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Chemical-Environmental Aspects of Measures to Eliminate the Chemical Weapon Destruction Consequences

CORRESPONDENCE →

AUTHORS & AFFILIATIONS

Dr. Alexey V. Trubachev ¶*

Expert of the Federal Register of Experts

Dr. Larisa V. Trubacheva ‖

ζ Head

¶ Expert of the Federal Register of Experts of the Scientific Research Institute – Federal Research Center for Projects Evaluation and Consulting Services,Russia

‖ Department of the Institute of Natural Sciences, Udmurt State University, Izhevsk, Russia (OA)

ABSTRACT

The paper presents the basic requirements for carrying out measures to eliminate the consequences of activities at chemical weapons destruction facilities, describes technological approaches for implementing measures to eliminate the consequences of the destruction of skin abscesses and phosphorus-organic toxic substances, and evaluates their effectiveness. The chemical-toxicological characteristic of the waste generated during the implementation of liquidation measures is given, the environmental risks of these measures are analyzed, including the risks of long-term storage of toxic waste in appropriate storage areas. The ways to reduce the negative environmental impact of the consequences of carrying out liquidation measures at the facilities for the destruction of lewisite, sarin and soman are proposed

Index Terms: chemical weapons destruction facilities • environmental risks • liquidation measures

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AUTHOR CONTACT QR LEDGER

Dr. Alexey V. Trubachev¶∐*

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RESEARCH ARTICLE

Chemical-Environmental Aspects of Measures to Eliminate the Chemical Weapon Destruction Consequences

Dr. Alexey V. Trubachev[¶∐*] **and Dr. Larisa V. Trubacheva**[‖ζ]

QUALIFICATIONS / ROLES

∐ Expert of the Federal Register of Experts
ζ Head

AFFILIATIONS

¶ Expert of the Federal Register of Experts of the Scientific Research Institute – Federal Research Center for Projects Evaluation and Consulting Services,Russia
‖ Department of the Institute of Natural Sciences, Udmurt State University, Izhevsk, Russia (OA)

Abstract

The paper presents the basic requirements for carrying out measures to eliminate the consequences of activities at chemical weapons destruction facilities, describes technological approaches for implementing measures to eliminate the consequences of the destruction of skin abscesses and phosphorus-organic toxic substances, and evaluates their effectiveness. The chemical-toxicological characteristic of the waste generated during the implementation of liquidation measures is given, the environmental risks of these measures are analyzed, including the risks of long-term storage of toxic waste in appropriate storage areas. The ways to reduce the negative environmental impact of the consequences of carrying out liquidation measures at the facilities for the destruction of lewisite, sarin and soman are proposed

Keywords: *chemical weapons destruction facilities, environmental risks, liquidation measures*

Correspondence: Dr. Alexey V. Trubachev

1 Introduction

During 2005-2017, in accordance with the Federal Target Program "Destruction of Chemical Weapons Stocks in the Russian Federation", chemical weapons were completely destroyed in all 7 storage arsenals in Russia. In order to involve the property complexes of former chemical weapons destruction facilities in economic turnover, a number of measures was carried out to eliminate the consequences of their activities - liquidation measures (hereinafter referred to as LM). The main task of LM was to perform the following works: reducing the content of the toxic substances residual amounts in the buildings, structures on the territories of industrial sites to hygienic standards, neutralizing and disposing the waste generated during the implementation of chemical safety measures at the storage landfills. The achievement of the necessary parameters for the fulfillment of these tasks was largely determined by the nature of the technologies used to destroy toxic substances, ensuring the environmental safety of these technologies implementation, and creating new approaches to organizing and conducting environmental-analytical monitoring in the areas where the chemical weapons destruction facilities were located[1-3].

The main technological approaches to eliminating the consequences of the destruction of skin-abscess (hereinafter referred to as SATS) and phosphorus-organic (hereinafter referred to as POTS) toxic substances (hereinafter referred to as TS) are largely identical. These approaches include operations of decontamination, dismantling, fragmentation and thermal neutralization of the construction materials and metal structures, technological and engineering equipment, communications, and appliances in the rooms where the chemical weapons are stored and destruction operations are carried out[4,5]. Of great importance in carrying out such work is the effectiveness of decontamination of the technological and other surfaces that have come into contact with the detoxification products of TS, the reliability of the isolation of compacted waste, and precision chemical and analytical control of the TS residual amounts[6].

