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INVESTIGATION OF SUSPENSIONS BASED ON GALVANIC SLUDGES

Chemical and phase composition, dispersity of slurries formed during reagent treatment of waste water by using lime and caustic soda are investigated. The properties of suspension on the bases of the slurries, in particular, viscosity, flowability, sedimentation velocity, final volume of sediment are examined depending on the method and producing conditions of the sludge. It is shown that builders make it possible to adjust rheological properties of the sludge suspensions. Features of the slurries preparation for processing in the technical materials are analyzed.

Introduction. One of the major environmental problems to be solved in Belarus is the disposal of the growing waste amounts of worked-out solutions and sludges to produce technical materials for various industries. Analysis of published in the literature researches devoted to sludge utilization formed in the process of wastewater treatment in electroplating industry shows that currently there are several key areas of galvanic sludges using as secondary raw materials for industrial materials [1–3]. One of the directions is the use of sludge in the production of building materials, particularly of expanded clay, tile, pottery, bricks [4], but some experts prefer technologies including thermal treatment of sludge in which the formation of a thermally and chemically stable compounds that provides ecological security for their further use takes place. A number of studies [5–8] demonstrate the expediency of thermal reworking of galvanic sludges into pigment materials in which migratory ability and toxic activity of heavy metals is reduced to acceptable values by means of high-temperature synthesis of formed insoluble spinels, silicates and other compounds. In the case of sludge processing into the pigment materials by "wet way" one of the stages is the preparation of a suspension with the required chemical and technological indexes.

Mostly galvanic sludges suspension is a complex colloidal-chemical system. Their properties are defined by chemical composition, degree of dispersion of the solid phase, the content of water-soluble substances and the ratio of the solid and liquid phases. The investigation of the system "sludge – water" and of the rheological properties of formed suspensions allow to determine the conditions under which it is possible to transfer sludge to the в yielding state for its further processing. The main characteristics permitted to regulate the properties of sludge suspensions are the ratio of the solid and liquid phases or the moisture content and viscosity.

The aim of this work is the study of the rheological properties and sedimentation stability of galvanic sludges suspension resulting from the reagent wastewater by electroplating.

Experimental techniques. The objects of the study were galvanic sludges formed during wastewater treatment woth milk of lime to STPTS-1 of OJSC "Byelorussian steel works" (BSW), Zhlobin (sludge N 1) and soda ash at the Baranovichi Transfer Lines Plant (BTLP) (sludge N 2). Investigated galvanic sludge are pasty mass characterized by complexity and instability of the composition from dark gray to dark brown in color with a density of 1.16–1.24 g/cm^3 and humidity of 60 to 85 wt %, pH of the suspension is equal to 3.2–7.9.

Sample taking of galvanic sludges was carried out periodically (every 1–2 months). Then they were averaged and studied. Granulometric sludges analysis was carried out on laser microanalizer of particle-size distribution Analysette 22 made by FRITSH.

Settling velocity and volume of the final sludge precipitation is determined by measuring of the thickness of the time taken up by the sludge solids of equal volumes of suspensions [9]. Under the final volume of the sludge precipitation is conventionally understood a percentage of the volume of a suspension of known concentration which it will take after 16 h of sedimentation. Determination of the viscosity of sludge suspensions were carried out with using of Engler viscometer withvolume of 100 ml.

Ten gram of sludge sub-sample in terms of bone-dry solids were placed in the glass, added some water adjusted to 100 ml and stirred until a homogeneous suspension. The suspension was poured into the Engler's vessel to the mark and the duration of the running-out of the suspension from the hole of viscometer was measured by a stopwatch. Viscosity value was expressed in Engler's degrees (°E) which was calculated by dividing the duration of the running-out of the suspension by the duration of the running-out of the same volume of water.

