Methods of Purification of Polluted Water from Ammonia Compounds at Nitrogen Fertilizer Plants

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Abstract. This article discusses the possibilities of wastewater purification polluted with ammonia compounds at enterprises producing nitrogen fertilizers by various chemical methods, as well as using air in a scrubber installation. In wastewater generated during the production of nitrogen fertilizers at the "Fergana Azot" enterprise of the Republic of Uzbekistan, the content of ammonia in the dissolved state is higher than normal. Due to the fact that ammonia compounds also have a high degree of binding to gases such as CO_2, NO_2 and SO_2, which are in a gaseous state under various conditions, the possibility of cleaning such waters from ammonia compounds in a scrubber using flue gases containing CO_2, NO_2 and SO_2 gases, as well as the amount of air supplied in this technological process, the speed of its passage through the scrubber nozzles, what it will be, what height the nozzles will be, is indicated according to the data obtained as a result of the experiment.

1 Introduction

In the process of production of nitrogen fertilizers at enterprises such as "Fergana Azot" and "Navoi Azot" in the Republic of Uzbekistan, the structure of the enterprise on the data will store a large amount of wastewater as shown in Table 1 below. The norm of the concentration of ammonia combination in the composition as a result of purification of waste water of such a composition should not exceed 1 mg per liter. But under operating conditions, the amount of purified waste water content is around 8.40 mg/L. On this basis, in order to re-use the wastewater dressing in production enterprises as technical water in the conditions of the enterprise or to add to the disposal of municipal wastewater, such wastewater is required to be cleaned at a high level from the ammonia compound [1-7]. Table 1 below is presented the chemical composition of polluted and purified waters, which are characteristic of the enterprise for the production of nitrogen fertilizers "Fergana Azot".

Table 1. Chemical indicators of polluted and purified waters generated at the enterprise "Fergana Azot"

Substances contained in wastewater		Quantity after cleaning in the conditions of the enterprise
Indicators	Quantity	
Temperature, ^0C	20-22	
pH value,	7.6	6.5-8.5
The amount of hanging granules, mg/l	328.7	150
Dry residue, ml/l	847.75	2000
Petroleum products	0.31	1
Chlorides, mg/l	48.6	350
Sulfates, mg/l	361.2	100
Nitrates, mg/l	6.4	9.1
Compound NH_4^-, mg/l	8.4	8.1
(II,III) iron compounds, mg/l	0.3	0.03

As can be seen from the information provided, the water purified in the conditions of the enterprise is not completely purified from ammonia compounds. To add such water to the city sewer system or, at the request of the administration of the enterprise, for reuse, it is necessary to thoroughly clean the wastewater from the ammonia

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compound contained in them. Currently, in our republic at enterprises producing chemical products and nitrogen fertilizers, are formed in large quantities of water polluted with nitrogen and ammonia compounds.

2 Methods and Materials

Therefore, the addition of such waters to natural water sources is environmentally prohibited. It is known that ammonia compounds are contained in wastewater in the form of ammonium ion (NH_4^+) and ammonia in the free state (NH_3) in equilibrium:

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

The change in equilibrium in this state is mainly due to the pH of the water, when the pH of the water is >10, 85% of the NH_4^+ ions are converted to the NH_3 compound in the free state based on the following equilibrium.

$$NH_4OH \leftrightarrow NH_3 + H_2O$$

Currently, various methods are used to purify water from the ammonia compound contained in it. In this method, 10 mg of hypochloride is consumed for the complete addition of 1 mg of ammonia compound in each liter of water. When water is purified in this way, the content of the NH_3 compound in it can be reduced to 0 [8, 9].

But the chlorinating substances used in this method are consumed in very large quantities. As is known, ammonia compounds combine well with gases present in the free state, such as carbon dioxide (CO_2), nitrogen oxide (NO_2) and sulfur oxides (SO_2). The compounds of ammonia compounds in the water with gases CO_2, NO_2 and SO_2 occurs on the basis of the following reactions.

$$CO_2 + NH_3 + H_2O = NH_4HCO_3 \qquad 4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$$

$$NH_3 + NH_4HCO_3 = (NH_4)_2CO_3 \qquad 6NO_2 + 8NH_3 = 7N_2 + 12H_2O$$

$$SO_2 + NH_3 + H_2O = NH_4HSO_3$$

$$NH_3 + NH_4HSO_3 = (NH_4)_2SO_3$$

If ammonia compounds are in the state of ammonium gidro oxide (NH_4OH) dissolved in water, the purification of waste waters from NH_4OH as a result of the combination of the compound with such gases occurs on the basis of the following reactions.

$$NH_4OH + CO_2 = NH_4HCO_3$$

$$NH_4OH + SO_2 = NH_4HSO_3$$

$$NO + NO_2 + 2NH_4OH = 2N_2 + 5H_2O$$

$$4NO_2 + 2H_2O + O_2 = 4HNO_3$$

$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O$$

As a result of these reactions, 1 mg of the NH_3 compound contained in the water is spent on CO_2 gas in the purification process using CO_2 gas, 2.58 mg of CO_2 gas, and 3.76 mg of SO_2 gas in the purification process using SO_2 gas.

