International Journal of Health Sciences June 2019, Vol. 7, No. 2, pp. 15-20 ISSN: 2372-5060 (Print), 2372-5079 (Online) Copyright © The Author(s). All Rights Reserved. Published by American Research Institute for Policy Development DOI: 10.15640/ijhs.v7n1a3 URL: https://doi.org/10.15640/ijhs.v7n1a3

# Hazard Analysis at Liquid Oxygen Storage Facilities

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# Abstract

This paper assesses the risks on the site of liquid oxygen storage, considering the absence of tank trays. For risk analysis the main groups of possible emergency situations scenarios were identified, for each a qualitative and quantitative risk assessment were conducted. Based on the obtained results, compensatory measures were proposed to reduce the risk to an acceptable level. It was found the implementation of the proposed measures and the regulation requirements the required level of security is ensured.

Keywords: Risk analysis, Liquid oxygen, Liquid oxygen storage, Cryogenic tanks

# 1. Introduction

Liquid oxygen is widely used in many industries, as well as in medicine. The main source of its production is natural air: air is liquefied and then separated into nitrogen and oxygen. After separation oxygen is stored in cryogenic tanks, which are high-risk objects, since oxygen is a strong oxidizer until it is sent to the consumer. In case of leakage from the liquid oxygen storage tank, there are risks associated with increased of ignition possibility and spread of fire. The goal of this work is to analyze the risk at the liquid oxygen storage site in the absence of a tray under the cryogenic tank with liquid oxygen.

# 2. Main Part

# 2.1. Brief description of the object of study

Liquid oxygen is stored in tanks with a capacity of 2000 m<sup>3</sup> at a temperature of about -180 °C. A cryogenic tank consists of an internal tank, an external tank, pipelines, insulation, ladder, platform and valves. Safety and measuring instruments are installed in the tank. The design of the tank is shown in Figure 1.

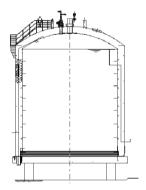


Figure 1. Design of cryogenic liquid oxygen storage tank

The tank has a vertical double wall with a flat bottom and a domed roof. The inner tank corresponds to the nominal capacity at the operating temperature.

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# 2.2. Characteristics of liquid oxygen

Oxygen is a chemically active nonmetal. Simple substance oxygen under normal conditions is a gas without color, taste and smell, the molecule of which consists of two oxygen atoms (formula O<sub>2</sub>). Liquid oxygen has a light blue color, and solid crystals are light blue [1]. Oxygen is a strong oxidizer, the most active non-metal after fluorine that forms binary compounds (oxides) with all elements except helium, neon and argon. As a rule, the oxidation reaction proceeds with the heat release and is accelerated with increasing temperature. It is known that ordinary materials burn in the air, but when the oxygen concentration increases, combustion will proceed faster. The rate of combustion, the ease of ignition and the spread of fire increase nonlinearly with increasing oxygen concentration. In general, these effects are slightly manifested at 25% oxygen, expressed at 40% oxygen, and reach a maximum at a concentration of about 50% oxygen - Table 1 [2].

Table 2. The	fire probability	at high oxygen	concentrations
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Oxygen	The probability of presence of	The probability of clothing	The proportion of fires
concentration, %	ignition source, %	ignition, %	causing death
25	4	5	0,1
30	4	75	0,2
35	4	90	0,44
40	4	100	0,98

Prolonged inhalation of pure oxygen at ambient temperature can cause hallucinations but does not lead to poisoning. If there was a spill of liquid oxygen, its vapors evaporating from the surface of the pool will be very cold. This cold cloud can affect people who were not prepared for the effects of low temperatures. This can lead to injuries and cryogenic burns [3].

# 2.4. Risk assessment methodology

To carry out risk assessments at liquid oxygen storage facilities in the this paper, qualitative and quantitative methods were used. Criteria for qualitative risk assessment were developed in accordance with [4, 5]. Data from tables 2-4 were used to assess the level of risk, probability of occurrence of an incident, development of an incident into an accident and qualitative assessment of its consequences.