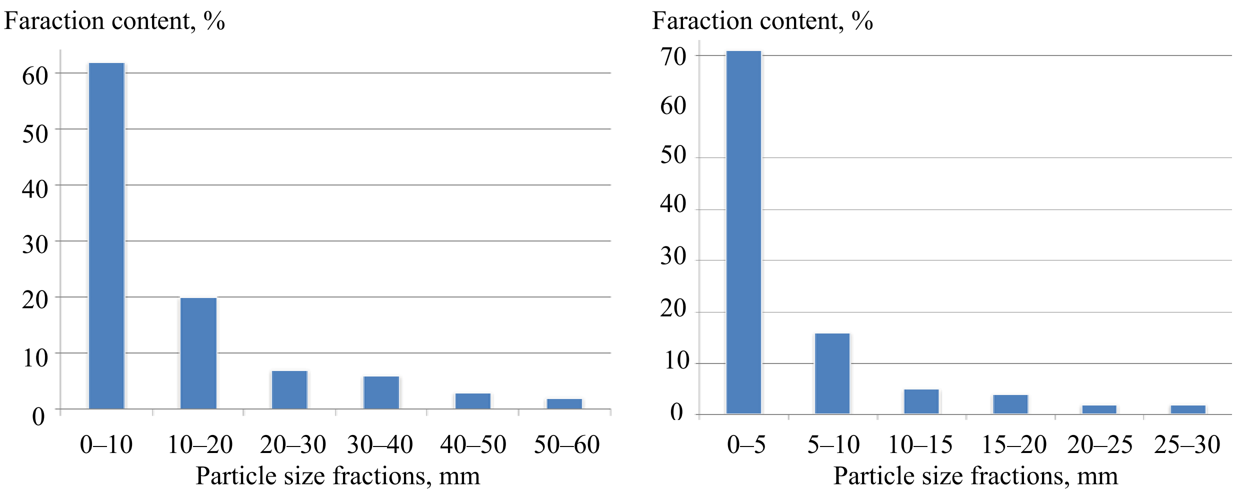
The original sludges were modified by adding a modifier to the paste materials. A 5% dilute sulfuric acid on the basis of 2% H_2SO_4 to absolutely dry sludge or water glass with module 2.9 were used as a modifier.

Experimental procedure. Ferriferous and calcic sludge N 1 (of OJSC "BSW" StPTs-1) according to XRD contains calcium sulfate in the form of $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 0.5H_2O$, and carbonate $CaCO_3$. Taking into account the fact that the sludge contains a significant amount of phosphorus, one can suppose that iron is presented in the sludge in the form of de hydroxophosphates $x Fe_2O_3 : y P_2O_5 : z H_2O$. Sludge N 2 formed by BTLP has a X-ray diffraction pattern characteristic for X-ray amorphous compounds. The content of iron compounds in terms of Fe_2O_3 in the sludge N 1 is 20–40 wt % which are in the amorphous state there is the calcium compounds in the form of CaO – 20–37 wt % and other metals, particularly zinc, copper, – 0.5–7.0 wt % nickel, manganese – 0.3–0.8 wt %. The sludge N 2 contains wt % up to 58% of iron compounds; 20% of zinc; 3% of chromium; 5% of copper in terms of their oxides.

Microscopic studies showed that these iron-containing sludges are characterized by polydisperse composition comprising particles and their agglomerates of various shapes with sizes ranging from fractions to tens of micrometers. For the test sludges some diagrams of the particle distribution depending on the size were constructed based on the results of the microscopic analysis (Fig. 1). The presence of particles of different size is a consequence of sludges complexity. The results showed that the sludge N 1 is dominated by particles of 0–10 µm, and the sludge N 2 – 0–5 µm. It's typically that average particle size of the sludge N 1 is a little bit larger than of the sludge N 2. It is associated with the content of crystalline compounds. They are calcium sulfate and calcium carbonate. The results of the investigation of settling velocity of solid phase and its volume according to the duration are shown in Fig. 2.

