COMBINED ENVIRONMENTALLY SAFE METHOD OF DETOXICATION OF SOILS CONTAMINATED WITH UNSYMMETRICAL DIMETHYLHYDRAZINE AND ITS TOXIC DERIVATIVES

Adylkhan D. Tovassarov [a], Sharipa S. Bissariyeva [a], *, Merey E. Nursultanov [b], Nazgul K. Kassymova [b]

[a] Central Asian Institute for Ecological Research LLP, Almaty, KAZAKHSTAN

[b] Kazakh National Research Technical University after K.I. Satpayev, Almaty, KAZAKHSTAN

Abstract - The article provides the data on cleanup of contaminated soil from the rocket fuel by combined method. The catalytic and microbiological methods of cleaning soil from rocket fuel components were developed and tested. Laboratory and natural researches are carried out. The obtain results of using of the combined method of detoxification of soils showed the promise of this method compared to the currently used methods of detoxication of soil potassium permanganate. At the same time after microbiological tertiary treatment, almost completely it is possible to rehabilitate a soil cover. Use of a biological method considerably accelerates process of restoration of soil microflora.

Keywords - components of rocket fuel, Baikonur cosmodrome, launch vehicle Proton-M, unsymmetrical dimethylhydrazine, soil detoxication.

1. Introduction

In Kazakhstan in all spheres of activity, including space, there is a transition to strategy of ecologically sound and sustainable development of economy and society, which takes into account both global and national interests. Creating environmental and hygienic standards, developing express-methods for determining the components of rocket fuel (CRF) and ecologically safe methods of detoxication of soils contaminated with CRF and its derivatives, to ensure environmental safety of rocket-space complexes, reducing damage to the environment and human health, are among the most relevant issues we are facing today.

Baikonur Cosmodrome is the most active spaceport in the world. It is known that environmental problems stem from its location in the inner part of Eurasia and the scale of space-rocket activity. The launches of the space rockets puts significant part of the territory of Kazakhstan under ecological risk.

One of the serious problems of protecting the natural environment is the elimination of soil pollution in the area of falling of separating parts from launch vehicles (AF SP LV), in the old impact areas (IA), in a zone of LV accidents. To date, there are no effective methods of neutralization of unsymmetrical dimethylhydrazine (UDMH) (1,1-dimethylhydrazine, heptyl) and derivatives of its chemical transformation, although research studies in this area are maintained for many years.

The search for effective ways of destruction of UDMH in soil continues to be relevant, because the proposed technologies are few and have some serious drawbacks [1].

The main requirements that apply to the methods of detoxication include: the effectiveness of decontamination, environmental friendliness, minimal cost, simplicity in hardware design and promptness. Particular attention is given to developing methods, tools and techniques of detoxication and neutralization of UDMH.

Development of environmentally sound methods and technologies of detoxication of soils contaminated with toxic propellant components and derivatives of their transformation is a complex scientific task that requires analysis and consideration of many factors: usage intensity, spatial position, climate, landscape and other local conditions of AF SP LV, operational and economical characteristics of the technological tools necessary for implementing the method. We must also take into consideration the properties of UDMH, the mechanisms of oxidation, sorption capacity of UDMH and its degradation products and chemical transformation and the possibility of methods to increase self-cleaning capacity of the soil [2].

Promising areas for developing new technologies are the methods based on both the oxidation of UDMH to form a simple and low-toxic degradation products, and methods which involve the binding of UDMH in durable and low-toxic derivatives. Priority should be given to those methods which not only cause degradation of pollutants, but also stimulate the factors that ensure self-cleaning of the soil [3].

Developed at different times and used to present day, ways of disposal of soils contaminated with UDMH represent a fairly wide range - chemical, physicochemical, thermochemical, adsorptional, radiational, membranal, biochemical, biological, etc.

All the methods in various operating conditions, along with the advantages have disadvantages that prevent their use under the existing constraints.

In reality, detoxication of soil in the places where spill of UDMH occured in AF SP LV was done by processing the soil with chlorine oxidants, in spill places - thermal treatment of contaminated soil did not provide the required level of detoxication with a high degree of air pollution and the destruction of soil's organic matter and soil microflora.

Catalytic methods, as well as chemical methods, are based on expressive reducing properties of UDMH. Reduction of the UDMH pollution is done by using various oxidants. Among them - hydrogen peroxide, oxygen, air, ozone [4-6], chlorine oxidizers, sodium nitrite, etc.