In the process of conducting the liquidation measures not only the residual amounts of toxic substances themselves can have a negative impact on the ecosystem and human health, but also the products of their neutralization, such as inorganic arsenic compounds (in the case of lewisite detoxification[7]), as well as the derivatives of methylphosphonic acid and inorganic fluorides (in the case of sarin and soman detoxification[8,9]), trapped into the aquatic environment, the air environment (during the incineration of relevant waste), as well as the soil horizons. In this regard, the task arises of operational control of these substances content in various matrices at the level of maximum permissible concentrations.

The purpose of this work was to analyze the effectiveness of technological approaches in the implementation of LM at the facilities for the destruction of chemical weapons "Kizner" (POTS), "Kambarka" (SATS) in the Udmurt Republic and "Maradykovsky" (POTS, SATS) in the Kirov region, to present the characteristics of the products of toxic substances neutralization formed during the implementation of technological operations, as well as to make an assessment of the associated environmental risks and possible ways to minimize them.

2 The main stages of the liquidation measures

The activities to eliminate the consequences of chemical weapons destruction are a set of measures aimed at making the chemical weapons destruction facilities and the territories they occupy safe for the environment and humans[10].

Before the start of LM in the working spaces of the facility, sampling and analysis of samples for the content of TS on the surfaces of the building structures and technological equipment was carried out. After the residual amounts of TS had been detected, the surfaces were decontaminated. According to the research results, the working spaces were divided into three groups: I hazard group – the «dirty rooms» in which toxic substances were found on the surface, in the samples "bulk" and scrapings in the concentrations above the hygienic standards; II hazard group – the «conditionally dirty rooms» in which the concentrations of toxic substances did not exceed the hygienic standards; group III - the «clean rooms» where no toxic substances were detected on the samples surface and in which no work with toxic substances had previously been carried out. When confirming the absence of the TS in the "deep" samples, after removing the contaminated layers of the building structure material, the rooms were "opened" for the actual LM.

The main stages of LM in the elimination of the consequences of the destruction of POTS were:

- dismantling and fragmentation of the technological equipment and construction structures of the buildings of hazard groups I and II;
- thermal neutralization of the metal waste and construction dust from after the removal of the top contaminated layer from the rooms of groups I and II;
- isolation of the neutralized waste obtained as a result of LM by encapsulation and their removal to a solid waste storage landfill;
- performing laboratory tests to determine the contamination of the soil of the industrial site and the sanitary protection zone with residual amounts of toxic substances, their degradation products and general industrial pollutants. In case of exceeding the established hygienic standards certain measures were taken to dispose of soil and remediate the site of the facility.

The main stages of LM in the elimination of the consequences of the destruction of SATS were:

- dismantling the technological equipment, cutting the tanks in the storage facilities and at the storage sites of the reaction masses into fragments;
- decontamination and detoxification of the metal fragments, building structures and soil;
- thermal neutralization of the solid waste and wastewater (by the fire method);
- isolation of the neutralized waste obtained as a result of LM by encapsulation or concreting and their removal to the solid waste storage landfill;
- analysis of the soil contamination on the territory of the industrial site and the sanitary protection zone for the content of the residual amounts of organic pollutants, their degradation products and general industrial pollutants. In case of exceeding the established hygienic standards, certain measures were taken to dispose of soil and remediate the territory of the facility.

3 Technological solutions implemented during liquidation measures

To ensure the safe implementation of LM, the use of thermal neutralization of the metal structures fragments, production equipment and other fireproof waste contaminated with POTS was proposed as a priority[7].

