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# SYNTHESIS AND PROPERTIES OF DETERGENT REAGENT FOR CLEANING FROM ACCUMULATED MINERAL SALTS

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**Abstract**

In this work, the process of sulfomethylation of aniline, the optimal parameters of the sulfirovanie process are defined, the obtained products are tested and the quality of the steaming solution is otlogeny mineralnyx soley with the surface of the heat exchange apparatus.

**Keywords:** *aniline, sodium bisulfite, formaldehyde, monosulfomethyleneaniline, mechanism reaction, cleaning of steam boilers of mineralnyx otlogeny*

## Introduction

The correct selection of "water-chemical reagent" standards for the water treatment system of thermal power stations, the main — turbine, condensers and secondary -compressors, pumps ensures efficient operation of the devices — prevents the accumulation of mineral salts, eliminates corrosion. For each type of circulating cooling systems, an individual approach to the selection of "water-chemical reagents" is required, and this is primarily related to the material of the components in the system and the type of reagents. Adding concentrated hydrochloric acid, sulfoamines, and phosphates to the environment is considered a traditional method and does not allow complete elimination of accumulated mineral salts and corrosion. Mineral salts collected on the surface of heat exchange devices affect vacuum weakening in technological systems, including heat exchange processes, which are considered the main economic indicator of energy devices. At the same time, special attention is being paid to the determination of effective components for "water-chemical reagent" correction-circulation cooling systems, production of competitive products based on organic synthesis from available raw materials, and determination of their properties.

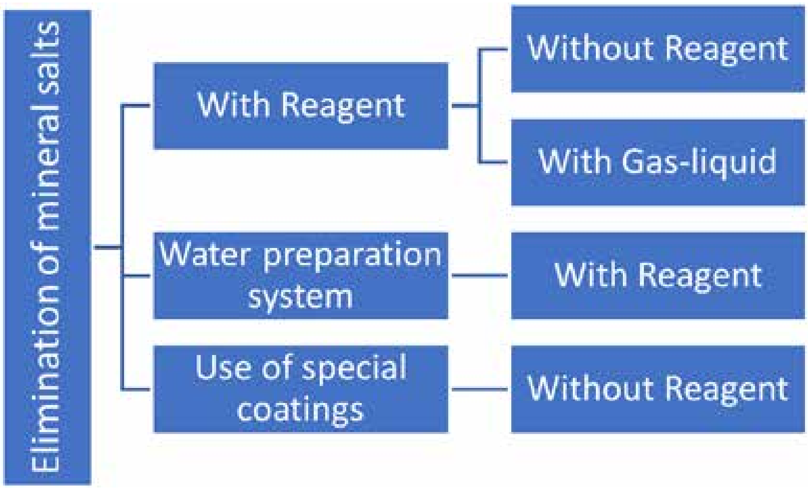
In practice, periodic cleaning of steam boilers is carried out on average once in

1–2 seasons. Boilers with a service life of 20 years (Levitin I. V., et al. 2011; Glazyrin A. I., Kostrikina E. Yu. 1987) are cleaned approximately 10–15 times before decommissioning.

The formation of salts is different due to the difference in mineral salts in the water, the method of its purification and the operating modes of the boilers. According to their chemical composition, salts can be divided into four main groups: 1) salts of alkaline earth metals — $SaSO_3$, $CaSO_4$, $CaSiO_3$, $5CaO\text{-}5SiO_2\text{-}H_2O$, $Mg(OH)_2$, etc.; 2) iron oxide and iron phosphate — FeO, $Fe_2O_3$, $Fe_3O_4$, $NaFePO_4$, $Fe_3(PO_4)_2$; 3) brass and 4) aluminum (RD 34.37.403–91; RD 34.20.591–97; Baranov V. N. 2013).

To clean boiler heating surfaces from salt deposits, reagent-based and reagent-free cleaning methods are applied depending on the structure of the contaminating layer, the degree of contamination of the heat exchange surface, and the type of boiler. The classification of methods to combat salt formation is shown in Figure 1, based on sources (Materials of OJSC 2014; Margulova T. Kh. 1969; GOST 24005–80). The choice of the method depends on the duration of the shutdown of the boiler, the availability of special equipment, chemical reagents, the flexibility of the technological scheme, and the availability of specialists and trained personnel.