On each occasion the concentration of solids in the test suspensions was 5 wt %. The volume of iron and calcium sludge N 1 formed in the process of neutralizing of waste water by lime milk rapidly decreases in the process of settling. Within the hour its seal occurs and further mature of suspension does not affect the volume of a solid or liquid phase. Volume of the final sludging is 29%. High-speed settling of the sludge can be explained by phase composition and dispersion. As it was noted above this sludge consists of X-ray amorphous compounds of iron and other metals as $CaSO_4 \cdot 2H_2O$, $CaCO_3$ mainly with the size crystals about 4.7–7.1 mm which settle and free quickly. Normally the smaller X-ray amorphous particles of iron and other metals are precipitated very quickly in this case. It should be explained bythe influence of the salt environment (in particular as a result of the solubility of $CaSO_4 \cdot 2H_2O$ rendering the coagulating action. The settling of the solid phase of the sludge N 2 doesn't practically take place because of it contains the particles with the sizes of sols and therefore the settling caused by gravitational forces is very slow.

Modification of sludges by sulfuric acid and preparation of suspensions on their basis leads to some changes of technological characteristics of precipitation. It is evident from the results shown in Fig. 3.



a *b*

Fig. 1. Diagrams of particle size sludge distribution on fractions:
a – sludge N 1; *b* – sludge N 2

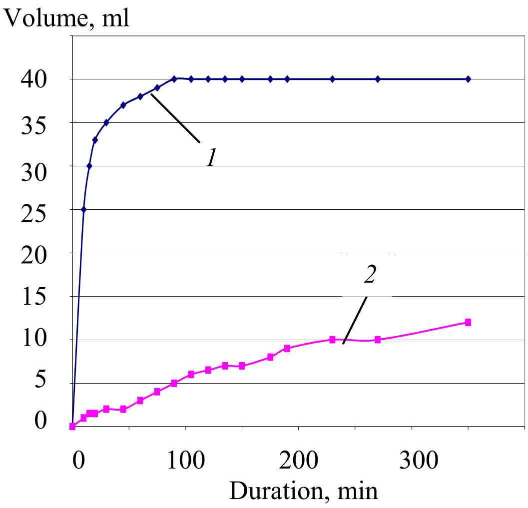


Fig. 2. The correspondence of volume of the clarified liquid phase in the suspensions of sludge to the duration of settling: *1* – sludge N 1; *2* – sludge N 2

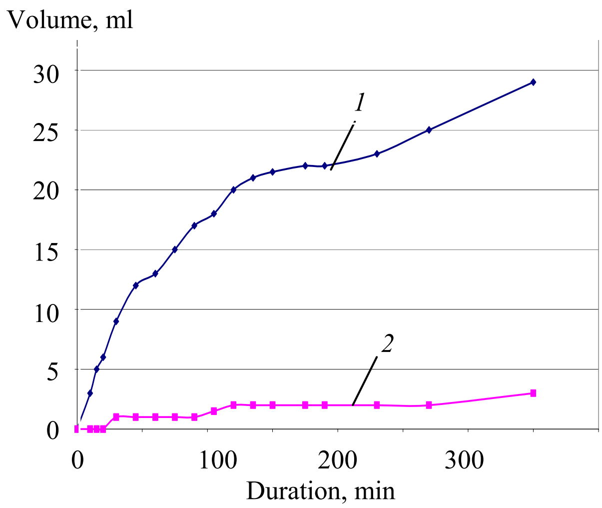


Fig. 3. The correspondence of volume of the clarified liquid phase in the suspensions of sludge modified H_2SO_4 to the duration of settling: *1* – sludge N 1; *2* – sludge N 2

The characteristic property of these suspensions is a lower capacity to settling of the dispersed phase (especially in the first few hours). It is eve dentally associated with the peptizing action of sulfuric acid. It results in the structuration and formation of stable free-dispersible system. The investigated sludges having the same moisture content have different viscosity. It indicates to the differences in mineral granulometric distribution.