Table 2. Qualitative assessment of the events probability

Level	Level	Description	Numerical estimation of the probability, year-1
А	high probability, possible repeated events	Will occur in most cases	more 10 -3
В	probable	Likely to occur in most cases	from 10 -4 to 10 -3
С	possible	May occur	from 10 -5 to 10 -4
D	unlikely	May occur but not expected	from 10 <sup>-6</sup> to 10 <sup>-5</sup>
Е	highly unlikely	Will occur under exceptional circumstances	less 10 -6

Level	Level	Effects in human	Impact on the environment	Economic damage, million rubles
5	catastrophic	numerous accidents	emergency environmental damage	over 150
4	considerable	non-renewable permanent disability, individual accidents	significant environmental damage	from 30 to 150
3	moderate	significant injury or harm to health, such as loss of working days	moderate environmental damage	from 15 to 30
2	insignificant	minor injuries or harm to health	local environmental damage	from 1.5 to 15
1	minor	minor harm to health	minimal environmental damage	less than 1,5

Probability, level of events		Evaluation of the consequences of events			
	1	2	3	4	5
А	R <sub>pr</sub>	R <sub>un</sub>	R <sub>un</sub>	R <sub>un</sub>	R <sub>un</sub>
В	R <sub>acc</sub>	R <sub>pr</sub>	R <sub>pr</sub>	R <sub>un</sub>	R <sub>un</sub>
С	R <sub>acc</sub>	R <sub>acc</sub>	R <sub>pr</sub>	R <sub>pr</sub>	R <sub>un</sub>
D	R <sub>acc</sub>	R <sub>acc</sub>	R <sub>acc</sub>	R <sub>pr</sub>	R <sub>pr</sub>
E	R <sub>acc</sub>	Racc	Racc.	R <sub>acc</sub>	Rpr
R <sub>acc.</sub> – acceptable risk; R <sub>pr</sub> - practical risk; R <sub>un</sub> – unacceptable risk					

#### Table 4. Risk assessment matrix

For a quantitative risk assessment, indicators such as potential risk, individual risk, and collective risk are used [6]. The potential risk is calculated as follows:

$$\mathbf{R}_{\rm pot} = \mathbf{P}_{\rm Ci} \cdot \mathbf{P}_{\rm d} \tag{1}$$

Where:

P<sub>Ci</sub>- the probability of the implementation of the i-th accident scenario;

 $P_d$  - the proportion of damage to people of various manifestations of the effects of liquid oxygen and its vapors. The individual risk of death from a fire caused by an increased oxygen content in the atmosphere is calculated using the following formula:

$$\mathbf{R}_{\text{ind}} = \mathbf{q} \cdot \mathbf{R}_{\text{pot}} \tag{2}$$

Where:

q - coefficient of human presence in the zone of impact of damaging factors.

Collective risk is calculated using the following formula:

$$R_{\rm col} = n \cdot R_{\rm ind} \tag{3}$$

Where:

n - the number of people exposed to the hazard.

The value of individual risk equal to 10<sup>-6</sup> year<sup>-1</sup> is taken as a quantitative criterion of acceptable risk [7].

### 2.3. Scenarios for accidents at liquid oxygen storage facilities

When operating storage tanks of liquid oxygen without trays, there is a danger of oxygen spilling onto an unlimited surface. The main groups of scenarios leading to the spillage of liquid oxygen are listed in table 5.

Table 5. Main accident scenario	s
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Script designatio n	Name	Description
C <sub>1</sub>	Instant full tank destruction	Instant complete destruction tank $\rightarrow$ the strait of oxygen from the tank on an unlimited surface $\rightarrow$ cryogenic effect of the Strait on the equipment and personnel $\rightarrow$ the evaporation of oxygen and the distribution of clouds $\rightarrow$ Ignition of organic materials in the presence of ignition source
C <sub>2</sub>	Depressurizati on of the internal tank	Hole formation in the inner tank $\rightarrow$ after the liquid oxygen supplied into the interstitial space $\rightarrow$ the evaporation of oxygen in the atmosphere $\rightarrow$ Ignition of organic materials in the presence of ignition source
C3	Tank overflow	Failure of the automatic system to switch off the supply of liquid oxygen to the tank $\rightarrow$ overflow of the tank $\rightarrow$ cryogenic impact of the Strait on the equipment and personnel $\rightarrow$ evaporation of oxygen and the spread of the cloud $\rightarrow$ Ignition of organic materials in the presence of ignition source
C <sub>4</sub>	Depressurizati on of the pipeline	Depressurization of the inlet pipeline during filling of the container $\rightarrow$ the Strait of liquid oxygen $\rightarrow$ cryogenic effect of the Strait on the equipment and personnel $\rightarrow$ the evaporation of oxygen and the distribution of clouds $\rightarrow$ Ignition of organic materials in the presence of ignition source

The main striking factors in accidents with liquid oxygen tanks are:

- cryogenic effects of liquid oxygen spill on equipment and personnel;

- combustion of organic materials in an atmosphere with high oxygen content.