**Figure 1.** *Classification of methods to combat salt formation*



It should be noted that the methods used may cause some negative phenomena, as a result of which the further operation of the boiler may be associated with a high rate of formation of salts or increased wear. For example, as a result of mechanical cleaning, the roughness of the surface increases and the oxide protective layer is destroyed, during chemical cleaning, partial melting of the oxide film and metal, hydromechanical wear of the surface, etc. may occur. The problem of effective cleaning of heating surfaces and increasing the wear resistance of the equipment is closely related to each other (Degremont, 2007).

The main advantage of the chemical cleaning method is that it does not require complete disassembly of the equipment being cleaned, and in some cases this salt is the only possible way to break up the sets.

## Experimental part

Currently, chemical cleaning methods widely use organic acids (citric, adipic, maleic, oxalic, formic, acetic, and sulfamic), mineral acids (hydrochloric, sulfuric, sulfamic, and phosphoric), and chelating agents (such as disodium salt of ethylenediaminetetraacetic acid (Trilon B), hydroxyethane diphosphonic acid, and others) as well as compositions based on them. These methods are applied in open or closed cycles using forced circulation techniques or natural circulation of the solution.

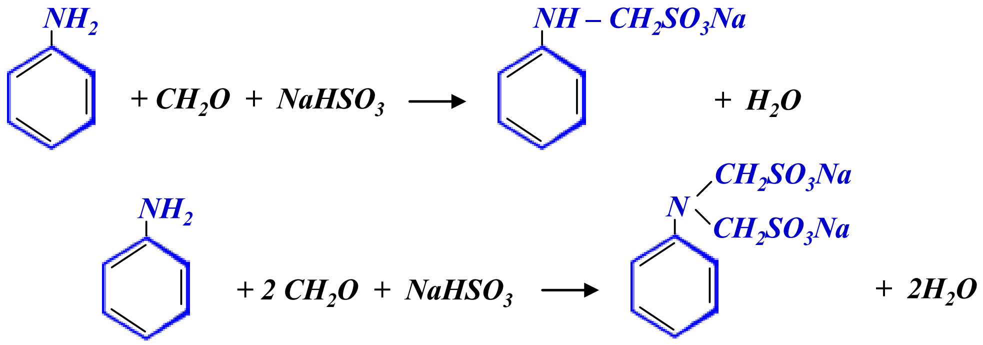
The purpose of this article is to improve the efficiency of water supply systems by eliminating existing scale deposits and to develop affordable and effective compositions of reagents for removing accumulated mineral salts.

To achieve the goal, the process of sulfomethylation of aniline was studied to produce reagents for removing accumulated mineral salts. A three-neck flask with a volume of 250 ml, equipped with a mechanical stirrer and a reflux condenser, was used. Into the flask, 10 ml of $H_2O$ and 85 g of sodium metabisulfite ($Na_2S_2O_5$) were added. 80 mL of 37% formaldehyde solution was added with vigorous stirring. 5 ml of 50% caustic soda solution was poured there. After the formaldehyde odor dissipates, 47.5 ml of aniline is gradually added to the mixture while stirring intensively. The mixture is then heated at a temperature of 60–70 °C for 3 hours. After appropriate treatment and subsequent drying in a drying oven at a temperature of 100±5 °C for 5 hours, 80% of the final product is obtained in powder form. The authenticity of the substance was proven using IR spectroscopy and GC–MS methods and confirmed by elemental analysis.

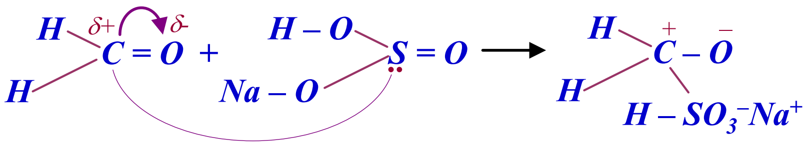
## Analysis of results

This section examines the sulfomethylation process of aniline, systematically studies the factors affecting its yield, and evaluates the effectiveness of the obtained products both in their pure form and as an inhibited acidic formulation in removing accumulated mineral salts from boiler surfaces. The analysis of the resulting scientific findings is also provided.

