# Research into the Process of Neutralization and Precipitation of Waste Solutions Generated in the Chemical Industry

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**Abstract.** The article studies the chemical composition of acidic and alkaline waste solutions generated in the chemical industry, and the possibilities of their mutual neutralization are investigated. The study of the precipitation process as a result of neutralization showed that it is possible to separate metals up to 98%.

**Keywords:** chemical industry, metals, neutralization, precipitate composition, chemical analysis, technological.

In recent years, the legislative framework for ensuring environmental safety in Uzbekistan has been strengthened [1-3]. In the metallurgical and chemical industries, a large amount of waste is generated during the production of finished products from raw materials, the main part of which is wastewater. These wastewaters are generated during the extraction, preparation and processing of organic and inorganic raw materials. The sources of wastewater formation during industrial technological processes are the following [4-8]: wastewaters formed as a result of chemical reactions, containing residues of starting materials and reaction products; waters released as a result of free or bound moisture in the composition of raw materials and starting materials; technical washing waters formed during the washing of raw materials, intermediate and finished products, equipment and devices; aqueous solutions used in production processes; extracts and absorbers formed during the extraction and absorption processes; cooling waters used in cooling systems; wastewater solutions and other technical wastewaters generated in the production of acids, alkalis and salts in the chemical industry.

The composition and amount of wastewater varies directly depending on the industry, production volume, chemical properties of the raw materials used and technological processes. These wastewaters may contain various organic and inorganic polluting compounds. International health organizations divide pollutants in industrial wastewaters into the following classes [9]: non-biologically stable organic compounds; inorganic salts of low toxicity; petroleum products and their derivatives; biogenic compounds (nitrogen and phosphorus components); special chemical compounds of high toxicity, in particular heavy metals, non-biodegradable synthetic substances.

Industrial wastewaters consist not only of dissolved organic and inorganic substances, but also contain colloidal dispersed mixtures and suspended coarse particles with a density greater or less than the density of water, heavy metals [10].

The level of ecological hazard of wastewaters is determined by the toxicity properties and concentration of pollutants contained in them. In particular, the presence of heavy metals (for example, mercury, lead, cadmium), cyanides, phenols, hydrogen sulfide and carcinogenic substances determines the high toxicity of wastewaters. Such waters are also characterized by a sharp unpleasant odor [11].

Pollution of the natural environment with heavy metals poses a serious threat to the stability of the biosphere. Ions of these metals have the property of accumulating in plant and animal organisms, and their toxic effect persists for a long time. Heavy metal ions that enter water bodies remain in a colloidal state, in the composition of bottom sediments or in other poorly soluble forms for a long time, becoming a source of environmental hazard [12].

To effectively remove heavy metal ions from wastewater, their purification is carried out by converting them into poorly soluble hydroxides or carbonate compounds. This is done using alkaline reagents such as calcium, sodium, magnesium hydroxides, oxides or carbonates [13].

Experience in studying waste solutions shows that waste electrolytes from the electrolysis process, spent acid-based electrolytes formed in metal production, are classified as environmentally hazardous pollutants of category 1–2, but they are an important secondary source for the recovery of non-ferrous metals. The mechanism of precipitation of Cu(II) ions in spent copper solutions in the form of hydroxo-compounds and the possibility of their processing by obtaining clean and easily separated precipitates have been identified [14-15].

A complete study of the composition of wastewater, a comprehensive application of treatment methods depending on the physicochemical parameters and the nature of pollutants, provides the highest efficiency. Hydroxide and carbonate-based precipitation gives high results in the recovery of copper ions, but the technological conditions (pH, reagent consumption, precipitate quality) must be carefully selected [16-17].

The results of spectrometric analysis of wastewater from the 201st thiourea production plant of Navoi Azot JSC show that there is a possibility of isolating valuable components such as iron (2800 µg/l), nickel (320 µg/l), copper (1200 µg/l), lead (1200 µg/l), and others.

Neutralization of waste solutions with each other is a process of reducing harmful substances, acids, alkalis, metal ions, and organic additives in them to a safe level, and its advantage is its economic cost-effectiveness. Initially, in the experiments, samples of AKN waste solutions and wastewater from the thiourea production plant in different ratios (7.5:1, 5:1; 3:1; 2.5:1; 1.875:1; 1.67:1; 1.5:1; 1:1; 1:1.33) were taken and mixed. The mixing process was carried out in an experimental reactor. The process was carried out at room temperature. As a result, mainly hydroxide and partially rhodanide ions react with metal cations as follows:

$CuCl_2 + 2CNS^- = Cu(CNS)_2 + 2Cl^-$ (1)

$CuCl_2 + 2OH^- = Cu(OH)_2 + 2Cl^-$ (2)

$ZnCl_2 + 2CNS^- = Zn(CNS)_2 + 2Cl^-$ (3)

$ZnCl_2 + 2OH^- = Zn(OH)_2 + 2Cl^-$ (4)

$FeCl_2 + 2OH^- = Fe(OH)_2 + 2Cl^-$ (5)

$FeCl_2 + 2CNS^- = Fe(CNS)_2 + 2Cl^-$ (6)

After one hour, the mixing was stopped and the solution was filtered (Figure 3.6). The composition of the filtered solution was determined. The appearance and color of the filtered solution and the remaining precipitate were studied (Table 1).

