Toxicological evaluation of the waste of carbonitration process at the machine building enterprise

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Abstract. Nowadays, the principle of balanced development of the machine building industry and, at the same time, the preservation of the natural environment is fundamental in the modern world. The processes used in the technological cycles of machine building enterprises should be safe both for humans and for the natural environment. One of the types of chemical and thermal treatment of metal is the process of liquid carbonitration, which allows improving the exploitation properties of treated pieces. As a result of this technology, two types of waste are generated. For a toxicological evaluation of the waste of carbonitration process, two test cultures were chosen as model organisms: Daphnia magna and Scenedesmus quadrauda. In the course of the study, it was found that wastes from the process of carbonitration in certain concentrations have an acute toxic effect and belong to the 3rd and 4th hazard classes.

1. Introduction

In modern machine building, the task of comprehensive improving of the exploitation properties of metallic materials is largely related to the development of new technological processes for surface hardening of pieces.

One of the types of chemical and thermal treatment is liquid carbonitration, which allows increasing the wear resistance and strength of pieces by 2.5-3 times. The use of this technology instead of gas nitriding makes it possible to reduce the processing time and improve the properties of the processed pieces [1, 2]. In many cases, carbonitration technology is an alternative to such processes as surface hardening, galvanic chrome plating, cementation and carbonitriding, etc.

The purpose of this work is the toxicological evaluation of the waste of carbonitration process at a machine building enterprise. To achieve this goal it is necessary to solve the following tasks:

- to conduct a literature review of carbonitration technology;
- to evaluate the toxicity of the technology;
- to perform sampling;
- to conduct researches of waste and analysis of results.

2. Results

The essence of carbonitration is that the machine pieces are kept in the molten salt (cyanate and potassium carbonate) at a temperature of 560-600°C, the duration of the technology depends on what amount of hardened layer is necessary to achieve [1, 3]. Pure cyanates are used as starting materials for the preparation of active melt. It was found that potassium cyanate, having a melting point of 320 °C, is more suitable for conducting the carbonitration process at 540–570 °C than sodium cyanate [4].

In the process of carbonitration there are oxidation reactions [2]:
The formation of a small amount of toxic cyanides is also possible by the reaction:

$$4\text{KCNO} = \text{K}_2\text{CO}_3 + 2\text{KCN} + 2\text{N}$$

(6)

For the oxidation of cyanides to cyanates in carbonitration baths, air sparging is performed and the reaction takes place according to formula 7.

$$2\text{KCN} + \text{O}_2 = 2\text{KCNO}$$

(7)

As a result of the ongoing reactions, a gradual accumulation of potash $\text{K}_2\text{CO}_3$ and a decrease in the content of the active salt $\text{KCNO}$ - potassium cyanate occurs. For regeneration, one of the following substances is periodically added to the bath: $\text{C}_3\text{H}_6\text{N}_6$ - melamine, or $\text{C}_3\text{H}_5\text{N}_5$ - melem. In this case, the percentage of potassium cyanate $\text{KCNO}$ is restored to 85-95% in the bath.

Further, the processes of decomposition of potassium cyanate, saturation of the metal surface with nitrogen and carbon, regeneration are continuously repeated during the operation of carbonitration baths. Liquid carbonitration technology does not require complex equipment, this method is simple to implement and allows achieving high surface strength of pieces. Also in many scientific works it is said that carbonitration technology itself is not a dangerous production and is environmentally friendly [1, 4]. Those chemicals in the reaction and waste from this process should be safe for both humans and the environment.

Potassium carbonate is a moderately hazardous substance; its dust can cause diseases of the gastrointestinal tract and respiratory tract, as well as prolonged contact leads to the damage of the skin [6]. Potassium cyanate is a substance that is highly soluble in water, non-toxic, explosion-proof and fireproof. The toxic effect is manifested in impairment of oxidative phosphorylation. This substance is a methemoglobin former. When a lethal dose is partially introduced into mice and rats, it first has a sedative effect, then increased motor activity, tremors, and convulsions develop [7].

Melamine is slightly toxic and does not irritate the skin and eye mucosa. When tested on mice, the carcinogenic properties were not found. As a result of the carbonitration process, two types of production waste are generated:

- waste during cleaning of carbonitration baths of metal surfaces;
- wastewater from washing metal products after carbonitration.

To determine the toxicity of waste, biotestings of waste were carried out according to approved methods [8-10]. As model organisms for biotesting were used:

- daphnia magna;
- scenedesmus quadrauda.

Daphnia magna belongs to the order of cladocerans, lower crustaceans. Daphnias are often found in freshwater, standing, and low-flow water bodies in Russia. The length of their body varies from 0.2 to 6 mm. The essence of the document “Toxicological control methods” is presented. The method of

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2\text{KCN} + \text{O}_2 = 2\text{KCNO} \\
2\text{KCNO} + \text{O}_2 = \text{K}_2\text{CO}_3 + \text{CO} + 2\text{N} \\
2\text{CO} \leftrightarrow \text{CO}_2 \uparrow + \text{C}
\]
measuring the amount of Daphnia magna Straus to determine the toxicity of drinking, fresh natural water and wastewater, water extracts from soil, ground, wastewater sludge and production and consumption waste by direct counting method" [8] consists in determining by the direct counting method daphnias mortality during toxic exposure of investigated substances.

By definition of acute toxic effect in short-term experiments (48 hours) they establish:

- acute or moderate toxicity with the death of 50% of test objects or more;
- harmless concentration of a substance, with the death of no more than 10% of test objects [8].