For the sulfomethylation reaction of aniline, the initial raw materials aniline, formaldehyde, and sodium bisulfite condense in weakly acidic environments. The reaction proceeds according to the following scheme:

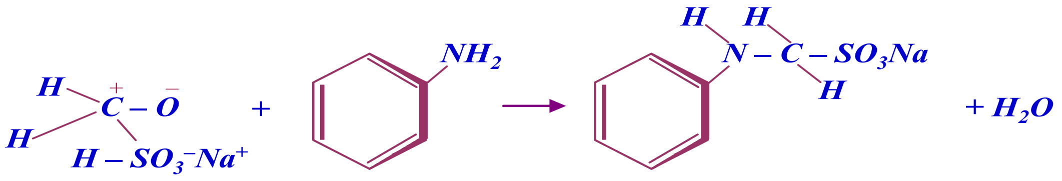


Studies on the dependence of the yields of mono- and disulfomethyl aniline on the ratio of initial raw materials show that the maximum yield of MSM (monosulfomethyl aniline) in its pure form is observed at a ratio of 1:1:0.5 at 70°C. With an increase in the amount of sodium bisulfite or temperature, the amount of DSM (disulfomethyl aniline) in the reaction mixture increases, reaching up to 57.4% at a 1:1:1 ratio at 90°C. The experimental results show that the condensation of aniline with formaldehyde in the presence of sodium bisulfite is independent of the amount of formaldehyde. This can be explained as follows: in the initial stage of the reaction, formaldehyde reacts with sodium bisulfite, which can be considered as a reaction where the hydrosulfite anion interacts with the nucleophile S.

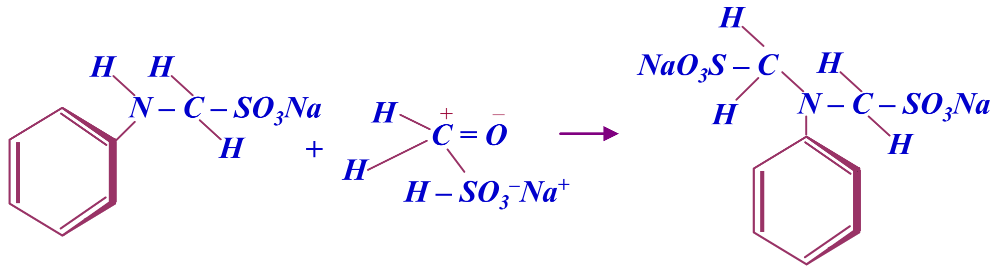


Since the carbonyl group of formaldehyde is a strongly polar group, it easily undergoes polarization. At the same time, the hydrosulfite, with its delocalized electrons, attacks the carbon of the carbonyl group, resulting in the formation of a new carbon-sulfur bond.

Since the resulting intermediate compound is highly unstable, the elimination of the hydroxyl group and the migration of the hydrogen from the hydrosulfite anion occur simultaneously. At the same time, the presence of aniline in the reaction environment leads to the interaction of the amino group with the hydroxyl groups of the ionized hydrogen, resulting in the formation of protonated water ions. As a result, monosulfomethyl aniline molecules are formed as the final product.



As the reaction progresses in this sequence, the concentration of monosulfomethyl aniline increases, which in turn leads to an increase in the amount of disulfomethyl aniline in the reaction mixture.



The reaction was carried out with various ratios of the initial raw materials. It was found that at a mole ratio of aniline: formaldehyde: sodium bisulfite of 1:1:0.5, the main product in the reaction mixture is monosulfomethyl aniline (MSMA). At a 1:1:1 ratio, disulfomethyl aniline (DSMA) is formed. The dependence of the yield of sulfomethyl aniline on the ratios of the initial reagents is presented in Table 1.

