OZONE TREATMENT OF HYDRAZINE-CONTAINING WATER SOLUTION

*V.I. Golota, *G.V. Taran, *A.A. Zamuriev, *M.A. Yegorov, **L.L. Mikhalskaia, **E.E. Prokhach

*National Science Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine;
**"Kharkov Research Center of Military Ecology", Kharkov, Ukraine
E-mail: tarang@kipt.kharkov.ua

The results of experimental investigation on decomposition of 0.1 and 0.2% hydrazine-containing standard test water solution by bubbling ozone-oxygen mixture through the water solution are presented. It was shown, that the time of hydrazine decomposition to the concentration lower than the MPC under the influence of ozone concentration of 15…40 gO_3/m^3 was 10 min for 0.1% hydrazine-containing water solution and 30…45 min for 0.2% hydrazine-containing water solution.

PACS: 82.30.Lp

Hydrazine and its derivatives – unsymmetrical dimethyl hydrazine (UDMH), amines (triethyl amine) and boranes are a family of the combustible substances that are widely used as a rocket fuels. Hydrazine and hydrazine-containing water solutions are highly toxic. Mucous membranes, eyes and respiratory tract are irritated by hydrazine. Exposure to high concentrations of hydrazine can damage the central nervous system and liver. The maximum permissible concentration for hydrazine and its substitutes (e.g. hydrazine hydrate) in the air of populated areas is 0.001 mg/m^3, and in water solution is 0.01 mg/l [1].

Therefore, the objective of the experimental studies was to recognize an effective, environmentally friendly method for the treatment of hydrazine-containing water solutions. The results of these studies are presented in the article.

It is well-known that there is a large number of chemical and physical methods for the treatment of hydrazine-containing water solutions [2, 3]. The chemical methods include: treatment with chlorine-based oxidants, treatment with hydrogen peroxide, bromide and copper chloride oxidation, potassium permanganate oxidation, nickel hydroxide oxidation, treatment with mineral or organic acids, ozone treatment [4].

Thermal decomposition is one of the physical methods for the treatment of hydrazine-containing waste water [5]. This method is based on complete oxidation of hydrazine by oxygen at the high temperature (850…1000°C).

Physical and chemical method for the treatment of hydrazine-containing waste water is UV radiation combined with oxidation (by ozone or hydrogen peroxide). According to [1], the simultaneous treatment of waste water by UV radiation and oxidants increases oxidation rate of hydrazine and its derivatives by 100…1000 times. During such treatment, synergistic effect of the oxidants and UV radiation arises. However, this method can be effective only at the stage of post-treatment, when hydrazine concentration is less than ~5mg/l (~0.0005%).

Therefore, ozone treatment is the most effective and ecologically-friendly method for the treatment of hydrazine-containing waste water.

The efficiency of hydrazine decomposition in water solutions under the influence of ozone was studied on the experimental stand (Fig. 1), which included:

- oxygen generator AirSep-12 (1) with the flow rate of oxygen-enriched gas mixture (up to 95% O_2) 0…0.6 m^3/hour;
- gas flow meter (2) RM-02 0,63 GUZ;
- ozone generator (3) StreamOzone OzW-10/18, which generates ozone-oxygen gas mixture with ozone concentration of 10…60 g/m^3 [6, 7];
- ozone monitor (4) TELEDYNE-API, model 465 H.
- fine bubble diffuser (5) with porous glass plate which provides intensive and uniform bubbling of the water solution to be treated;

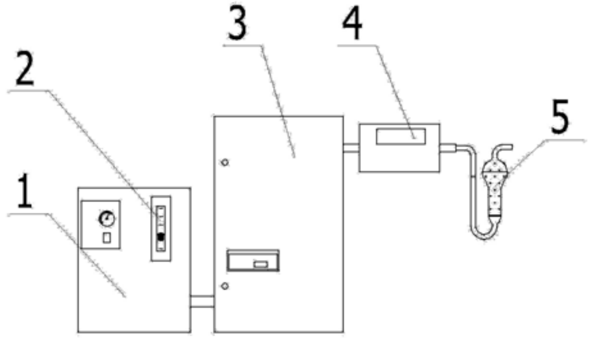

Fig. 1. Schematic diagram of the experimental stand

All the experiments were carried out in a fume hood to protect the working area from residual ozone, vapors and decomposition products of hydrazine.

