Conference Paper

Chemical Selection for Flocculation of the Sludges Produced During Lime Neutralization of Acidic Spent Pickling Solutions and Rinse Water from Steel Pipe Mill

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Abstract

Acidic spent pickling solutions and rinse water are produced during steel pipe acid pickling. They are usually neutralised with lime in a neutralisation plant and pumped in the form of a wet sludge to a landfill. This is one of the main environmental issues of Russian steel mills. The implementation of sludge treatment units, including equipment for sludge polymer conditioning and dewatering, is an import consideration when seeking to reduce the impact of steel mills on human health and the environment. The researches results of polymer conditioning of the aggressive wastewater sludges by flocculants are reflected in the paper. Sludge samples were obtained from the neutralisation plant of an Ural's steel pipe mill. Sludges of two types were investigated: the sludge which is formed in clarifiers during spent pickling solutions neutralization with lime and the sludge which is formed in clarifiers during rinse water neutralization with lime. During the work non-ionic, cationic, and anion flocculants Praestol® efficiency was estimated. The shortest time of water capillary suction from the flocculated sludge was accepted as efficiency criterion of flocculant processing. It was defined with use of the capillary suction timer Fann® and Whatman® 17 chromatographic paper. It is established that: non-ionic focculant Praestol® 2500 dose of 4–5 g/kg dry solids is effective for conditioning of the sludge produced during lime neutralization of acid spent pickling solutions; the anionic flocculant Praestol® 2540 dose of 1.5–2 g/kg dry solids is effective for conditioning of the sludge produced during lime neutralization of acid rinse water. The empirical response surfaces and the contour plots showing the relationship between capillary suction time and a dosage of flocculant and a charge density (% hydrolysis) of a flocculant were reveived.

Keywords: steel pipe mill, acid pickling, wastewater, sludges, flocculants, capillary suction time

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1. Introduction

The 21st century is called the flocculants century, and in some sense it is fair. They are irreplaceable at water and wastewater treatment, sludge conditioning — in any parts of various systems of water industry

Flocculants, promoting aggregations formation due to association of several particles through macromolecules of the adsorbed or chemically connected polymer, belong to high-molecular-weight polymers [1]. Flocculants promotes bridges formation between micro-flocs and macro-flocs forming.

All flocculants can conditionally be divided into three groups: natural high-molecular substances; inorganic polymeric substances; synthetic high-molecular substances. Chemistry development gives the chance to expand the third (main) group of flocculant practically in unlimited scales, that is one of the main factors of the ever-increasing demand for them.

Flocculants are successfully used for a long time in ore enrichment processes, where, perhaps, the widest practical experience is accumulated [2–5]. Here also should be mentioned selective flocculation — the most promising method of concentrating and enriching minerals, extracting particularly valuable substances from raw materials [6, 7]. Flocculants are used for cell suspension concentration [8], different concentrated solutions (syrups [9], brines [10]) treatment, etc.) In the works [11–16] flocculants receiving ways, the main properties and practical use are considered. It's should be noted that flocculants amount going on sale constantly grows, yet there are no signs of this process reduction (as well as interest in flocculants).

One of the main application areas of flocculants is industrial wastewater sludge conditioning [17, 18]. As for Sverdlovsk region an actual task is ferrous metallurgy enterprises negative impact on human health and the environment, we chose the research subject devoted to sludge processing, which is formed during metal surface chemical treatment aggressive wastewater purification.

2. Materials and Methods

2.1. Sludges characteristics

The sludges samples for experiments were obtained from a neutralisation plant of an Ural's steel pipe mill. The sludges were collected:

1. sludge A — the sludge, which was formed in clarifiers during spent pickling solutions neutralization by calcium hydroxide;

2. sludge B — the sludge, which was formed in clarifiers during rinse water neutralization by calcium hydroxide.

The properties of the sludge collected from an industrial wastewater treatment plant are listed in Table 1.