For the test, scenedesmus quadricauda was also chosen, recommended by a number of documents for biotesting [9]. Scenedesmus quadricauda is a species of green protococcal algae of the genus Scenedesmus, which are the most common of freshwater genera. Scenedesmus quadricauda have relatively large cells and are widely distributed in water bodies of Russia. This is a type of coenobial organism, reproduction occurs through the formation inside the maternal cell of 2, 4, less 8 and 16-cell coenobia.

According to the method [9], with acute toxicity of substances within 72 hours there is a decrease in the number of cells by 50%. Sampling of waste was carried out according to the method [10]. Biotesting of solid waste was carried out on a water extract with a solid phase: liquid phase ratio of 1:10. To obtain the extract air-dry sample of solid waste and distilled water were used. Further, cultivation water was used to prepare dilutions of the studied waters. The sample "waste from cleaning of carbonitration baths of metal surfaces" was investigated in the following concentrations: 1:1, 1:100, 1:1000, 1:10000.

At toxicological research on determination of the mortality and fecundity of daphnia, the sample "Wastewater from washing metal products after carbonitration" was analyzed in 100, 33, 11, 3.7 and 1.2% concentrations with dilution with cultivation water, and at researches using test object - The Scenedesmus quadricauda sample was examined in the following dilutions: 1:1, 1:3, 1:11, 1:33, 1:100.

According to the method [8], the researches on Daphnia magna were conducted on synchronized daphnia culture, i.e. culture obtained from one female, even age was used. Thus, the culture was genetically homogeneous. Each test was conducted in three parallels using 10 test objects (daphnia).

According to the conditions of the method [9], studies using the scenedesmus quadricauda were carried out in two parallels of each concentration. Biotestings of samples were carried out in a neutral environment. The conditions under which the experiments were carried out are given in Table 1, 2.

**Table 1.** Test conditions of the sample “Waste from cleaning of carbonitration baths of metal surfaces”

| Extragent                                      | Characteristic of water extract of the sample |  
|-----------------------------------------------|-----------------------------------------------|  
|                                              | pH of extract before analysis | pH of extract after analysis | Temperature of extract, °C |  
| Fresh cultivated water (Daphnia magna)        | 8.1                                         | 8.1                          | 20                          |  
| Fresh cultivated water (Scenedesmus quadricauda) | 8.1                                         | 8.2                          | 22                          |

**Table 2.** Test conditions of the sample “Wastewater from washing metal products after carbonitration”

| Extragent                                      | Characteristic of water extract of the sample |  
|-----------------------------------------------|-----------------------------------------------|  
|                                              | pH of extract before analysis | pH of extract after analysis | Temperature of extract, °C |  
| Fresh cultivated water (Daphnia magna)        | 7.8                                         | 8.0                          | 20                          |  
| Fresh cultivated water (Scenedesmus quadricauda) | 7.8                                         | 7.9                          | 22                          |

The results of the test on test organisms of Daphnia magna in each parallel of different dilution concentrations of the studied samples are illustrated in Figures 1, 2.
According to figure 1, the death of more than 50% of test organisms (Daphnia magna) in the water extract sample “Waste from cleaning of carbonitration baths of metal surfaces” occurs in all parallels of the study at a dilution concentration of 1:1 and 1:100.

The death of more than 50% of test organisms (Daphnia magna) in the water extract of the sample “Wastewater from washing metal products after carbonitration” occurs at a dilution concentration of 1:1 (figure 2).

The number of algae cells after testing the samples according to the method [9] is presented in Figures 3, 4.
In Figure 3, it can be seen that when testing the sample of water extract “Waste from cleaning of carbonitration baths of metal surfaces”, the decrease in the number of algae cells by 50% and more is observed in two parallels at concentrations of 1:1 and 1:100.

**Figure 4.** Percentage of living algae cells after testing the sample “Wastewater from washing metal products after carbonitration”

**Table 3.** Test results of the biotesting of sample “Waste from cleaning of carbonitration baths of metal surfaces”

| The ratio of dilution of the water extract | Scenedesmus quadralcauda | Test culture | Daphnia magna |
|------------------------------------------|--------------------------|--------------|---------------|
|                                          | Deviation from control, % | Acute toxic effect | The death of test culture | Acute toxic effect |
| 1:1                                      | 78.4                     | yes           | 100.0          | yes            |
| 1:100                                    | 59.3                     | yes           | 93.0           | yes            |
| 1:1000                                   | 43.0                     | no            | 7.0            | no             |
| 1:10000                                  | 23.5                     | no            | 0              | no             |
Table 4. Test results of the biotesting of sample “Wastewater from washing metal products after carbonitration”

| Test culture          | Scenedesmus quadrauda | Daphnia magna |
|-----------------------|------------------------|---------------|
| The ratio of dilution of the water extract | Deviation from control, % | Acute toxic effect | The ratio of dilution of the water extract | The death of test culture | Acute toxic effect |
| 1:1                   | 65.8                   | yes           | 1:1               | 77                   | yes                   |
| 1:3                   | 40.4                   | no            | 1:3               | 3                    | no                    |
| 1:11                  | 37.9                   | no            | 1:9               | 0                    | no                    |
| 1:33                  | 36.3                   | no            | 1:27              | 0                    | no                    |
| 1:100                 | 34.2                   | no            | 1:81              | 0                    | no                    |

In the study of the sample “Wastewater from washing metal products after carbonitration” a decrease in the number of algae by more than 50% is observed in 2 parallels at a concentration of 1:1 (figure 4). The test results of biotesting are presented in tables 3, 4.

3. Conclusion
The results of biotesting of the sample “Waste from cleaning of carbonitration baths of metal surfaces” for two test objects Daphnia magna and Scenedesmus quadrauda showed that this waste is of the third hazard class, and the sample “Wastewater from washing metal products after carbonitration” is of the 4th class. Thus, the process of carbonitration of metal can not be called safe for the environment without safe technology of waste disposal.

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