Liquid oxygen is non-toxic, non-combustible and non-explosive, however, being a strong oxidizer, dramatically increases the ability of other materials to burn.

Liquid oxygen in contact with exposed skin causes frostbite, as well as affects the mucous membrane of the eyes [3].

#### 2.5 Risk assessment results

#### 2.5.1. Complete destruction of the liquid oxygen tank

The probability of instantaneous destruction of cryogenic tank ( $C_1$ ) shall be assumed as be 10<sup>-6</sup> year<sup>-1</sup> [6]. After the destruction of the tank, an oxygen spill on an unlimited surface with further evaporation will occur. Since the probability of such a scenario is small, only a qualitative risk assessment has been carried out within the framework of this research.

According to tables 2 and 3, the probability of depressurization of the internal receptacle is assessed as "Highly unlikely" (E) and the consequences as "Moderate" (3). Table 4 shows that the risk is acceptable and the development of additional compensatory measures is not required.

### 2.5.2. Depressurization of the internal liquid oxygen tank

The potential risk is assumed to be equal to the probability of depressurization of the internal capacity of the cryogenic tank  $R_{pot} = 10^{-4}$  year<sup>-1</sup>. According to formulas (1) and (2)  $R_{ind} = 2,2 \cdot 10^{-5}$  year<sup>-1</sup>,  $R_{col} = 1,8 \cdot 10^{-4}$  persons year<sup>-1</sup>. According to tables 2 and 3, the probability of depressurization of the internal container is estimated as "Possible" (C) and the consequences as "Moderate" (3). Table 4 shows that the risk is practically possible, therefore, it is necessary to develop compensatory measures that will reduce the risk to an acceptable level.

As a compensating measure, a safety system will be considered that ensures the emptying of the oxygen tank in the event of leakage into the interstitial space. The principle of operation of this system is that it provides permanent control of the environment in the inter-wall space. And with the possible leakage of oxygen into the interstitial space - instantly show the analysis changes. In this case, the operator will receive a signal about the accident. In the event of such a situation, the tank is emptied by supplying the entire volume of stored oxygen to the consumer. It is assumed that the probability of failure of such a system ( $P_{ss}$ ) is  $10^{-3}$  year<sup>-1</sup> [8]. Considering the implementation of this event there are two possible scenarios for the disaster caused by the depressurization of the inner tank ( $C_{2.1}$  and  $C_{2.2}$ ).

The scenario  $C_{2.1}$  can be presented in the following form:

Hole formation in the tank  $\rightarrow$  the expiry of liquid oxygen in the interstitial space  $\rightarrow$  alarm  $\rightarrow$  emptying and bringing it in for repair. At the same time, the probability of death of the personnel of the enterprise from the fire caused by the increased oxygen content in the atmosphere is accepted equal to zero.

The probability of implementation of this scenario  $P_{C2.1} = 10^{-4}$  year <sup>-1</sup> and is estimated as "Possible" (C), and the consequences as "Insignificant" (2), which corresponds to an acceptable risk.

Thus, the safety system will reduce the risk to an acceptable level by reducing the consequences of the accident.

It is also necessary to consider the scenario associated with a possible failure of the security system (C<sub>2.2</sub>):

The hole formation in the tank  $\rightarrow$  the expiry of liquid oxygen in the inter-wall space  $\rightarrow$  system failure security $\rightarrow$  evaporation of oxygen in the atmosphere.