Table 1: Properties of raw sludges (author's own work).

Sludge	Concentration of dry solids (kg/m^3)	Density of sludge (kg/m^3)	Density of solids (kg/m^3)	pH
A	26	1024	2242	8.5
B	18	1011	2630	9

2.2. Used flocculants characteristics

For studied sludge processing the Praestol® flocculants were used.

The Praestol® flocculants are organic, synthetic, high-molecular flocculation means, made on polyacrylamide basis. The Praestol® flocculants are manufactured non-ionic type, anion type, and cationic type.

Non-ionic flocculants represent technically pure polyacrylamide. In water solution they show natural — non-ionic behavior. Anion flocculants are acrylamide copolymers with increasing acrylate shares, giving to polymers in water solution negative charges and by that anion active character. Cationic flocculants are acrylamide copolymers with increasing shares of cationic somonomers. Cationic groups, bought by them in polymer, possess in water solution positive charges.

Flocculants characteristics, by which the sludges A and B were conditioned, are given in the Table 2.

Table 2: Characteristics of flocculants (author's own work).

Flocculant	Type of charge	Charge density (%)	Molecular weight (g/mole)	Form of flocculant	Bulk density (kg/m^3)
Praestol® 650 BC	Cationic	20–50	$6 \,.\, 10^6$	Dry	570–670
Praestol® 2540	Anionic	20–50	$14 \,.\, 10^6$	Dry	600–750
Praestol® 2500	Non-ionic	–	$14 \,.\, 10^6$	Dry	600–750

The flocculants doses varied from 0 to 2.5 g/kg dry solids during the sludges processing, which is formed at rinse water neutralization, and from 0 to 10 g/kg dry solids during the sludge processing, which is formed at spent pickling solutions neutralization. The 25 mL sludge samples were conditioned with the 2.5 g/L flocculant solutions. The magnetic stirrer was used for mixing flocculant with the sludge samples. The mixing time was 15 s. Mixing intensity (the root mean square velocity gradient) was G = 150 s $^{-1}$.

2.3. Capillary suction time measurement

The flocculant type and doses for sludge conditioning were determined with using capillary suction time (CST) device, represented in Figure. 1. CST device (model 440) provided by FANN (Houston, Texas, USA).

The CST device allows to evaluate sludge technological properties, processed by flocculant or not, by CST measurement, during which sludge fluid phase (water) moves on chromatographic paper capillaries. The less CST, the better sludge water giving properties.

CST device consists of the following main elements:

1. cabinet — controls, batteries, and connection for test head (acrylic unit);
2. test head — sensor plate (on top) with pins and cable connection into the instrument cabinet and the sensor tray (bottom);
3. chromatographic paper;
4. funnel;
5. battery and battery eliminator.

The device test head consists of the sensor plate and sensor tray (Figure 2). On the sensor tray (bottom) chromatographic paper is put. On sensor plate (on top) two rings, to which sensors are attached, are applied. In the sensor plate the funnel, filled by the analyzed liquid sludge, is established vertically. By the contact of a sludge with chromatographic paper fluid phase from the sludge begins to move on paper capillaries. At passages liquid via the first sensor time report begins, at passages liquid via the second sensor time report stops. Time is measured to within the tenth fractions of a second. CST is sludge fluid phase movement time on chromatographic paper from the first to the second sensor.

Funnels for CST measurement have the contact zone diameters 1 and 1.8 cm. For a well filtered sludge the 1 cm contact zone diameter funnel is used, for a hardly filtered sludge — the 1.8 cm. As the studied sludge is hardly filtered, the funnel with 1.8 cm contact zone was used.

As chromatographic paper Whatman® 17 (Whatman Plc., Brentford, UK) was chosen, it is used for wastewater sludge CST definition [19].