Hydrazine concentration in water solution was analyzed using the photocolorimetric method in accordance with the standard test procedure [8].

To examine the feasibility of hydrazine decomposition under ozone treatment, the 0.1 and 0.2% hydrazine-containing test water solutions were used. 0.1% hydrazine-containing test water solution contains 1.047 g hydrazine per 1 liter of solution at the pH value of 9.7. Distilled water was used for preparation of water solutions.

The experiments were divided into two stages. At the first stage, the oxidative ability of ozone to the full decomposition of the hydrazine-containing water solution was evaluated. Therefore, 0.1% hydrazine-containing water solution was used. The flow rate of oxygen-enriched gas mixture for ozone synthesis was 1 l/min. Ozone concentration $[O_3]$ in gas mixture was 20 and 40 g/m^3. The time of ozone treatment was $t_{treatm.}$ = 15, 30, 45 and 60 min. The temperature T_{sol} of hydrazine-containing water solution was 30°C. The data on residual hydrazine content in a treated test solutions are presented in Table 1.

Table 1

Residual hydrazine concentration in the treated test water solution

#	$[O_3]$, g/m^3	$[N_2H_4]_{initial}$, g/l	$T_{sol.}$, ^oC	$t_{treatm.}$ min.	$[N_2H_4]_{final}$, mg/ml
1	20	1.047	30	15	$< 5\cdot10^{-5}$
2	20	1.047	30	30	not detectable
3	20	1.047	30	45	not detectable
4	40	1.047	30	15	not detectable
5	40	1.047	30	30	not detectable
6	40	1.047	30	45	not detectable
7	40	1.047	30	60	not detectable

The table shows the following parameters of the experiment:

- $[N_2H_4]_{initial}$ – initial hydrazine concentration in water solution, g/l;
- $[N_2H_4]_{final}$ – final hydrazine concentration in water solution after ozone treatment, mg/ml.

Table 1 shows that almost in all cases the hydrazine was completely removed from water solution.

At the second stage, after a positive result of ozone treatment for destruction of hydrazine-containing test water solution had been verified, the dynamics of hydrazine decomposition under the influence of ozone has been studied. The gas mixture with ozone concentration of $[O_3]$ = 15 and 20 g/m^3 was used in the experiments. The time of treatment was $t_{treatm.}$ = 5, 10 and 15 min for 0,1% hydrazine-containing water solution, and $t_{treatm.}$ = 5, 15, 30 and 45 min for 0.2% hydrazine-containing water solution. Data of the experiments on destruction of hydrazine-containing water solution are presented in Table 2.

Table 2

Results of ozone treatment for 0,1% and 0,2% hydrazine-containing water solution

#	$[O_3]$, g/m^3	$[N_2H_4]_{initial}$, g/l	$T_{sol.}$, ^oC	$t_{treatm.}$ min.	$[N_2H_4]_{final}$, mg/ml
1	15	1.047	30	5	$2\cdot10^{-2}$
2	15	1.047	30	10	$5\cdot10^{-5}$
3	15	1.047	30	15	$5\cdot10^{-5}$
4	20	1.047	30	5	$7.5\cdot10^{-3}$
5	20	1.047	30	10	$5\cdot10^{-5}$
6	20	1.047	30	15	$5\cdot10^{-5}$
7	15	2.094	30	5	1.418
8	15	2.094	30	15	0.42
9	15	2.094	30	30	not detectable
10	15	2.094	30	45	not detectable
11	20	2.094	30^o	5	0.456
12	20	2.094	30^o	15	0.04
13	20	2.094	30^o	30	$3\ 10^{-4}$
14	20	2.094	30^o	45	not detectable

The diagrams which demonstrate the dependence of hydrazine concentration in water solution on the time of ozone treatment at different ozone concentrations in gas mixture are shown at Fig. 2.

