Modern technology of treatment and disposal of chromium- and sulfide-bearing wastes

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Abstract. There were discovered the main sources of chromium- and sulfide-bearing sludges as well as their influence on a man and the environment. Requirements to the environmental compliance of leather industry have grown all over the world. There arises a need for creating new resource-saving technological schemes of leather industry chromium- and sulfide-bearing wastes treatment and disposal in order to return the valuable components into production. The obtained experimental results allowed to make a conclusion that for transforming into a concentrate any chromium- and sulfide-bearing sludges can be appropriate in the natural condition, after drying, after freezing and after preliminary processing by flocculants and freezing. The presented technology of chromium- and sulfide-bearing sludges neutralization and disposal will allow to change over to the almost non-waste leather-making what complies with the modern requirements of environmental protection.

1. Introduction

Treatment of leather industry wastes is an integral part of the industrial complex and it allows to solve or defuse ecological and economic problems of the industry sector enterprises. This treatment assumes greater importance due to the strengthening of requirements for the ecological state of leather-making enterprises, deficit of hides and increase of their cost.

Modern requirements to the environmental protection call for the production of a sanitary safe product, qualitative composition, and properties of which ensure the possibility of its disposal, burial, and recycling in an environmentally sound manner. The composition of sludges, their quantity, moisture and volume weight of industrial wastewater vary widely [1].

Depending on the level of wastewater pollution and methods of treatment, the number of sludges can make up from 0.8 till 30 % of water volume and in case of increased pollution, it can be over 30 % of the wastewater volume [2]. Except for low-toxic iron and calcium compounds, in the composition of slag, there can be the compounds of such heavy metals like chromium, copper, lead, cadmium, manganese, and nickel [3]. In metallurgy, there is formed the ferrochromium slag which contains in its composition: calcium oxide 48-54.9 %, silicon oxide 18-22 %, magnesium oxide 7.8-11 %, chromium oxide 2-7.7 % [4].

In the leather industry, sulfide-bearing wastewater is formed at the stage of soaking, washing and liming. Solutions used for these operations contain sodium sulfide, surface-active substances,
ammonium sulfate, and calcium hydroxide. The volume of sulfide-bearing wastewater makes up 185 m3/day, and the concentration of sulfides thereafter averaging is 3.17 g/dm³ for sodium sulfide [5].

In view of the above, the concentration of chromium in wastes coming to the manufacturing enterprise treatment plant makes up the amount from 20 to 50 mg/dm³, and the concentration of chromium in wastes coming to a biological treatment plant varies within the limits of 15-25 mg/dm³. Herewith, as in the case of sulfide wastes, the seasonal change of chromium concentration has been observed – an increase in summer and decrease in winter months [6]:

- in winter, the concentration of sulfides and chromium (III) achieves the lowest values (~ 100 mg/dm³ for sulfides, ~ 33 mg/dm³ for chromium);
- in summer, the concentration of sulfides and chromium (III) in wastewater achieves the highest values (~ 110-120 mg/dm³ for sulfides, ~ 45 mg/dm³ for chromium);
- in fall, the concentration of sulfides and chromium (III) in wastewater decreases (~ 100 mg/dm³ for sulfides, ~ 35 mg/dm³ for chromium);
- in spring, the concentration of sulfides and chromium (III) increases (~ 120 mg/dm³ for sulfides, ~ 46 mg/dm³ for chromium);
- the seasonal component makes the greatest contribution to the variety of the concentration of sulfides (55-64%) and chromium (III) (69-76%).

The obtained data shows that in the leather enterprises wastewater, there is a significant quantity of chromium. Moreover, in the course of the ordinary organization of the process, great losses of valuable reagent take place, which in accordance with the most modest calculations make up 158 t/year for Cr₂O₃ at Sterlitamak Leather Plant. The solution of a problem of extracting chromium from the sludges of wastewater and its recycling in the technological process is urgent.