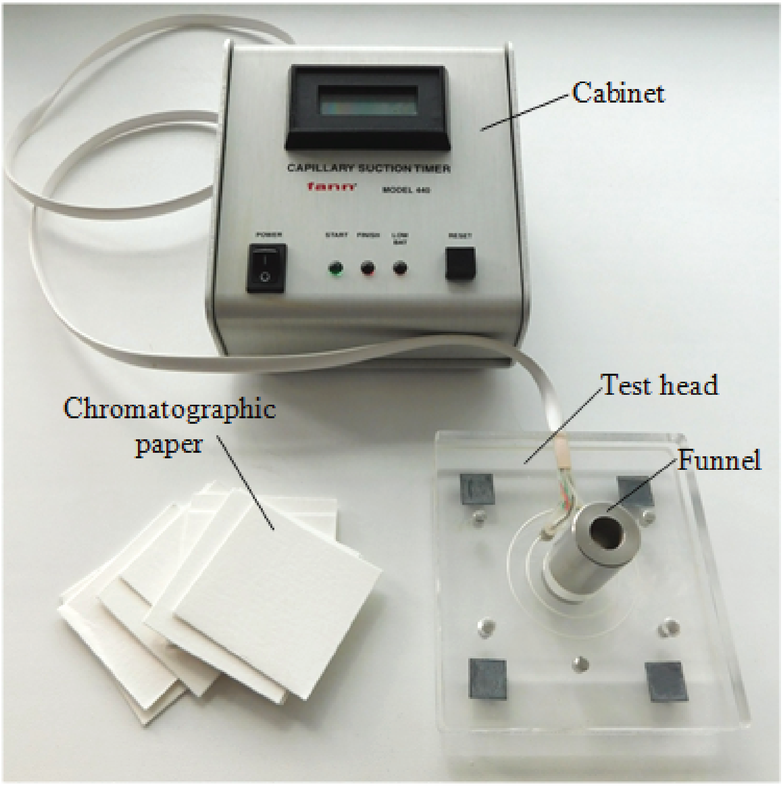

Figure 1: Capillary suction time device (author's own work).

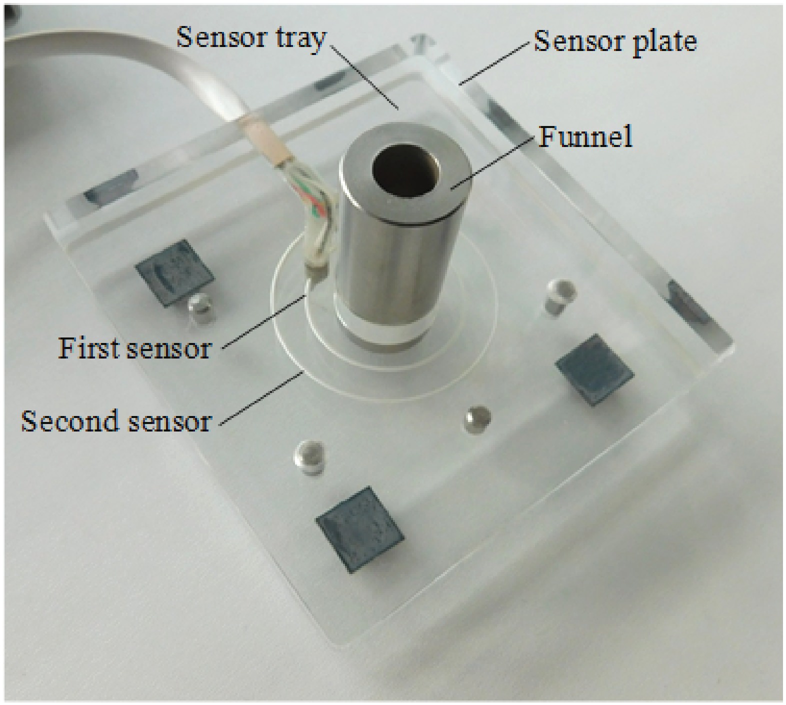

Figure 2: Test head (author's own work).