The probability of implementation of scenario  $C_{2,2}$  is defined as the product of the probability of depressurization of the capacity and failure of the security system and is equal to  $10^{-7}$  year<sup>-1</sup>. In this case, the potential risk from scenario  $C_{2,1}$  is

 $10^{-7}$  year<sup>-1</sup>. The values of individual and collective risk are determined by formulas (2) and (3) are  $R_{ind} = 2,2\cdot10^{-8}$  year<sup>-1</sup>,  $R_{KOA} = 1,8\cdot10^{-7}$  per year<sup>-1</sup>. The calculated values of the individual risk of personnel death are significantly less than the permissible values.

When implementing compensatory measures, there will be a decrease in the probability of a dangerous event – the probability of the event is estimated as "Extremely unlikely" (E), the consequences are "Moderate" (4), which corresponds to an acceptable level of risk.

On the basis of qualitative and quantitative risk assessment, it can be concluded that the risk of an accident after the implementation of compensatory measures is reduced to an acceptable level.

the calculated collective risk R number =  $2,4 \cdot 10^{-6}$  per year<sup>-1</sup>.

According to tables 2 and 3, the probability of a tank overflow is estimated as "Possible" (C) and the consequences as "Insignificant" (2). Table 4 shows that the risk in the implementation of the  $C_3$  scenario is acceptable, and the development of additional compensatory measures is not required.

#### 2.5.4. The depressurization of the pipeline

The probability of implementation of the scenario  $C_4$  – depressurization of the inlet or outlet pipeline - is equal to the probability of depressurization of the processing pipeline, which in turn depends on the length of the supply pipeline and the frequency of its depressurization:

$$P_{C4} = L \cdot \lambda \tag{6}$$

Where: L – the length of the considered section of the pipeline, m. The length of the considered pipeline should be at least 10 m. At a shorter length, it is considered to be equal to 10 m [10].  $\lambda$  – the frequency of depressurization of the pipeline, m<sup>-1</sup>-year<sup>-1</sup>.

In this scenario, only the pipeline section directly near the tank is considered. Therefore, the length of the process pipeline section will be taken as 10 m. The frequency of pipeline depressurization is assumed in accordance with [10] depending on the diameter of the pipeline. For the considered pipeline with a diameter of 3 inches (76.2 mm), the depressurization frequency is  $-3 \cdot 10^{-7}$  (year·m)<sup>-1</sup>, the probability of depressurization of the pipeline will be in accordance with the formula (6)  $-3 \cdot 10^{-6}$  year<sup>-1</sup>. The maximum possible flow rate at the expiration of oxygen from the supply pipeline is equal to the maximum flow rate when filling the tank with oxygen from the air separation column – 2,683 Nm<sup>3</sup>/hour. The maximum possible leakage time is taken for 3 hours – in case of failure of the carbon dioxide circuit signaling the leakage of the cryogenic medium and the detection of leakage only by personnel on the site. Even under the worst conditions, i.e. a complete rupture of the pipeline and oxygen leakage within 3 hours, there is a gradual flow of a small amount of substance in the surrounding space that manages to mix with the air. Due to this, high concentrations of oxygen are not achieved, and the threat of fire is created only at small distances from the emission site. Individual risk, in this case, is  $R_{ind} = 1,84 \cdot 10^{-6} roA^{-1}$ . It is assumed that at the same time about the tank can be 3 workers.

Based on this, the collective risk is calculated:

 $R_{col} = 5,5 \cdot 10^{-6} \text{ persons} \cdot \text{year}^{-1}.$ 

According to tables 2-4, the probability of pipeline depressurization is assessed as "Possible" (C) and the consequences as "Insignificant" (2), the risk is acceptable. Based on the results of the qualitative assessment, it can be concluded that the risk in the implementation of scenario  $C_4$  is acceptable and the development of additional compensatory measures is not required.

#### 3. Conclusion

The paper considers the accidents that may occur at the liquid oxygen storage facility in the absence of the trays under the tanks. The qualitative and quantitative risk assessment methods were used to assess the risks arising from such accidents. It was found that the risk exceeds the permissible values only for the case of depressurization of the inner tank capacity and the flow of oxygen into the interstitial space. To reduce the risk, it is proposed to use a system that provides constant monitoring of the environment in the inter-wall space and emptying the container when a leak occurs. This measure has reduced the risk to an acceptable level. According to the results of the study, it can be concluded that it is possible to operate cryogenic tanks with liquid oxygen without trays, provided that compensating measures are taken, as well as the requirements of regulatory documents and recommendations for the cryogenic tanks manufacturer.

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