The greatest ability to fluidity with the moisture content of 80 wt % is noted in electroplating sludge N 1 while the sludge N 2 does not have any fluidity. To improve the sludge fluidity silicate liquid glass with module 2.9 was used as a fluxing ingredient.

The ability of sludge to flow with the introduction of diluting agent was illustrated by the curve in Fig. 4.

According to the research at the flow of 0.9–1.0% of sodium silicate suspensions fluidity based on the sludge N 1 and 2 is 1.3 and 2.9°E, respectively.

Significant difference in fluidity of suspensions containing water glass can testify the fact that the particles of the solid phase of sludge have different surface activity to ion exchange and micelle formation. As you know, free-disperse systems including galvanic sludge are able to maintain a uniform distribution of the dispersed phase in terms of the dispersion medium and the stability of the distribution of the phases and consequently the aggregative stability.

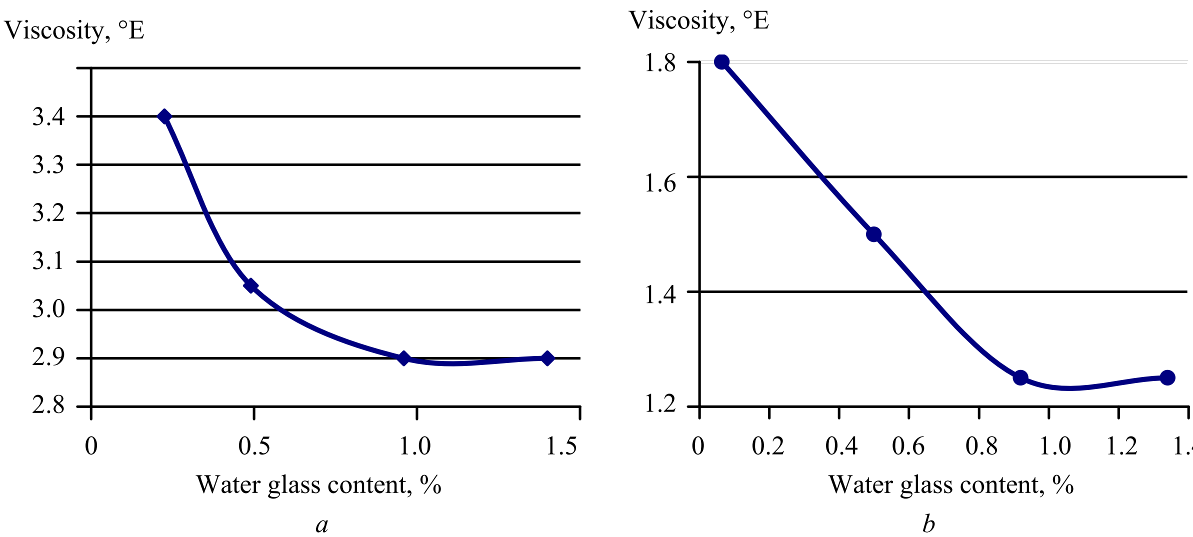


Fig. 4. Correspondence of viscosity of sludge suspension to the water glass content: *a* – sludge N 2; *b* – sludge N 1

Conclusion. It was found that the sludges formed in the process of the treatment of wastewaters in electroplating industry by reagent method has different rheological properties, dispersion and, therefore, sedimentation stability. This method is notable for the nature of the sedimentator. It was presented that the galvanic sludges formed in the process of the treatment of wastewaters by lime milk contain a crystalline phase in the form of calcium compounds with particles size of 10 μm. They precipitate and densify very quickly. Sludges formed in the process of the treatment of wastewaters by calcinated or caustic soda are free-dispersible, sedimentally stable systems where the size of the particles of the solid phase is at the level of the nanoparticles.

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