3. Results and Discussion

The sludges A and B, formed during lime neutralization of the aggressive wastewater from the processes of metal surface chemical treatment, represent a concentrated system containing mainly mineral particles. The characteristic feature of the sludges A and B is the colloidal structure of their volume individual elements due to the presence of iron hydroxides, nickel hydroxide, chromium hydroxide and hydroxides of other metals in the sludge. Water in the sludges A and B are in free and bound states, outside and inside colloidal structures. Bound water is mainly understood as water mechanically enclosed in colloidal structures and, to a lesser extent — water of hydrated shells of hydrophilic sediment particles.

Polymer conditioning of the sludges A and B with the properly selected flocculants will improve their water-yielding properties due to changes in the composition, structure and forms of water-solid phase particles.

We studied the effects of the flocculant dosage and the charge density (% hydrolysis) of the flocculant on the CST. The goal was to minimize the CST. The charge density of a flocculant is an important parameter affecting the adsorbtion of the flocculant.

Figures 3 and 4 show graphically relationship between CST and the dosage of flocculant and the charge density (% hydrolysis) of the flocculant.

Based on examination of fitted surface in Figure 3, it is clear that CST of the sludge A decreases as the dosage of flocculant increases up to the dose of 6 g/kg dry solids and the charge density (% hydrolysis) of the flocculant decreases. The lowest CST value of the sludge A achieved by using uncharged flocculant Praestol® 2500 (we assume that the charge density is zero) dose of 4–5 g/kg dry solids. With further flocculant dose increase the CST increases, this is explained by sludge stabilization due to flocculant excess in sludge liquid phase (after saturation of adsorption).

Based on examination of fitted surface in Figure 4, it is clear that CST of the sludge B decreases as the dosage of flocculant increases and the anionic charge density (% hydrolysis) of the flocculant increases. The lowest CST value of the sludge B achieved by using the Praestol® 2540 (the anionic charge density is 20–50 %) dose of 1.5–2 g/kg dry solids. With further flocculant dose increase the CST remains virtually unchanged. The effective dosage is lower for the charged flocculant Praestol® 2540 than for a corresponding uncharged flocculant Praestol® 2500. The advantage of using charged flocculants compared to uncharged flocculants is that they often exhibit a much stronger electrostatic affinity to surfaces in aqueous solution [20].

The sludge colloidal structure collapses during flocculant treatment. Large easily separable from water hydrophobic flocs are formed. At the same time there is bound