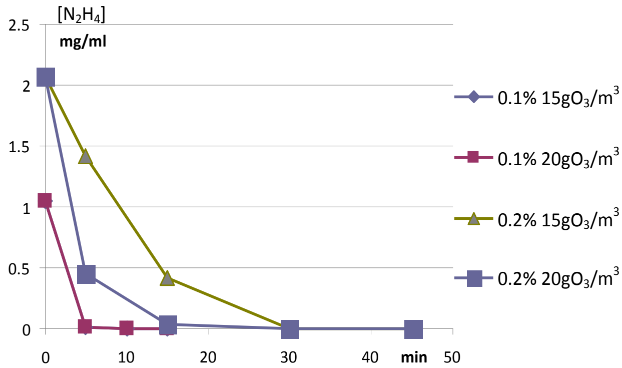

Fig. 2. The dependence of hydrazine concentration on the time of ozone treatment

The given experimental data show, that the time of complete hydrazine decomposition in water solution increases together with hydrazine concentration. As ozone concentration in the gas mixture used for the treatment of hydrazine-containing water solution increases, the time of hydrazine decomposition decreases. In general, the time of the full hydrazine decomposition under experimental condition was 10 min for 0.1% hydrazine-containing water solution and 30…45 min – for 0.2% hydrazine-containing water solution.

Today there is no complete theory to explain the mechanism of hydrazine oxidation. During the process of oxidation, various intermediate products are formed depending on oxidation conditions and pH value. In the end, either molecular nitrogen and water, or ammonia, nitrates and nitrous acid are formed. In general, less toxic compounds are formed as a result of hydrazine oxidation.

It is difficult to describe all stages of hydrazine decomposition under the influence of ozone by one equation. However, the reaction of hydrazine and ozone can be presented in generalized form by the following equation:

$$2\,O_3 + 3\,N_2H_4 = 6\,H_2O + 3\,N_2. \qquad (1)$$

If assumed that the hydrazine reacts with ozone in water solution according to reaction (1), when the changes in hydrazine concentration can be presented by the following equation:

$$d[N_2H_4]\Big/dt = k[N_2H_4]^x[O_3]^y, \qquad (2)$$

where k is chemical reaction rate constant, x and y are constants that, in general, do not correspond to stoichiometric coefficients of the reaction;
$[N_2H_4]$ is hydrazine concentration in water solution;
$[O_3]$ is ozone concentration in water solution.

Under an assumption that ozone concentration in water solution was constant during the whole experiment, the solution of differential equation (2) can be written as follows:

$$[N_2H_4] = [N_2H_4]_0 * e^{-Kt}, \qquad (3)$$

where $[N_2H_4]_0$ is initial hydrazine concentration in water solution, K is constant of hydrazine decomposition. This constant depends on ozone concentration in ozone-oxygen gas mixture used for the treatment of hydrazine-containing water solution.

For confirmation the above mentioned assumption about type of kinetic reactions for hydrazine decomposition in water solution under the influence of ozone the change of hydrazine concentration with the time of ozone treatment is presented in logarithmic scale at Fig. 3.

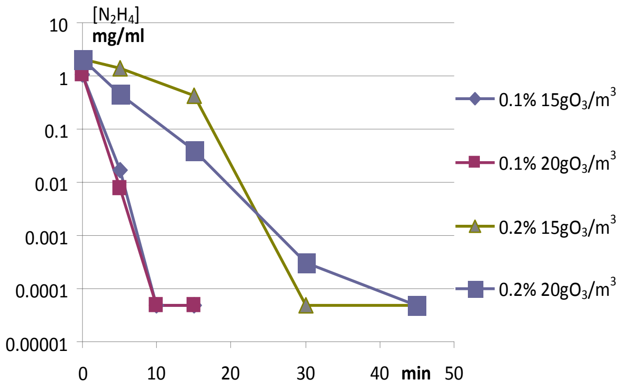

Fig. 3. The dependence of hydrazine concentration on the time of ozone treatment in logarithmic scale

The diagrams on Fig. 3 show that in logarithmic scale the dependence of hydrazine concentrations on the time of ozone treatment is almost linear in the wide range of changing of hydrazine concentrations from 1 to 0.0005 g/l. This conforms that the dynamics of hydrazine decomposition in water solution can be described by the exponential dependence. Therefore, hydrazine decomposition in water solution under the influence of ozone-oxygen mixture follows the first-order kinetic equation.