**Table 1.** *Dependence of the yield of mono- and disulfomethyl aniline on the ratio of initial raw materials, reaction duration: 3 hours*

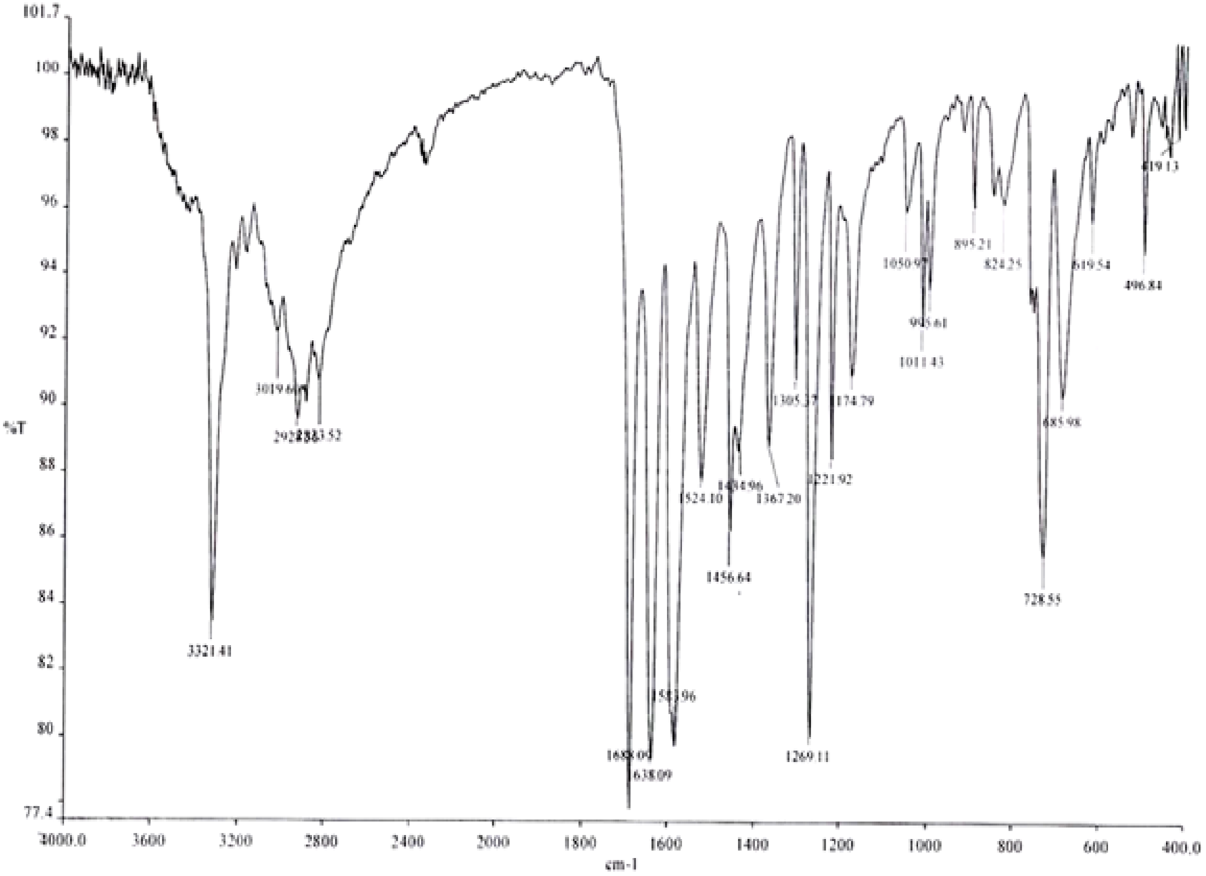
| $C_6H_7N$: $CH_2O$: $Na_2S_2O_7$ mol ratios | Temperature, °C | Productivity, % | |
|---|---|---|---|
| | | MSMA | MSDA |
| 1:1:0,5 | 30 | 26.4 | 4.8 |
| 1:2:1 | | 7.8 | 18.0 |
| 1:1:0,5 | 50 | 47.3 | 7.8 |
| 1:2:1 | | 16.2 | 25.5 |
| **1:1:0,5** | **70** | **80.0** | **0.8** |
| 1:2:1 | | 24.6 | 49.8 |
| 1:1:0,5 | 90 | 78.1 | 1.9 |
| 1:2:1 | | 22.2 | 57.4 |

The structure and composition of the obtained sulfomethyl aniline products were determined using elemental analysis, IR spectroscopy (Figure 2), and 1H NMR spectroscopy (Figure 3).