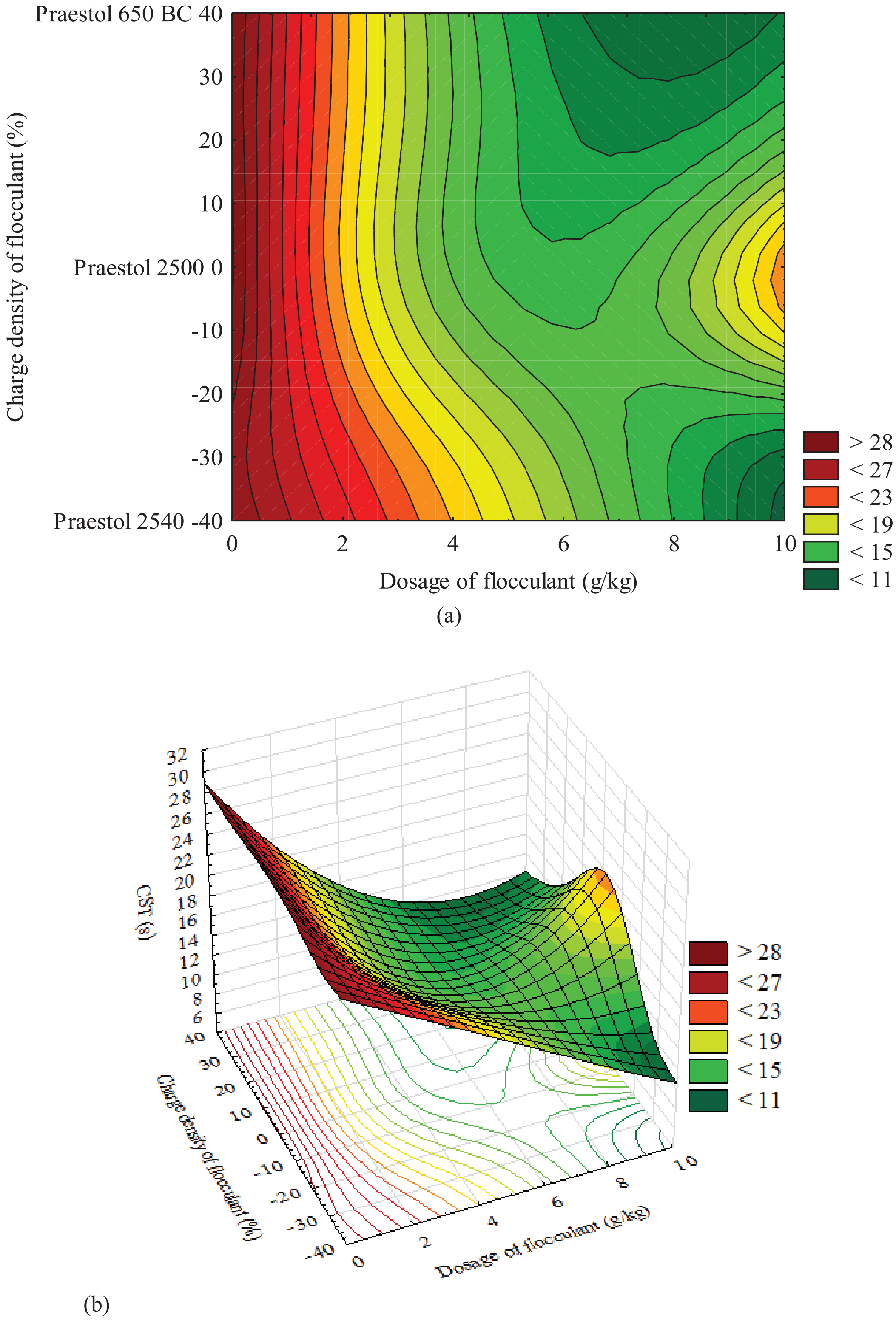

Figure 3: Contour Plot (a) and Response Surface Plot (b) of the CST value of the flocculated sludge A produced during neutralization of spent pickling solutions (author's own work).

water decrease in the sludge, the rate of capillary suction increases, and, accordingly, the CST decreases.