Using methods based on the oxidation of pollutants by shown oxidants and alkyl halides will result the formation of some toxic UDMH transformation products that do not fit modern requirements of environmental safety.

The priority should be the methods that not only cause the destruction of pollutants, but also stimulate the factors that ensure soils self-cleaning. For this purpose, it is necessary to use methods or combination of methods, which should increase the self-cleaning capacity of the soil. This approach will reduce the cost of restoring the soil cover.

To clean the soil from UDMH most effective can be a rational combination of different ways as there are concentration limits that do not allow, for example, use microorganisms to highly contaminated soils, as well as the penetration of UDMH deep in soil to anaerobic conditions. In this situation, the microbiological method may be most effective in the final stage of purification of contaminated sites where other methods become uneconomical.

At the same time, for the purification of soils, use of native microorganisms isolated from the field of pollution, which allow more efficient and deeper utilize a variety of complex substrates that are inaccessible to monocultures.

This article presents the results of research work, which aimed to develop a combined method (catalytic and microbiological) of the detoxication of soils contaminated with UDMH.

2. Materials and methods or experimental

In the first phase of work in the laboratory, experimental work on the development of complexones and disposal of soil from UDMH and its derivatives was completed. Based on the results, the detoxication of soils in the places of UDMH spill by hydroperit catalytic oxidation method in the presence of d-metals (copper and iron) was done, to establish its effectiveness [7].

In the second phase, from the upper horizon soil of AF SP LV and sites of emergency falling of launch vehicle “Proton-M” in the Ulytau area of the Karaganda region, isolated microorganisms capable to absorb UDMH as a sole carbon source were extracted.

The optimal association of microbial cultures was done. Laboratory experiments on cleaning UDMH pollution by using selected associations of microbial cultures was conducted.

To isolate microorganisms, which are able to assimilate UDMH, cultures of microorganisms were grown on solid and liquid medium with the addition of UDMH at concentrations corresponding to 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.25, 2.5, 5.0, 10.0 maximum permissible concentration (MPC – 0.1 mg/kg).

Morphological, cultural and biochemical properties of selected microorganisms were studied by standard methods. Identification of microorganisms was carried out by Bergey’s Manual of Determinative bacteriology [8]. From the contaminated soil propellant samples 63 isolates were extracted.

Selected cultures of microorganisms were grown on mown nutrient agar plate. Afterwards, cultures of microorganisms were plated on solid nutrient medium containing UDMH as a sole carbon source in concentrations corresponding to 10, 5, 2.5 maximum permissible level (MPL). Cultivation was performed for 7 days in an incubator at 30 °C. Grown colonies of microorganisms (32) were placed in nutrient broth. Good growth was seen in 4 colines of culture - 7, 15, 26, 29. The possibility of assimilation of isolated cultures of microorganisms at lower concentrations of UDMH, namely 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 MPL was revealed. The studies obtained dry product of association of microorganisms for the detoxication of the soil.

In the third stage, in the area near to the Baikonur cosmodrome in control and experimental sites field tests were conducted. We used the methods of detoxication of soil from UDMH and products of its chemical transformation by “catalyst-oxidant” system and cultures of microorganisms.

The study used a homogenous system, which is an aqueous solution of iron complexonate. Then the soil was processed by microorganisms to recycle residual UDMH and its toxic derivatives, and to restore the soil microflora.

Tests of both methods were performed on two soil types (4 control and 4 experimental sites) at two initial concentrations of UDMH. Section 1 - on the sandy desert soil in **Fig. 1.** Section 2 – on the gray-brown desert soil in **Fig. 2.** Selected areas characterized by deep groundwater.

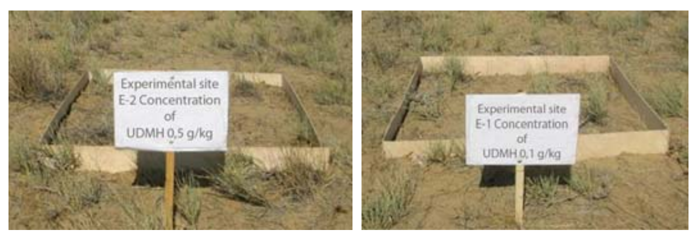


Figure 1. Experimental sites (E-1 and E-2) on the sandy desert soil. Section 1

Figure 2. Control sites (K-3 and K-4) on the gray-brown desert soil. Section 2.