Based on this data, if use gases CO_2, NO_2 and SO_2 gases with more smoke gases in the composition when cleaning wastewater from ammonia compounds, the amount of these toxic gases emitted into the atmosphere in combination with smoke gas decreases as waste water is purified from ammonia compounds.

3 Results and Discussion

The pH indicator of the water that is being cleaned when cleaning wastewater with the help of air in water purification devices from the ammonia compound has a big importance. what state will the ammonia compounds be in the composition of water in the case when the pH indicator of water changes from 6 to 12 shown in following Figure 1.

As can be seen from the picture, in the process of increasing the pH of water from 6 to 12, the quantity of NH_4^+ ions contained in the water decreases, and the quantity of NH^3 compound in the free state increases. The rate at which the NH^3 compound in the free state is separated from the water depends on the surface tension of the water surface and the difference in the concentration of the ammonia compound in the water and in the air [10-14].

Table 2 below shows the amount of reduction in the content of the ammonia compound in the process of water purification with the help of air at a water purification installation with a height of 6 meters.

According to the data obtained on the basis of experience, when cleaning polluted water from ammonia compounds in the quantity of 1 m^3, the quantity of air supplied to the water purification installation should not be less than 1600 m^3, and the pH indicator of water should be around 10,5.

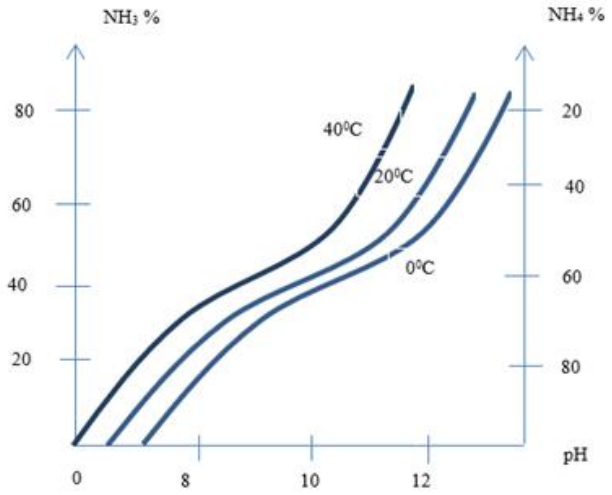

Fig. 1. Changes in ammonia compounds with increased water pH indication

Table 2. Reducing the content of ammonia compounds as the pH increases in water purification installations.

pH	Temperature ^{0}C	The quantity of ammonia in the purified water, mg/l	Indicators of purified water		
			Temperature, ^{0}C	Reduction of ammonia, mg/l	Degree of reduction, %
8,0	22	26,8	16	18,2	37
8,6	21	26,6	17	15,8	41
9,3	23	26,2	18	5,3	80
9,7	21	30	16	2,1	93
10,8	22	25,5	17	0,6	98

The following Figure 2 shows the level of water purification from ammonia, depending on the height of the water purification installation and the quantity of air supplied to it. In the abscissa axis in the picture is given quantity of air for cleaning 1 m^3 of water. Ordinate arrow indicates the degree of decrease in ammonia accumulation in the purified water.

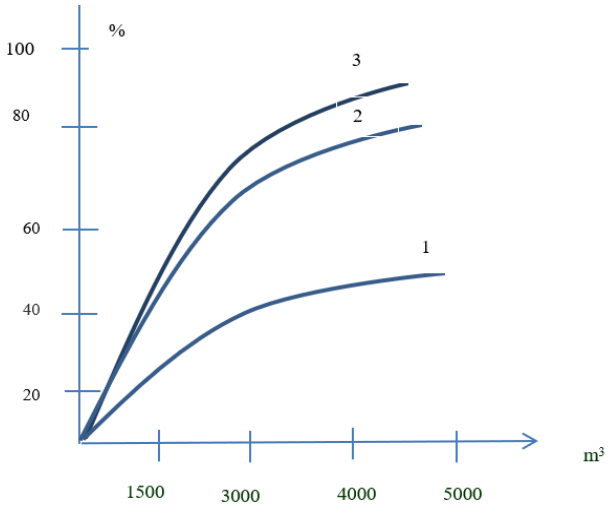

Fig. 2. 1-the height of the tower is 3,6 m; 2 – 6 m; 3 – 7.0 m.

The maximum level of water purification from ammonia, in towers with a height of 6 or 7.0 m, as indicated in the picture, is determined by the results of the experiment.
Figure 3 below shows the pH indicator of the water being cleaned in the tower with a height of 1.5 to 7.5 m when it is 9.7; 10.5; 11.3 and 11.7 the level of purification from the ammonia compound.

