Integrated Microanalysis of Sediment Composition Waste Water with Heavy Metals Ions

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Abstract. The comprehensive analysis results of sediment, containing heavy metal ions using standardless methods of X-ray phase (XRD) and X-ray spectral (XRD) analyzes to determine the elemental and phase composition of sediment samples, obtained during reagent treatment of industrial wastewater are shown. The analytical results of the processes that take place in these precipitation under the influence of certain temperature regimes are presented, which contributes to a change in the physicochemical properties of these precipitates and allows the most accurate qualitative and quantitative analysis of these precipitation. The obtained results are further used to determine the hazard class of precipitation and to develop a modern scheme for processing and disposal of precipitation, which makes it possible to reduce the technogenic load on the environment.

1. Introduction
One of the most toxic pollutants is heavy metals that enter the environment in a waste form from galvanic wastewater. The maximum permissible concentrations of metal ions are very low, the requirements for the treatment of industrial effluents are quite stringent, and so increasing the degree of industrial wastewater treatment is one of the main tasks at most industrial enterprises. The main method of galvanic production wastes purification from heavy metal ions is the reagent one [1]. Its essence comes down to the formation of hydroxides or heavy metals salts, which are removed by settling, filtration or other separation methods of solid and liquid phases, however, the current reagent treatment scheme requires a large consumption of expensive chemicals (for example, FeSO₄ consumption is at least 2 mg / dm³ per 1 mg of copper). In this case, large amounts of precipitation are formed. The total salinity increases and water cannot be used in circulation without an additional stage of post-treatment. All this necessitates the development and implementation of modern technologies to ensure high efficiency of cleaning processes, as well as the possibility to create a closed cycle of water consumption on their basis.

The study object was a wastewater model with different initial concentrations of copper, zinc and nickel ions C_in^{ Cu²⁺} =60 mg/dm³; C_in^{ Zn²⁺} =15 mg/dm³ and C_in^{ Ni²⁺} =20 mg/dm³, because most metal processing enterprises were characterized by the presence of common wastewater flows after electroplating operations.

Among the promising new reagents is the patented product Amersep MP7, manufactured by Ashland Specialty Chemical Company Drew Industry (Netherland) [2,3]. Amersep MP7 is precipitating reagent containing 25-40% solution of sodium polythiocarbonate (Na₂CS₄). It is widely...
used in Western Europe to remove heavy metal ions from wastewater and has low toxicity compared to traditional precipitators.

The reagent, based on sodium polythiocarbonate $\text{Na}_2\text{CS}_4$, forms compounds with various heavy metal ions due to the strong complexing effect because of S-S cystine bond decomposition. In most cases, the AMERSEP MP7 precipitating reagent does not react with chelating and sequestering additives, therefore, it can be used as a replacement for existing reagents or at the final stage of the cleaning process to remove residual metals in wastewater. $\text{SO}_2$ and $\text{SO}_3$ gases are released during thermal decomposition of the reagent. Preliminarily, $\text{Ca} (\text{OH})_2$ was used for neutralization.

2. Mathematical and Methods
Thermo gravimetric analysis of the reagent dried at 1000 °C was carried out on a STA 449 F1 instrument (synchronous thermal analyzer), NETZSCH company (Germany), heated to 10000 °C (Figure 1) in order to study the physicochemical properties of the reagent. Thermo gram is complex with many endo-effects and exo-effects.

Figure 1. Thermo gram of the reagent: TG - thermo gravimetric curve, which shows the change in mass during the heating process (mass increases or decreases); DTA is differential thermal analysis; DSC is differential scanning curve (DSC and DTA show endo- and exo effects that occur when heated).

Endo-effect of $t = 103 \, ^{\circ}\text{C}$ is accompanied by the release of water and occurs with a decrease in mass. Exo- effects in the temperature range of 350 - 625 °C occur with a sharp decrease in mass due to the emission of $\text{SO}_2$ and $\text{SO}_3$ oxides and carbon dioxide $\text{CO}_2$. Exo -effects of $t = 784 \, ^{\circ}\text{C}$ and $804 \, ^{\circ}\text{C}$ are accompanied by an increase in mass, possibly due to the formation of metal oxides (mainly $\text{Na}_2\text{O}$).

As a result of the model wastewater treatment, it was possible to reduce the heavy metal ions' content in the wastewater and to determine the optimal dose of the reagent.

In most cases, this chemical - natured precipitate is a mixture of hydroxides, oxides, hydrated salts, or other sparingly soluble compounds, removing heavy metal ions by converting them into an
insoluble precipitate [4,5]. They are the main sources of heavy metals entering the environment [6,7], therefore, the problem of galvanic sludge disposal in its significance follows directly radioactive waste disposal. However, at present, the questions on modern methods use for studying the chemical composition and structure of the resulting precipitation are insufficiently covered, so this determines the presented work relevance.