In the IR spectrum of the condensation products of aniline, formaldehyde, and sodium bisulfite in weakly acidic environments, the following characteristic absorption bands for sulfomethyl aniline can be identified:

1. A stretching vibration at 1190––1205 cm$^{-1}$ corresponding to the -C–N bond,
2. A stretching vibration at 1048––1075 cm$^{-1}$ associated with the O=S=O group,
3. Absorptions at 3422–3448 cm$^{-1}$ corresponding to the -N-H group in the aromatic ring,
4. A stretch at 1663.2 cm$^{-1}$ for the C–C bond in the aromatic ring,
5. Deformation vibrations in the range of 1454–1472 cm$^{-1}$, characteristic of the methylene group.

**Figure 2.** *IR spectrum of the condensation products of aniline, formaldehyde, and sodium bisulfite in weakly acidic environments*



The rate of removal of accumulated mineral salts on the internal surface of the boiler was calculated using the gravimetric method (Antikain P. A., 1969) with the following formula:

$$W = \frac{\Delta m_{mt}}{S_t \cdot t} \qquad (1.1)$$

Where:

- W is the rate of removal of mineral salts (g/m$^2$·h),
- $m_{mt}$ is the mass of the dissolved accumulated mineral salts (g),
- $S_t$ is the surface area being cleaned (m$^2$),
- t is the time for the removal of the accumulated mineral salts (hours).

The effect of the reagents on metal corrosion during the washing process (Mk) was determined using the following formula:

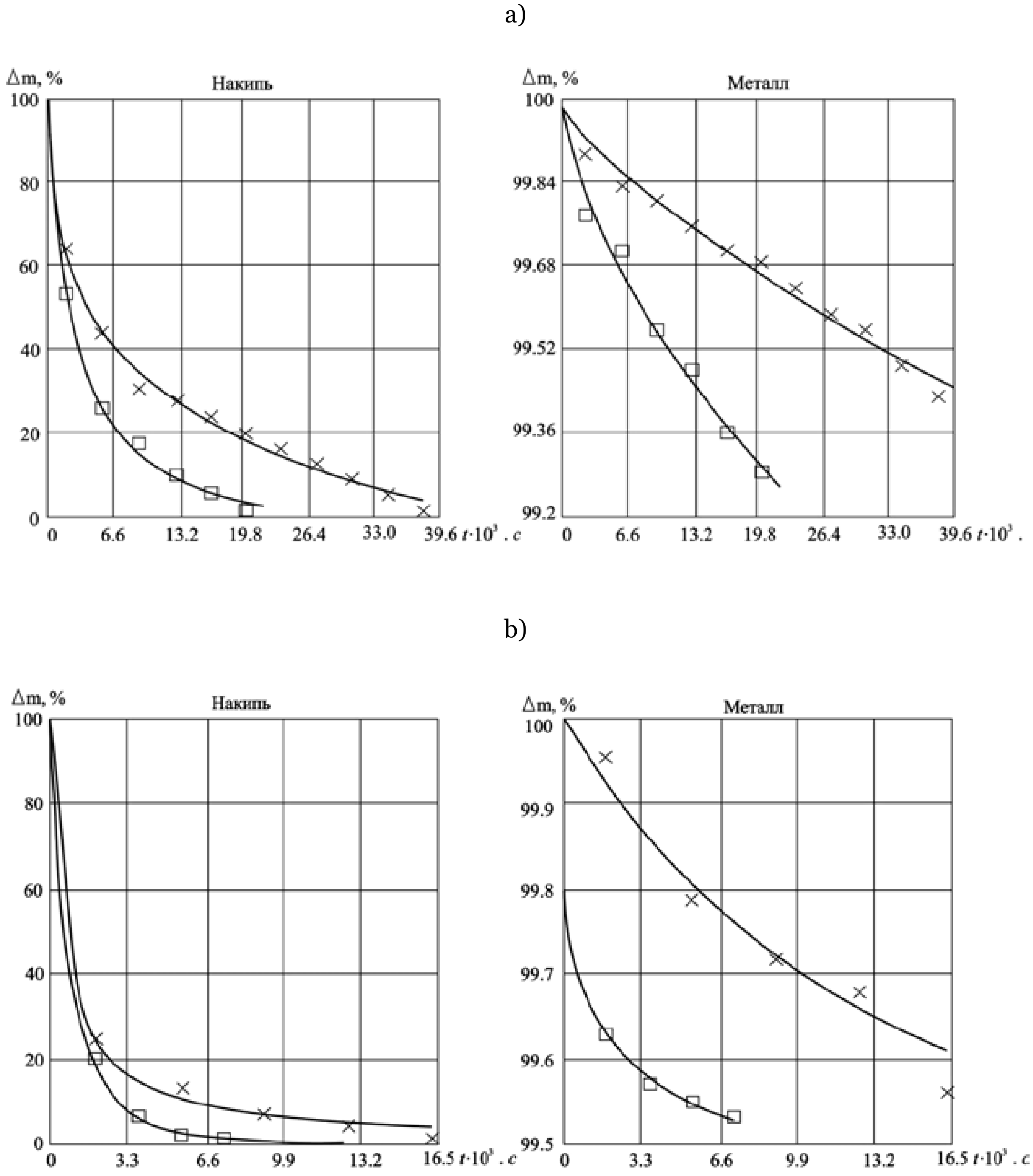
$$K_M = \frac{\Delta m_{mt}}{S_t \cdot t} \qquad (1.2)$$