CONCLUSIONS

The performed experimental research on decomposition of 0.1 and 0.2% hydrazine-containing test water solution by bubbling with ozone-oxygen mixture (15…40 gO_3/m^3) have shown that the complete hydrazine removal from water solution can be realized.

The time for the complete hydrazine decomposition was 10 min for 0.1% test water solution and 30…45 min for 0.2% test water solution. Thus, ozone with average concentration of 10…40 g O_3/m^3 is a highly efficient for hydrazine decomposition in water solution.

REFERENCES

1. Maximum allowable concentrations (MACs) of chemicals in the water of water objects used for drinking and domestic-recreation purposes. Hygienic rating HR 2.1.5.1315-03 (in Russian).
2. O. Pestunova, G. Elizarova, V. Parmon. Treatment of water solutions containing 1,1-dimethylhydrazine by catalytic oxidation with hydrogen peroxide // *Journal of applied chemistry*. 1999, v. 72, № 7, p. 1147-1151 (in Russian).
3. N. Kundo, V. Ivanchenko, N. Kuksanov, et al. The Use of Electron Beam Radiation Treatment for Decomposition of Nitrogen-Containing Compounds in Waste Water // *Journal of applied chemistry*. 1999, v. 72, № 7, p. 151-1154 (in Russian).
4. I. Ismagilov, M. Kerzhentsev, Z. Ismagilov, et al. New technologies for heptyl neutralization // *Abstracts of All-Russian Scientific conference with international participation "Catalytic technologies for environmental protection at industry and transport" (St. Petersburg, 11-14 December 2007)*. St. Petersburg, 2007, p. 133-135 (in Russian).
5. Ukrainian Patent 69515A IPC[7] S01V21/16, S01V21/20. Hydrazine-containing liquid rocket fuel utilization / O. Panasyuk, A. Ransky, V. Ilchenklo, et al. Published: 09.15.04, Bull. № 9 (in Ukrainian).
6. V. Golota, O. Yegorov, V. Mykhaylov, V. Mukhin, G. Taran, S. Shilo. *Ozone generator*. US Patent #6,544,486 B2, date 04/08/2003.
7. V. Golota, E. Sukhomlin, G. Taran. Ozone generators, developed in the NSC KIPT // *Proc. of conf. "New technologies for health improvement with natural and preformatted factors (physical therapy, ozone therapy, balneotherapy)"*. Kharkov, 2002, p. 36-38 (in Russian).
8. *Methods for measurement the liquid rocket fuel components at industrial facilities and surrounding environment* / Edited by Razbitna L.M., 1988, p. 338 (in Russian).

Article received 16.05.2013

РАЗЛОЖЕНИЕ ГИДРАЗИНА В ВОДНОМ РАСТВОРЕ МЕТОДОМ ОЗОНОВОЙ ОБРАБОТКИ

В.И. Голота, Г.В. Таран, А.А. Замуриев, М.А. Егоров, Л.Л. Михальская, Э.Е. Прохач

Приведены результаты экспериментальных исследований по разложению 0.1 и 0.2% модельных водных растворов гидразина при барботировании озоно-кислородной газовой смесью. Показано, что время разложения гидразина озоном с концентрацией 15…40 $гO_3/м^3$ до уровня ниже ПДК составляло 10 минут для 0.1% водного раствора гидразина и 30…45 минут для 0.2% водного раствора гидразина.

РОЗКЛАДЕННЯ ГІДРАЗИНУ У ВОДНОМУ РОЗЧИНІ МЕТОДОМ ОЗОНОВОЇ ОБРОБКИ

В.І. Голота, Г.В. Таран, О.О. Замурієв, М.О. Єгоров, Л.Л. Михальська, Е.Ю. Прохач

Наведено результати експериментальних досліджень по розкладанню 0..1 та 0.2% модельних водних розчинів гідразину при барботуванні озоно-кисневою сумішшю. Показано, що час розкладання гідразину озоном з концентрацією 15…40 $гO_3/м^3$ до рівня нижче НДК складав 10 хвилин для 0,1% водного розчину гідразину та 30…45 хвилин для 0.2% водного розчину гідразину.