The research objective was to determine the elemental and phase composition of the sediment samples, obtained by reagent neutralization of wastewater containing heavy metal ions.

Due to the standards lack, standard-less methods of X-ray phase (XRD) and X-ray spectral (XRD) analyzes were used for this purpose. X-ray research methods are the most universal, objective and accurate. Using x-ray phase analysis is the way to determine the qualitative and quantitative composition of a material [8].

Radiographs were taken using Shimadzu XRD-7000S automated X-ray diffract metric equipment (CuKα radiation). X-ray diffraction analysis was carried out using an information retrieval system for X-ray phase identification of materials (IPS), combining high-quality and semi-quantitative (according to the “corundum numbers” method) analysis. The fundamental parameters method was used (X-ray fluorescence energy dispersive spectrometer ARL Quant’X) for semi-quantitative SAR Thermal analysis was performed on a SDT Q600 synchronous thermal analyzer, combined with a Nicolet380 IR Fourier spectrometer with a TGA / FT-IR interface (an attachment for gas phase analysis). This complex made it possible to simultaneously obtain DThA, TG, and the composition of the evolved gas phase.

From the obtained IR spectra, the time dependence of the optical density for released gases was constructed. According to thermo gravimetry, the maximum content of organic compounds was approximately estimated. Thermal analysis was carried out in air; heating one was carried out from room temperature to 1000°C at a speed of 20 K / min.

The results of spectral analysis are shown in table 1 and Figure 2. The diffract gram of the obtained precipitate is shown in Figure 2.

| Element | Fe | Ni | Cu | Zn | S  | K  | Ca | Na | Mg |
|---------|----|----|----|----|----|----|----|----|----|
| Concentration, mass. % | 0.37 | 15.66 | 55.34 | 16.41 | 1.45 | 0.99 | 9.14 | 0.13 | 0.51 |

The determination of zinc by the X-ray spectral method on energy dispersive spectrometers is greatly hindered by copper presence in the sample, since α is the line of zinc overlaps with β is the line of copper. Therefore, the joint determination of zinc and copper is best done in the sample by another method.

As if the presented samples contained organic compounds that were difficult analyzed by XRD and XRD methods, we additionally performed thermo gravimetric analysis of the samples, which made it possible to study 3D kinetics of the exhaust gases during precipitate pyrolysis (Figure 3).
Nature and number of phases in various substances mixtures is determined using a qualitative differential thermal analysis [9]. The mixture components in can be detected by the thermal effects inherent in each substance.

Thermal analysis is one of the fast enough research methods that allows you to track the progress of physicochemical transformations with temperature [10] and serves to study the substance properties and the processes that occur in it, heated or cooled according to a given program.

The essence of thermal analysis is to determine (using the heating or cooling curves of the sample) the substances’ transformation and interaction temperatures, accompanied by thermal effects that is a heat absorption (endothermic processes) or heat generation (exothermic). Using the heating curves, one can study the effects of phase transformations in reversible and irreversible processes, an amorphous substance conversion to crystalline one, decomposition and formation of solid solutions, melting, boiling, decomposition, dehydration, oxidation, reduction, exchange, etc.

Figure 3. 3D-IR spectrum of exhaust gases during pyrolysis of sediment (optical density-wave number-time).

Recording weight method (thermo gravimetric analysis) is used in the heating process, studying physical and chemical processes along with the method of heating curves (DThA). The TG curve makes it possible to judge the kinetics of the process of oxidation, reduction, dehydration, dissociation, and also to determine the amount of a particular mineral in the mixture.

The obtained spectra of concentration curves showed a change in concentration over time, i.e. the possibility of linking the mass change along the mass loss curve with the release of these substances, but the nature of the gases themselves could not be identified. The analysis was carried out on a SDTQ 600 synchronous analyzer combined with the IR Fourier spectrum of the Nicolet 380 c TGA / FT-IR interface (an attachment for gas phase analysis). Recording weight method (thermo gravimetric analysis) is used in the heating process, studying physical and chemical processes along with the method of heating curves (DThA). The TG curve makes it possible to assess the kinetics of the oxidation process, reduction, dehydration, dissociation, and also to determine the amount of a particular mineral in the mixture.

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This method made it possible to simultaneously obtain DhTA, TG, and the composition of the evolved gas phase. The time dependence of the optical density for the released gases was constructed from the obtained IR spectra. According to thermo gravimetry, the maximum content of organic
compounds was approximately estimated. Thermal analysis was carried out in air; heating one was carried out from room temperature to 100°C at a speed of 20 K/min.

