task during the operation of reservoir parks is to maintain the quality and quantity of the product stored.

This requires the maximum sealing of all drainage, filling and storage processes. The majority of evaporation losses are in the tanks. All losses of oil and oil products are classified into the following types:

Quantitative losses occur as a result of leaks, spills, incomplete drainage of transport tanks and tanks. Quantitative losses are made possible by the leakage of the walls and bottoms of the tank, malfunction of the shut-off valve, non-observance of the technology of operations and other reasons.

The losses include the incomplete discharge of petroleum products, especially viscous originating through structural defects in transport capacities (insufficient inclination of the bottom of the container - to the drain pipe), oil sticking and film formation on the walls of the tank, which requires extra time for drainage.

As it was mentioned above, hydrocarbons released due to evaporation losses effect both humans and natural environment. The main sources of hydrocarbons release are standard operations of a retail gasoline outlets and tank farms and also vehicles refueling. Gasoline vapors contain significant fractions of harmful chemicals such as benzene, toluene, ethylbenzene, and xylene. These chemicals are believed to be of the great concern for human health. At the same time, vapors significantly contribute to environmental contamination and especially to atmospheric pollution.

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