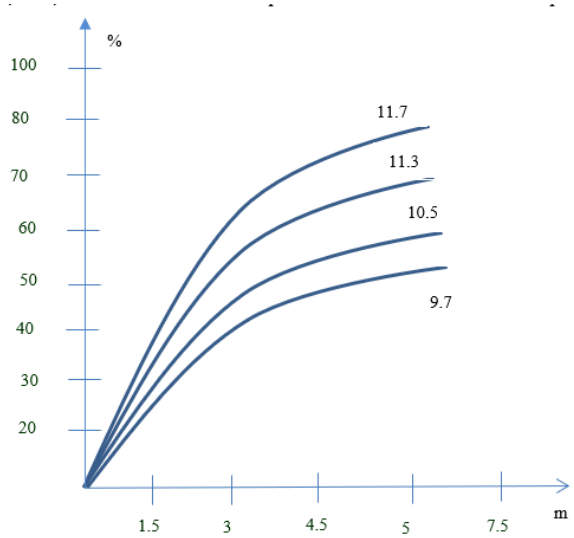

Fig. 3. pH indication of the water being purified in the tower with height from 1.5 to 7.5 m

As the results of the experiment show, when the pH indicator of the purified water is 11.7, the level of purification of water from ammonia is 86.2%. When the water pH decreases from 11.7 to 10.5, its ammonia purification rate drops from 86.2% to 80,2%. But while the water pH decreased from 11.7 to 9.7, it was found that the case of ammonia purification fell sharply from 86.2% to 51.8 %. For this reason, in order to fully clean the water from the ammonia compound, it is necessary that the height of the water purification installation nozzles should be less than 6-6.5 m while the pH indicator is around 10.5.
The following 4-th figure shows the appearance of the installation used in cleaning water from ammonia.

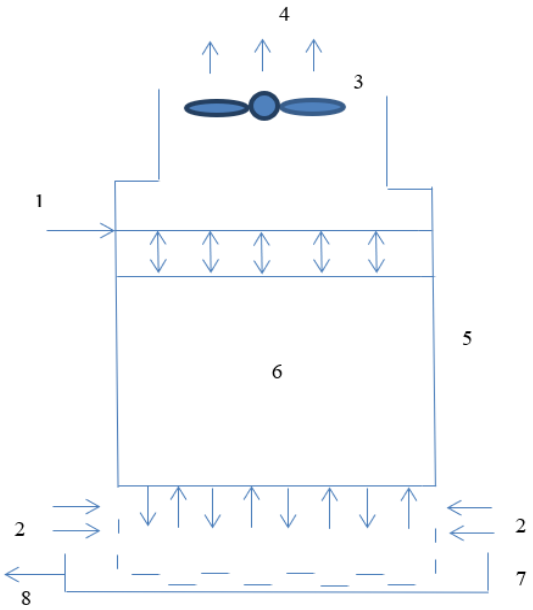

Fig. 4. Scheme of the scrubber device for purification of water from ammonia: 1-supply of purified water; 2-supply of air or smoke gas to it; 3 – fan; 4 – output of air; 5 – case; 6 – nozzle for converting water into droplets; 7 – collection of purified water; 8-output of purified water.

The efficient operation of this a water purification scrubber device will depend on how many tiny droplets of water the nozzles in it decompose and the chances of colliding with the fragments of water in the supplied air. It is necessary to make so small that the holes in the nozzles to turn out how much water into tiny droplets. But in this case, the air, which passes continuously through the nozzles, causes the carbon acid balance in the water to shift to the right. In the process, when the air passing through the nozzles in the flow opposite to the water, together with the CO_2 gas contained in the water, is carried into the atmosphere, the amount of CO_3^{2-} ions forming a precipitate

increases in the purified water, as a result of which the release of deposition products of the $CaCO_3$ compound increases in the breathable surface parts of the nozzles and the water permeability of the nozzles sharply decreases.
According to the results of the experiment, it was noticed that the efficiency of the water purification device decreases to 75% in the presence of scale in the cracks of the nozzles for 20 days of continuous operation. In order that a precipitate of the $CaCO_3$ compound does not form between the nozzles of the scrubber installation, the amount of CO_2 gas in the composition of the treated water should not exceed the equilibrium concentration index. When water is purified from ammonia compounds in combination with a high degree of water purification from ammonia compounds when flue gases are supplied instead of air in the scrubber device, the formation of a sedimentary compound $CaCO_3$ in the intervals of the scrubber nozzles is sharply reduced. This is due to the fact that H_2SO_3 and H_2NO_3 acids, formed on the basis of NO_2 and SO_2 gases contained in flue gases, reduce the concentration of the sedimentary compound $CaCO_3$. In such water treatment plants, due to the deposition products formed between the nozzles, it is possible to wash the nozzles of the water treatment plant with a 3-4% solution of sulfuric acid, while its efficiency is higher than this indicator. The dissolution of the precipitation products formed in this case under the action of acid occurs on the basis of the following reaction.

4 Conclusion

As a result of the reaction of the $CaSO_4$ compound in an acidic environment, it passes into the composition of the washing water in a completely dissolved form in water. And under such conditions, the combination of H_2CO_3 decomposes into gases H_2CO_3 and CO_2.
Therefore, on the basis of the above information, it is worth noting that before sending polluted waters with ammonia compounds to natural water sources, or for the reuse of such waters in the conditions of the enterprise, cleaning of ammonia compounds with the help of air or smoke gas is both effective and economical in case of complete compliance with environmental requirements.

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