In the first case, the load on the soil of UDMH was 0.17-0.18 g/kg (1750-1800 MPC), in the second – 1.1-1.4 g/kg (11000-14500 MPC).

The size of each site - 1x1 m. The experimental area was divided into quadrants measuring 0.6 m^2 - for catalytic method and 0.4 m^2 - for the microbiological methods.

The experiment was conducted in August and September at a temperature of 12 - 35 ºC. Before UDMH filling, background soil samples to a depth of 1.0-1.2 m were extracted. Extracted samples of soil had UDMH, nitrosodimethylamine (NDMA), tetrametiltetrazen (TMT), dimethylformamide (DMF), 1-methyl-1H-triazole (MT), dimethyltirazole (DMT), dimethylhydrazone formaldehyde (DMGFA) which did not exceed 0.01 mg/kg. Background content of formaldehyde (FA) for sandy and gray-brown desert soil is almost the same and is 0.20 and 0.23 mg/kg, which is significantly lower than the MPC (7.0 mg/kg).

After the process of detoxication, samples of soil were selected after 10, 20, 30 and 40 days. Sampling was carried out by soil auger up to a depth of 80 cm depending on soil type.

Laboratory and analytical studies of soil samples was performed by spectrophotometric and gas chromatographic methods.

On the section 1 with the initial load to ≈ 11.000 MPC dynamics of decomposition of UDMH on the sandy soil was as follows. After 10 days of UDMH content in the soil decreased to of 0.05 mg/kg, whereas, the control soil still contained UDMH at concentrations 3.5 mg/kg.

Catalyst tillage allows to achieve almost complete detoxication of soil from UDMH (its content in soil is less than MPC) in 10 days.

Similar full-scale tests on the gray-brown soil (section 2) showed that UDMH decomposition proceeds more slowly than sandy. But an important difference is that under the catalyst effect, the ground with an initial load of 1599 mg/kg sharp decrease of UDMH to 300 mg/kg is observed, whereas in the control experiment reduction of heptyl in the soil is slower (down from the initial concentration of 1.311 to 1081 mg/kg).

These data clearly show the influence of soil type on the degradation of UDMH. Application of the catalyst on the gray-brown soil with an initial load of ≈ 1800 MPL has allowed in 10 days to reduce the content of UDMH to 30 mg/kg, while in control soil its content was 46 mg/kg, i.e. the efficiency of the catalyst was 1.5 times higher.

In general, the analysis of catalytic detoxication of UDMH contaminated soil shows that in all cases at experimental sites observed lower content of both the UDMH and its derivatives. The exception is data on formaldehyde, catalyst treatment resulted in a higher its content in comparison with the control. Apparently this is due to the action of the complex catalyst for UDMH and the products of its transformation: under the influence of the catalyst is oxidized organic products with the release of formaldehyde. In order to post-treatment residual UDMH and its products of transformation, on the tenth day after the catalytic detoxication carried out microbiological analysis of the experimental sites. Full-scale tests were cultures of microorganisms – *Micrococcus sp.7, Bacillus sp.15, Rhodococcus sp.26, Acinetobacter sp.29* detected in soil samples from AF SP LV.

Before microbiological detoxication, the concentration of UDMH on the 10 days after the catalytic detoxication ranged on the sandy desert soil from 0.05 to 29.25, on gray-brown desert soil - from 30 to 216 mg/kg.

Soil samples were taken on the 20th, 30th and 40th day. Sample results from experimental sites compared with control (Tables 1-4).

Table 1. Dynamics of UDMH and its derivatives after the microbiological treatment in sandy desert soil (experimental site E-1)

Time, days	Concentration, mg/kg								
	After detoxication								
	TMT	DMG FA	UDMH	DMT	NDMA	$NO3^-$	FA	DMF	MT
10 d	0	0.02	0.05	0.72	1.12	4.52	27.72	22.27	245.27
After microbiological processing									
20 d	0	0.01	0.02	0.01	0.01	2.02	5.94	0.69	3.53
30 d	0	0.01	0.02	0.01	0.01	1.62	4.75	0.55	2.82
40 d	0	0.01	0.02	0.01	0.01	1.94	3.8	0.44	2.26