where – $\Delta m_M = (m_0 - m_m)$ mass of the metal initially and after the washing process, g; $S_t$ – metal surface area, m$^2$; t – washing time, hours.

Studies of the composition and structure of accumulated mineral salts in steam boilers under the conditions of the Syrdarya TPP, as well as numerous conducted experiments, indicate that the washing process consists of two main stages: The initial stage occurs rapidly (covering about a quarter of the total washing duration) and dissolves 75–85% of the mineral salts. The second stage involves dissolving the strongly adhered, hard-to-dissolve portion of accumulated mineral salts on the metal surface. This stage takes longer, encompassing 75–80% of the reaction duration and is considered the phase that determines the qualitative efficiency of the washing process.

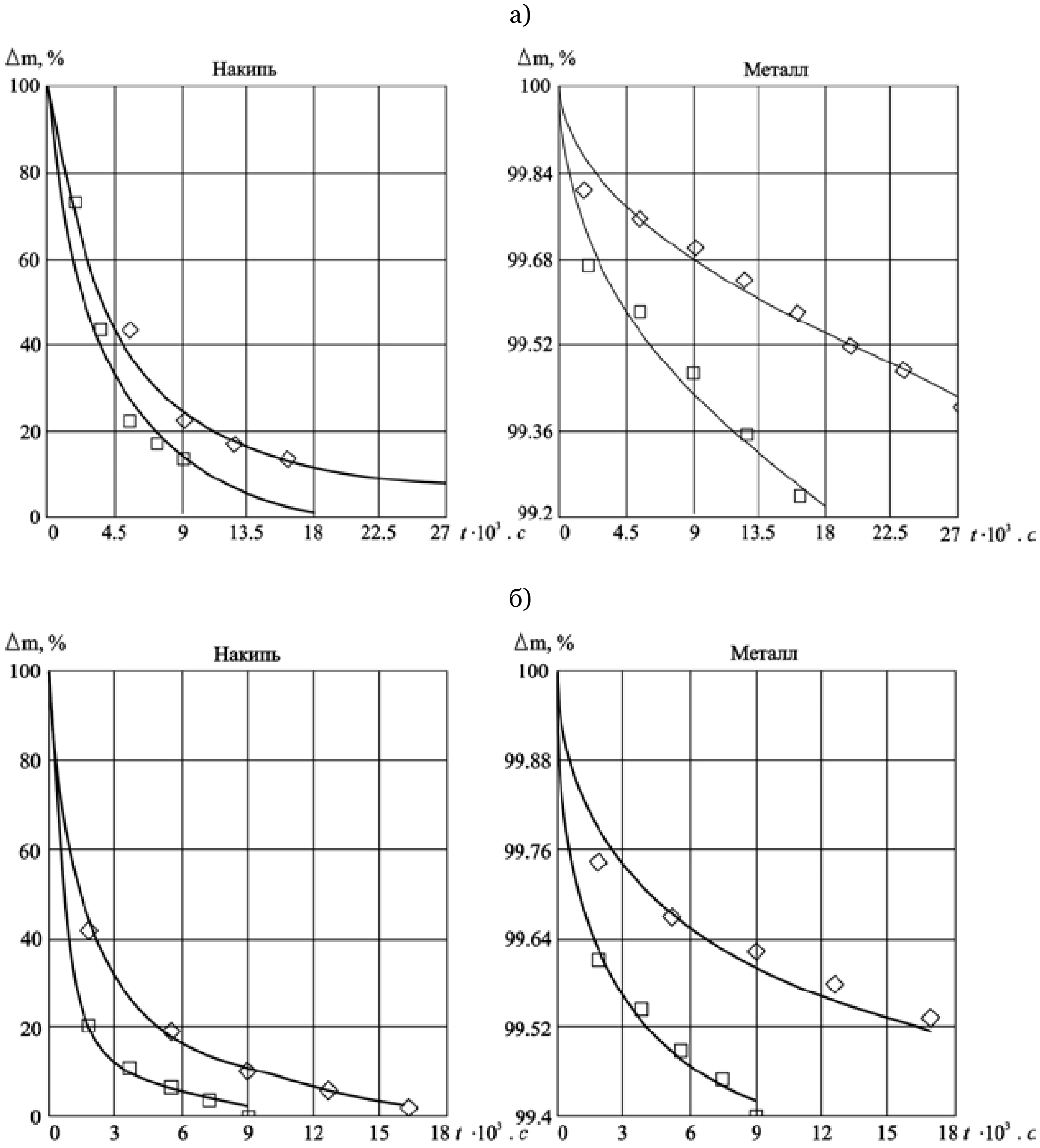
The upper layer of the accumulated mineral salts is relatively soft and mainly consists of carbonate compounds, while the layer closer to the metal surface contains a higher concentration of iron oxides.