**Table 1. Amount of solution and precipitate after filtration**

| № | AKN solution:thiourea solution | Mixed volumes (ml) | Total volume, ml | Filtration products | |
|---|---|---|---|---|---|
| | | | | Precipitate mass, gr | Solution, ml |
| 1 | 7,5:1 | 75:10 | 85 | 1,42 | 83 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 5:1 | 75:15 | 90 | 1,75 | 88 |
| 3 | 3:1 | 75:25 | 100 | 2,11 | 87 |
| 4 | 2,5:1 | 75:30 | 105 | 2,54 | 102 |
| 5 | 1,875:1 | 75: 40 | 115 | 2,77 | 110 |
| 6 | 1,5: 1 | 75:50 | 125 | 2,91 | 121 |
| 7 | 1:1 | 75:75 | 150 | 3,11 | 140 |
| 8 | 1:1,33 | 75:100 | 175 | 3,57 | 170 |

The proportions of AKN waste solutions and thiourea waste solutions mixed in the studied proportions with a total volume of 175 ml form an average of 2.5 gr. to 3.57 grams of precipitate, the main part of which is neutralized as a residual solution, as a result of which both solutions are cleaned of harmful metal ions and become environmentally safe waste. When AKN waste solutions and thiourea waste solutions were mixed in different proportions, the amount of metals in the solution increased, and the precipitation levels increased in the precipitation phase as the pH value increased (Fig. 1).

The mixing was carried out at different time intervals (in the range of 10-60 minutes), and the amount of copper, zinc, and iron transferred to the precipitate was determined. In the process, AKN waste solutions and thiourea waste solutions were mixed in a ratio of 1:1.33, and from the results obtained during the experiment, we can see that the amount of metals decreased (Table 2).

The experimental conditions were carried out at the following pH values, in the proportions of the two mixtures.

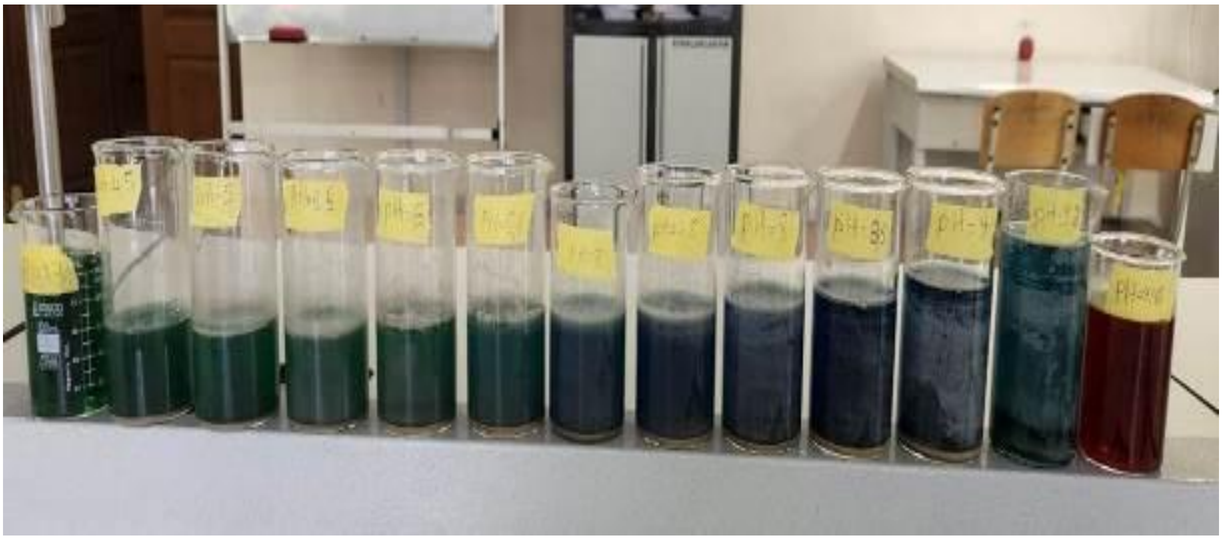

**Figure 1. Images of experimental tests conducted at different pH values of the process of precipitation of AKN solutions with thiourea solution**

**Table 2.**

Time dependence of the amount of metals in the solution

| Mixing time (min) | Amount of metals in solution (g/l) | | |
|---|---|---|---|
| | Cu | Fe | Zn |
| 0 | 4,036 | 2,8 | 1,2 |
| 10 | 2,96 | 1,55 | 1,05 |
| 20 | 2,15 | 1,22 | 0,92 |
| 30 | 1,88 | 1,05 | 0,78 |
| 40 | 1,05 | 0,92 | 0,62 |
| 60 | 0,83 | 0,74 | 0,42 |

No. 1: pH=4.5-5, when AKN waste solutions and thiourea waste solutions were precipitated, the compositions of the filtrates and precipitates formed as a result of precipitation were studied. In this case, the composition of the solutions was analyzed by X-ray fluorescence experiments, and the structure and composition of the precipitates were analyzed based on SEM analyses (Fig. 2-3).