Table 2. Dynamics of UDMH and its derivatives after the microbiological treatment in sandy desert soil (experimental site E-2)

Time, days	Concentration, mg/kg								
	After detoxication								
	TMT	DMG FA	UDMH	DMT	NDMA	$NO3^-$	FA	DMF	MT
10 d	0	0.04	16.25	13.21	10.48	4.87	37.86	188.22	1068.99
After microbiological processing									
20 d	0	0.02	0.22	4.36	1.05	1.80	18.74	21.62	158.74
30 d	0	0.02	0.18	3.49	0.84	2.34	14.99	17.30	126.99
40 d	0	0.02	0.11	1.09	0.36	0.82	4.32	8.30	76.09

Table 3. Dynamics of UDMH and its derivatives after the microbiological treatment in gray-brown desert soil (experimental site E-3)

Time, days	Concentration, mg/kg								
	After detoxication								
	TMT	DMG FA	UDMH	DMT	NDMA	$NO3^-$	FA	DMF	MT
10 d	0	0.05	30.00	0.79	0.78	6.26	36.16	16.43	278.86
After microbiological processing									
20 d	0	0.01	0	0.05	0.08	3.93	3.89	1.42	29.54
30 d	0	0.02	0	0.07	0.13	7.07	7	1.85	38.40
40 d	-	-	-	-	-	-	-	-	-

Table 4. Dynamics of UDMH and its derivatives after the microbiological treatment in gray-brown desert soil (experimental site E-4)

Time, days	Concentration, mg/kg								
	After detoxication								
	TMT	DMG FA	UDMH	DMT	NDMA	$NO3^-$	FA	DMF	MT
10 d	0	0.06	216.00	69.13	7.44	4.72	70.40	14306.0	1231.42
After microbiological processing									
20 d	0	0.01	0	0.04	0.41	5.89	6.33	8.28	86.22
30 d	0	0.01	0	0.04	0.37	5.30	5.70	7.45	77.60
40 d	0	0.01	0	0.03	0.30	4.24	4.56	5.96	62.08

3. Results and discussion

As a result, studies have shown that for complete removal of TMT in the soil is sufficient use of the developed catalyst, which was not observed when other methods of detoxication, and by the 10^{th} days of TMT in both soil types is almost undetectable. In the case of the heptyl for the initial load up to 2000 MPC catalyst reduces the content of UDMH to 0.5 MPC for sandy soils and up to 300 MPC on clay soil. These figures indicate the failure of only a catalytic method. The use of strains of microorganisms, actively assimilate nitrogen compounds, reduced content of UDMH to a level below MPC (0-0.2 MPC in soil for 40 days).

A significant increase in the load UDMH to 16000 MPC respectively affect the residual of its contents in the soil after the catalytic detoxication. By the 10^{th} day on the sandy soil content of UDMH 162.5 MPC and MPC 2160 on clay soil. As the load up to 2000 MPC action of the catalyst was more effective in sandy soil. The use of microbial detoxication method has reduced the content of UDMH in the soil to acceptable values 0-1.1 MPC.

Similar results were observed for NDMA. The analysis showed that at loads up to 2000 MPC UDMH microbiological method also proves to be effective and helped to reduce the content of NDMA to acceptable baseline in 1-13 MPC at initial 78-112 MPC. A different picture was at a load of up to 16000 MPC. In this case, reducing NDMA in soil occurred before 30-36 MPC. Despite these relatively high values, yet the use of microbiological method is justified, since there was a decrease in NDMA up to 30 times on both types of soil. Such dynamics of reducing the concentration of NDMA in soils to predict the reduction in the level of NDMA to the 3-month to a level below the MPC.

4. Conclusions

Obtained analysis show the high levels of MT and DMF in all areas. These data again confirm the relevance of their work on the regulation and the effect on living organisms and vegetation. Thus, the results obtained using the combined method of detoxication of soils, showed the promise of this method compared with currently used methods of detoxication of soils with potassium permanganate ($KMnO_4$). At the same time after the microbiological purification can be almost completely rehabilitate soil. Using the biological method significantly speeds up the recovery process of soil microflora. Technology developed by us belongs to innovation, and will continue to be used in the real world - in areas separating from parts of rockets in the regular and emergency situations for the detoxication of toxic spills CRF and products of its chemical transformation.