**Figure 4.** *Concentration dependence of the dissolution process in washing (solution flow rate U=1 m/s): -×-washing reagent concentration 5%; -washing reagent concentration 8%; a) temperature t = 24°C; b) temperature t = 30°C*



From the comparative graphs of washing temperature and washing solution dosage, it is evident that temperature increase has a greater impact on cleaning duration than dosage increase. For instance: At a 5% dosage and a temperature of 20°C, the cleaning duration for metal surfaces is 39.6 × 10³ seconds. Gradually increasing the temperature to 70°C at the same concentration reduces the cleaning duration to 16.5 × 10³ seconds, shortening it by up to 2.4 times. Increasing the washing solution dosage to 10% at 20°C results in a cleaning duration of 19.8 × 10³ seconds, reducing it by 2.1 times. This clearly demonstrates the aforementioned point.

**Figure 5.** Dependence of the dissolution process in washing on the speed of solution movement (temperature t = 30 °C): -×-washing reagent flow rate 0.1 m/s; – washing reagent flow rate 1.0 m/s; a) washing reagent concentration 5%; b) washing reagent concentration 8%



## Summary

Thus, the condensation products of aniline, formaldehyde, and sodium bisulfite in weakly acidic environments were studied using IR spectroscopy, elemental composition analysis, and PMR (proton magnetic resonance) spectroscopy. The synthesis of sulfomethyl aniline products aligns with the principles of organic chemistry theory, where it is based on the observation that with increased reaction time, sulfomethyl aniline produced in aqueous solutions undergoes hydrolysis, converting back to the initial products, which leads to a decrease in the reaction yield. The geometry and electronic structure of the obtained substances were studied using the semi-empirical quantum chemical method with PMZ (probabilistic molecular zone) analysis.

The optimal standards for washing the mineral salts accumulated on the internal surfaces of steam boilers have been determined, and the effectiveness of the salt dissolution rate (W) was calculated using the gravimetric method. Studies on the composition and structure of the mineral salts accumulated in steam boilers under the conditions of the Syrdarya Thermal Power Plant (TPP) and numerous experiments showed that the washing process consists of two main stages: The initial stage – a rapid phase (covering about a quarter of the total washing duration) in which 75–85% of the mineral salts dissolve. The second stage – the dissolution of the strongly adhered, hard-to-dissolve portion of the accumulated mineral salts on the metal surface (this stage is prolonged, covering 75–80% of the reaction duration, and is considered the stage that determines the qualitative effectiveness of the washing process).

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