Thermal neutralization was carried out in two stages: at the first stage the internal and external surfaces were decontaminated by complete immersion in baths with an aqueous peroxide-alkaline solution for 2 hours. After decontamination, the fragments were washed with water and blown round with compressed air, while the quality control of the decontamination was carried out according to the content of TS in the rinsing water in accordance with the hygienic standards. At the second stage the obtained fragments were neutralized in thermal neutralization units in the temperature range from 500 to 650°C. The mode of thermal neutralization in the specified temperature range was determined depending on the type of TS, fragments and substances to be neutralized according to the technological regulations. Chemical-analytical control of the decontamination level of the thermally neutralized fragments has shown that the content (C) in the rinses from decontaminated surfaces does not exceed the maximum permissible levels-MPL (e.g. for sarin $C < 0.4 \cdot 10^{-5}$ mg/dm^2, MPL = $1.0 \cdot 10^{-4}$ mg/dm^2; for soman $C < 0.1 \cdot 10^{-6}$ mg/dm^2, MPL = $1.0 \cdot 10^{-5}$ mg/dm^2). These neutralized fragments can be used as scrap metal at metal processing plants. The neutralized construction waste and spent sorbents are sent for isolation to the industrial waste storage landfills as production waste after the liquidation work.

In the process of implementation of the liquidation measures at the POTS destruction facilities, decontamination with mixtures based on monoethanolamine and waste encapsulation technology were used, resulting in bitumen-salt masses containing calcium salts of methylphosphonic acid and its acid ester, diisopropyl ether of methylphosphonic acid, aminoethylisopropyl-methylphosphonate, calcium fluoride, sarin in the amount of less than $1 \cdot 10^{-8}$% and bitumen (up to 97.5%)[9]. These bitumen-salt masses as waste of hazard class III were sent for burial at the special waste storage landfills.

The main operation when performing LM at the SATS destruction facilities was surface decontamination. Decontamination of fragmented parts of the technological equipment and construction fractions was carried out with a 3.0% aqueous solution of sodium hydroxide by soaking them in degassing baths for 24 hours (a 10.0% aqueous solution of NaOH was used for additional preventive decontamination). 1.0% aqueous solution of sodium hydroxide was used to treat the exterior surfaces of the equipment and building structures of the buildings in which arsenic-containing lewisite detoxification products were handled in order to decontaminate the rags, activated carbon, plastic and metal gaskets and plugs contaminated with arsenic, and personal protective equipment.

The water-polymer composition based on hydrogen peroxide containing a quaternary ammonium compound, acetic or oxalic acid, starch and water was used to decontaminate the external surfaces of equipment, pipelines and building structures. Decontamination of surfaces using this composition was carried out three times with a consumption of 0.3 l/m^2 per treatment, with 30% of the formulation being retained on the metal surfaces and 70% draining away. After decontamination the treated materials were dried at a temperature not lower than 20°C and the humidity not more than 60%. This composition was also used to decontaminate the fragmented equipment parts by soaking them in decontaminating baths for 1 hour. An aqueous solution of sodium hypochlorite with an active chlorine concentration of 5–10 g/l was used for soil decontamination, with 50–100 kg of solution being consumed per 1 ton of soil, depending on the achieved soil moisture. Spent decontaminating solutions were incinerated in a liquid waste incinerator.

To isolate arsenic-containing wastewater formed during the detoxification of lewisite, the technology of their encapsulation in the form of a concrete-salt mass was used, and concreting was used to isolate metal waste products. The concrete-salt mass was a solid product of the composition: 0.30% arsenic, 4.15% sodium sulfate, 1.85% calcium sulfate, 93.70% silicon dioxide (concrete), and the concreted metal waste consisted of 0.10% arsenic, 1.23% calcium sulfate, 19.13% metallic iron, 79.54% silicon dioxide (concrete). These concrete masses, as the waste of hazard class II, obtained as a result of LM operations at SATS destruction facilities, were sent for burial at the special landfills.

4 Environmental risks of the elimination of the chemical weapons destruction consequences and ways to minimize them

The chemical weapons destruction facilities where liquidation measures are carried out are classified as category II facilities (moderate negative impact), and waste disposal facilities resulting from LM (burial landfills) are classified as category I facilities (significant negative impact).

The impact on the environment during LM is caused by emissions into the atmosphere during the dismantling, fragmentation and decontamination of the technological equipment, metal and building structures, the combustion of decontaminating solutions and wastewater[11]. Thus, during the implementation of liquidation measures at SATS destruction facilities, the emissions of pollutants containing inorganic arsenic compounds may occur during operations for cutting and dismantling decontaminating baths, as well as during the incineration of spent decontaminating solutions at the thermal neutralization plant. Inorganic arsenic compounds have an acute toxic effect on human internal organs, cause skin diseases, and have a carcinogenic effect (their maximum permissible concentration in the air must be $3 \cdot 10^{-6}$ g/m^3).