* Corresponding author. Tel/fax.: + 8-10-7-7272-3671683.
E-mail address: bsharipa@mail.ru (Sharipa S. Bissariyeva).

References

[1] Y.V. Proskuriakov, T.V. Koroleva, A.P. Vorozheikin, G.S. Samoilova, "Soil pollution and the problem of asymmetric dimethylhydrazine their detoxication in areas falling residuals stages of launch vehicles": Proceedings of the 3rd International Meeting "Geochemistry of the Biosphere", Rostov-on-Don, Russia, 2001. (in Russian).

[2] N.A. Kruchinin, N.I. Nekhoroshev, G.M. Nikolaeva, and L.V. Andreeva, "Detoxication method of soil and ground from UDMH reagent Abiks", J. Dual technology, (3) 2000, pp. 51-59. (in Russian).

[3] A.P. Vorozheikin, T.V. Koroleva, Yu.V. Proskuriakov, and A.V. Puzanov, "Behavior of unsymmetrical dimethylhydrazine in landscapes areas falling residual parts of carrier rockets, launched from the Baikonur cosmodrome", Siberian Journal of Ecology, (2) 2001, pp. 167-175. (in Russian).

[4] I.Z. Ismagilov, M.A. Kerzhentsev, Z.R. Ismagilov, L.T. Tsikoza, E.V. Matus, O.B. Suhova, et.al., "New technologies decontamination of heptyl": Proceedings of the All-Russian Conference "Catalytic environmental technologies for industry and transport", Saint-Petersburg - Novosibirsk, Russia, 2007, pp.133-135. (in Russian).

[5] L. Carlsen, B.N. Kenessov, S.Ye. Batyrbekova, "QSAP/QSTR study on the Environmental health impact by the rocket fuel 1,1-dimethyl hydrazine and its transformation products", Environmental Health Insights, (1) 2008, pp. 11-20.

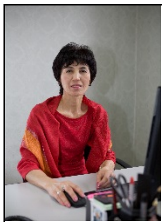
[6] D.N. Moskvin, I.A. Rodin, A.D. Smolenkov, O.A. Shpigun, "Transformations of asymmetric dimethylhydrazine in soils", Russian Journal of Physical Chemistry A, 82(6) 2008, pp. 1039-1044. (in Russian).

[7] N.M. Dyatlova, V.Y. Temkina, K.I. Popov, "Complexons and complexonates of metals", Moscow: Chemistry, 1988. (in Russian).

[8] J.G. Holt, N.R. Krieg, P.H.A. Sneath, J.T. Staley, S.T. Williams, "Bergey's Manual of Determinative Bacteriology", 9th Ed., Baltimore, Maryland: Williams and Wilkins, 1994.

AUTHORS PROFILE

Dr. Adylkhan D. Tovassarov, PhD in Chemistry, working as Project manager in Central Asian Institute for Ecological Research LLP, Almaty, Kazakhstan. He contributed more than 50 Research papers in International and National Journals and Conferences, including 3 monographs. It has 2 patents and 6 innovative patents RK. His area of research is the chemical, petrochemical, environmental protection. For many years was the executive in charge of the Russian-Kazakh environmental safety programs in the aerospace activities. He lectured course chemistry of oil and gas at the Kazakh National Research Technical University after K.I. Satpayev.
Tel.8-10-7-727-3671683,
e-mail: tovasarov_ad@mail.ru



Dr. Sharipa S. Bissariyeva, PhD in Biology, Associate professor, Chief of research Department at Central Asian Institute for Ecological Research LLP, Almaty, Kazakhstan. Author of more than 70 Research papers published in International and National Journals and Conferences, including 3 monographs and 2 books. Interests: biochemistry and environmental protection.
Tel. 8-10-7-727-3671683,
e-mail: bsharipa@mail.ru

Mr. Merey E. Nursultanov, Senior Lecturer, Department of Chemical Technology of oil refining and gas Kazakh National Research Technical University after K.I. Satpayev, Almaty, Kazakhstan,
Tel. 8-10-7-727-2577188,
e-mail: merey1980@mail.ru

Ms. Nazgul K. Kassymova is working as Lecturer in Department of geology and oil gas at Kazakh National Research Technical University after K.I. Satpayev, Almaty, Kazakhstan.
Tel. 8-10-7-727-2577131,
e-mail: kasymova.n@mail.ru