When AKN waste solutions and thiourea waste solutions were mixed, the amount of copper increased due to the presence of copper in the second solution, and at pH = 4.5-5, the amount of base metals was still preserved in large quantities in the residual solution. This indicates that the pH environment is not sufficient for the precipitation of heavy non-ferrous metals. In the study, the pH indicators of the initial and post-mixing solutions were measured with a laboratory pH meter.

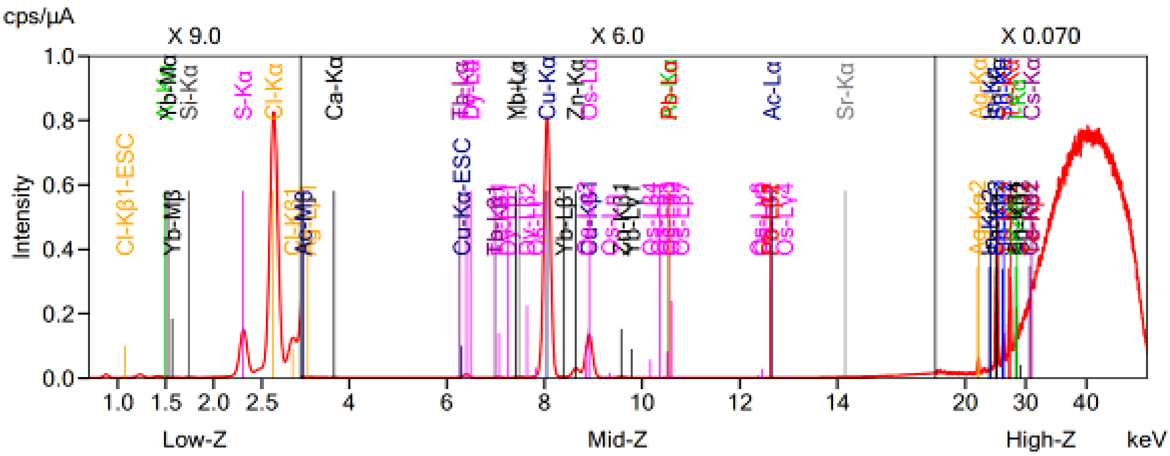


**Figure 2.** Results of analysis of the residual solution after precipitation at neutralization pH=4.5-5

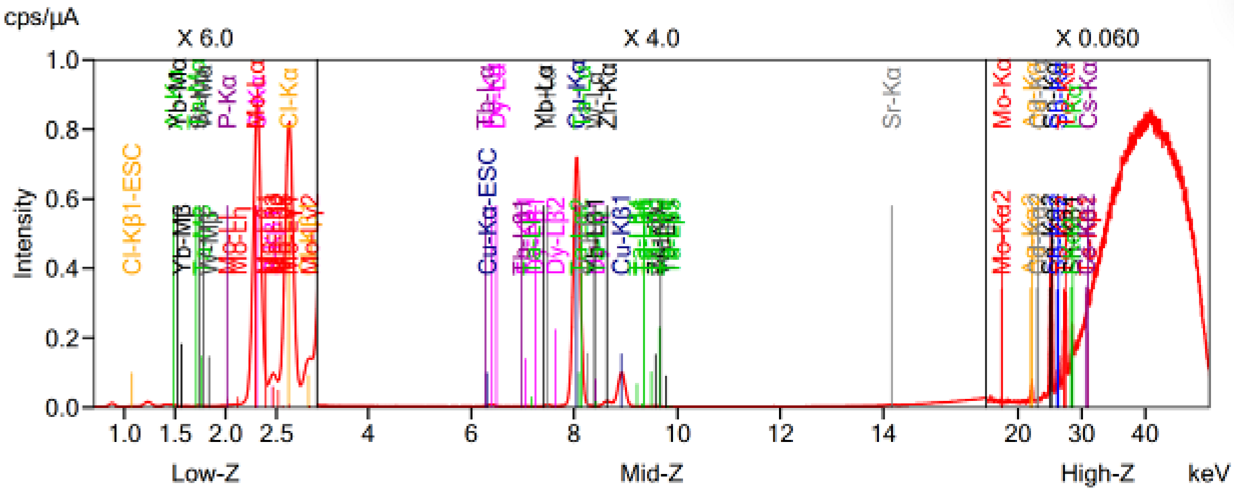

**Figure 3.** Results of analysis of the residual solution after precipitation at neutralization pH=7.5-8

From this it can be concluded that by increasing the pH from a strongly acidic environment of pH=3.6 to an alkaline environment of pH 8.7, it is possible to achieve a precipitation degree of up to 82.8% for copper.

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