As noted above, the mixtures for decontaminating the external surfaces of the equipment, fragmented parts and soil include organic substances (acetic acid, oxalic acid, starch), as well as the products containing active chlorine (sodium hypochlorite). For thermal neutralization of the waste mixtures, incineration by fire is used. It is known[12] that the simultaneous presence of chlorine, oxygen-, hydrogen-, and carbon-containing compounds in the reaction medium in the temperature range from 230 to 530°C significantly leads to the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans. Such conditions are realized at the plant for combustion of these mixtures, which leads to the formation of dioxins in the combustion products and their release into the atmosphere. Dioxins are one of the most highly toxic compounds, they are able to accumulate in the human and animal bodies without decomposition, exerting an embryotoxic and carcinogenic effect (the maximum permissible concentration of dioxins in air must be $5 \cdot 10^{-13}$ g/m^3).

Thus, one of the possible negative environmental consequences of LM implementation at facilities where SATS are destroyed is atmospheric air pollution with arsenic compounds and dioxins.

Concrete-salt and bitumen-salt masses, concreted metal waste containing arsenic compounds, methylphosphonic acid derivatives and other substances can pose a danger to the environment. For one reason or another, prolonged storage at burial landfills may result in depressurization of containers filled with these wastes, followed by leaching of arsenic-containing and other toxic components releasing into the environment (soil, water horizons). For example, the main migration products from bitumen-salt masses obtained during the neutralization of sarin are monoethanolamine and isopropyl esters of methylphosphonic acid. These substances, having sensitizing, gonadotropic, teratogenic and mutagenic effects on the body of warm-blooded animals, can integrally turn out to be toxic when released into the environment. This is also one of the possible negative environmental consequences of the liquidation measures implementation.

LM environmental safety should be ensured by a number of organizational, technical and technological measures aimed at the safe management of the working processes and the prevention of toxic emissions of chemicals. Among them, it should be noted there are such as: using the sealed equipment and materials; multi-stage flue gas purification of the thermal neutralization plants; equipping the places of mechanical processing and flame cutting of fragments with mobile filtration units to remove and filter the welding fumes and dust from the temporary and non-stationary work posts; protecting the underground part of the toxic waste storage bunkers from atmospheric precipitation infiltration and groundwater inflow, etc.

Industrial chemical-analytical control of the LM implementation, monitoring the pollution of the atmospheric air, soil, water horizons, snow cover at the industrial zone facilities and adjacent territories is important for minimizing environmental risks during the elimination of the consequences of the chemical weapons destruction. At waste disposal facilities, it is necessary to regularly monitor the atmospheric air pollution to check the content of the lewisite and inorganic arsenic compounds, the groundwater and soils pollution to check the content of the total arsenic, lewisite, phosphate and fluoride ions, as well as the content of the methylphosphonic acid derivatives and POTS themselves.

Performing precision chemical analytical measurements of the concentrations of the above-mentioned toxicants in multicomponent natural matrices requires the development and creation of new instruments and methods of analysis, including on-line sensors for monitoring their content in environmental objects that meet the requirements of high accuracy, expressiveness and selectivity.

Carrying out the work to eliminate the consequences of the chemical weapons destruction is an environmentally significant challenge that requires the use of specific technological approaches and methods of chemical and analytical control to minimize the associated environmental risks.

5 Conclusions

It has been shown that the measures to eliminate the consequences of the chemical weapons destruction are a number of organizational, technical and technological measures aimed at making the facilities for the destruction of toxic substances safe for the environment and humans. The possible negative environmental consequences of the liquidation measures have been analyzed. These effects may be associated with the release of inorganic arsenic and dioxin compounds into the environment during detoxification of residual amounts of lewisite, as well as the derivatives of methylphosphonic acid and fluorides during detoxification of residual amounts of sarin and soman. Burial landfills of concrete-salt and bitumen-salt masses as waste of hazard classes II and III obtained during the liquidation measures implementation can also have a negative impact on the environment. The ways to minimize possible environmental risks associated with the liquidation measures implementation at the chemical weapons destruction facilities have been described. These ways include the prevention of chemicals emissions and the creation of modern chemical-analytical methods and test systems to control environmental pollution with appropriate toxicants.

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