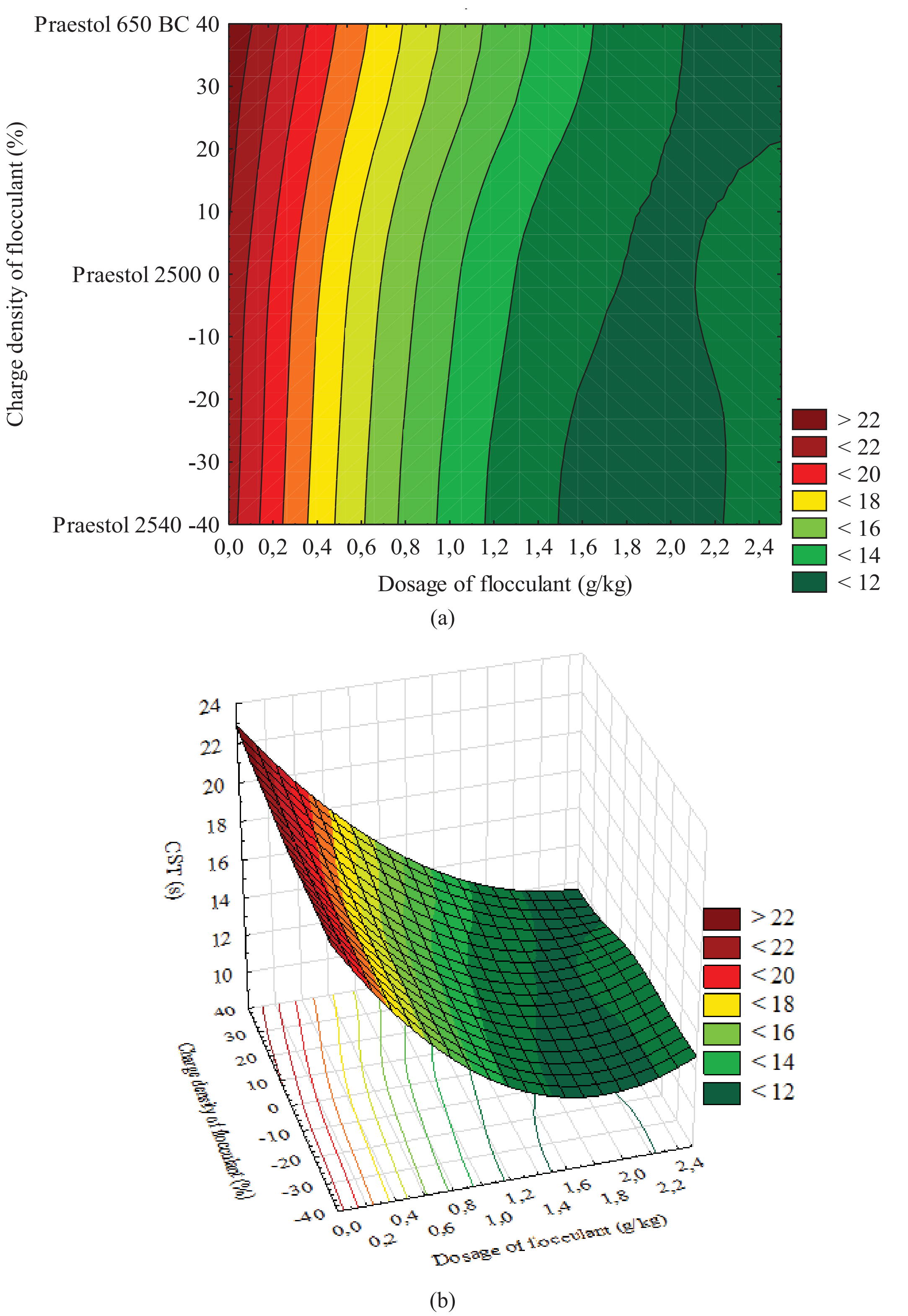

Figure 4: Contour Plot (a) and Response Surface Plot (b) of the CST value of the flocculated sludge B produced during neutralization of rinse water (author's own work).

Thus, for the sludge A and B the anionic flocculant Praestol® 2540 and non-ionic flocculant Praestol® 2500 are effective. It can be concluded that solid phase of the sludges A and B is positively charged. While the sludge A gives water worse than the sludge B. To the sludge A conditioning two times more flocculant is consumed.

4. Conclusion

The non-ionic focculant Praestol® 2500 dose of 4–5 g/kg dry solids is effective for conditioning of the sludge produced during lime neutralization of spent pickling solutions. The anionic flocculant Praestol® 2540 dose of 1.5–2 g/kg dry solids is effective for conditioning of the sludge produced during lime neutralization of rinse water. Necessity of using flocculants different types with different dosages for sludge conditioning justifies necessity of independent technological processing lines organization at sludge treatment facility of a neutralisation plant. In addition, this explains the reason of low efficiency of the aggressive wastewater neutralizations plants of the Russian industrial enterprises, where treatment of these sludge is carried out jointly. As a result of joint processing of such sludges, a mixed composition hard-to-filter sludge is formed, which is almost impossible to dewatered to acceptable sludge cake moisture content.

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