Based on 3D-IR spectra, we obtained the time dependence of the optical density for the released gases (Figure 4).

Figure 4. Gas evolution curves during pyrolysis of sediment.

Thermal analysis of the sediment and scanning the gas phase composition is going on synchronously. X axis is the designation both in temperature and in time, therefore, from time to time we can go to temperature and back. So the time interval is 10.8 - 17.6 minutes in the thermogram (Figure 4). It corresponds to 200 - 400°C.

The gas evolution curves indicate the presence of the organo-containing reagent decomposition during the sediment pyrolysis. In section 1, the TG curve decreases in weight by 6.5%. This effect is accompanied by water release. In section 2, the organic matter of the sediment is oxidized, which is accompanied by a small emission of carbon dioxide (10.8-17.6 minutes) and water. This effect is accompanied by heat generation (exothermic peak at 294.77°C). In section 3, carbon dioxide is released due to the decomposition of calcium carbonate. The decomposition of calcium carbonate corresponds to an endothermic effect with a beginning at 678.28°C. 10% CO2 was released in the process of calcium carbonate decomposing. Hence, the calcium carbonate content is 22.7%. The peak area on the gas evolution curve is 0.7, which is responsible for the emission of CO2 during the calcium carbonate decomposition and the peak area is 0.2 which is responsible for the combustion of organic carbon. A peak area of 0.7 corresponds to 10% CO2, meaning a peak area of 0.2 corresponds to 2.85% CO2 or 0.78% C. Thus, the organic carbon content in the sample is 0.78%.

Figure 5. Thermogram of sediment.
The elemental composition of the precipitate was determined by the semi quantitative method of X-ray fluorescence analysis by the method of fundamental parameters on an X-ray fluorescence wave dispersive spectrometer Shimadzu XRF-1800. The analysis’ results (in terms of oxides, since the analysis of oxygen directly makes a high error) are presented in Table 2 and in Figure 6.

Bremsstrahlung and characteristic radiation of the anode material of the x-ray tube are used to excite the characteristic radiation of the element in the sample material. Bremsstrahlung occurs when electrons are broken by the anode of an x-ray tube. It decomposes into a continuous spectrum, having a boundary on the side of small wavelengths. The position of this boundary is determined by the electrons energy falling on the substance and does not depend on the substance nature. Characteristic x-rays are formed when an electron is knocked out one of the atom’s inner layers, followed by a transition to a released electron orbit from its outer layer. They have a line spectrum.

3. Results
Excitation of the substances’ atoms in a sample occurs when the tube is exposed to x-rays. The sample begins to fluoresce, emitting characteristic x-ray radiation. A chemical element in a sample can emit x-ray radiation only when the energy of the exciting x-ray quanta is higher than the binding energy (absorption edge) of the element’s internal electron. In this case, the process of X-ray fluorescence excitation is probabilistic, i.e. the appearance of different lines is determined by probability of the corresponding transitions, and it determines “brightness” of the various spectrum lines. Another very important feature of the x-rays spectra characteristic is that each element gives its spectrum, whether it is excited to emit x-rays in a free state or as part of a chemical compound. This feature of the characteristic X-ray spectrum is used to identify various elements in complex compounds and it is the basis of X-ray spectral analysis, which allows determining the total content of this element in the sample.

| Table 2. Sediment Analysis’ Results. |
|--------------------------------------|
| Element (in terms of oxide)          | CaO | CuO | SiO₂ | C   | MgO | NiO | S   | ZnO | Al₂O₃ | Fe₂O₃ | P    | K₂O | Cr₂O₃ | Mn  |
|--------------------------------------|-----|-----|------|-----|-----|-----|-----|-----|-------|-------|------|-----|-------|-----|
| Concentration, mass%                 | 29.9| 32.6| 9.3  | 3.36| 6.32| 6.14| 4.70| 4.80| 1.11  | 1.05  | 0.50 | 0.12  | 0.10 | 0.05  |

Figure 6. X-ray fluorescence spectra: a) Cu – Intensity 290, b) Ni – Intensity 48, c) Zn – Intensity 54, d) Ca – Intensity 185, f) S – Intensity 28.
The studies showed that the obtained precipitate, as a result of the reagent treatment, mainly contains adsorbed water, calcium bicarbonate, calcium sulphate, copper, nickel, zinc, organic compounds and calcite.

4. Conclusion
The possibility of using a complex of modern analytical methods and instruments to study and fully understand the structure of sludge obtained as a reagent neutralization result of wastewater containing heavy metal ions, in particular Cu (II), Ni (II) и Zn (II), is shown. In the future, this makes it possible to better develop a modern scheme for utilizing the resulting precipitation and reduce the man-made load on the environment [11].

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