At present, chromium wastes are combined with the all-factory wastes whereupon chromium concentration decreases until the amount of 30-50 mg/dm³ [6]. Assuming that in the course of production the world leather industry uses 4.8 million tons of large hides at the average water consumption of 65 cubic meters per 1 ton of raw material, we will get the total amount of water consumed of 300 million cubic meters, and taking into consideration the amount of small animal hides, this amount will increase to 450 million cubic meters. 60% or 270 million cubic meters out of them fall on the preliminary processes and 40% or 180 million cubic meters fall on pre-tanning, proper tanning and dye and greasing processes [7]. Problems occurring in the process of treatment of wastewater of the leather industry enterprises are directly connected with the insufficient level of technology and low usage of chemical compounds used in leather-making from the modern point of view. According to the information of Leder und Haute Markt magazine in the course of chromium leather manufacture used for the upper parts of shoes, 47% of skin collagen - a valuable protein product - go into wastes and as for the chromium compounds, just 48% of them are used. The low degree of chromium usage is connected with not only the worsening ecological situation at the leather enterprises. The loss of such amount of chromium with the spent solutions should not be neglected due to its high cost - 800-1000 USD per ton. The leather industry consumes about 65 thousand tons of chromium compounds annually. According to BLMRA (British Leather Manufacturers’ Research Association), 20 thousand tons out of this amount go into the product and the rest is lost with the wastes. Wherein 25 thousand tons of them are drained with the spent solutions [8].

Influencing the composition and properties of natural waters, the chromium compounds lead to nonconvertible changes in the organisms of plants and animals and through them influence the whole biosphere [9]. On the other hand, some countries import high volumes of chromium compounds for the production activity [10].

Nowadays chromium-bearing wastes are most often placed in the landfills [11]. For the sulfide-bearing wastes of the leather industry, there are methods of disposal with elemental sulfur, hydrogen sulfide obtainment [12], as well as by means of acid hydrolysis with the further protein texturization in the presence of modifying additive [13].
We consider that the disposal of chromium- and sulfide-bearing wastes with the repeated use of the obtained products of the leather processing technology is a perspective direction.

2. Methods
Chromium- and sulfide-bearing wastes were treated by the diluted sulfuric acid in order to obtain the concentrates necessary for the leather treatment.

The acid affects the chromium- and sulfide-bearing wastes, which are formed at a treatment plant in different states such as initial sludge, sludge after drying, dewatered sludge (cake), sludge after storage area and freezing, sludge with the flocculant added.

For the research and in order to obtain the sludge, there was simulated a model of the chromium-bearing waste of the leather production which contains chromium sulfate (III). The concentration of chromium (III) content in a solution in the amount of 4 g/dm³ was chosen assuming the worst conditions of the leather production wastewater coming, and of the solution of ferric sulfate (III) with the concentration of iron (III) in the amount of 10 g/dm³.

Hereafter the sludge was directed for the determination of the specific resistance to filtration, the moisture, and density.

Drying and freezing were used for treating and conditioning of the sludge as if the sludge was placed in the open storage areas.

For determination of the sludge density, there were taken 160 ml of the sludge of 172.863 g weight. The density of the sludge made up 1.08 g/cm³.

After that, the chromium-bearing sludge and cake were left in a drying chamber for 24 hours at the temperature of 105°C. The moisture of the sludge made up 94.8 %, cake 78%, specific resistance of the sludge - 8.86•10¹⁰ cm/g.

The next stage is the series of experiments for determination of the necessary quantity of sulfuric acid in order to create the concentrate.

As a result of the research, the necessary quantity of sulfuric acid per gram of the treated sample was determined; so for the chromium-bearing sludge, this amount is 0.46 ml/g, for the dried chromium-bearing sludge, it is 39.07 ml/g, for the cake of the chromium-bearing sludge, it is 23.26 ml/g, for the frozen chromium-bearing sludge, it is 0.94 ml/g, for the frozen chromium-bearing sludge with the flocculant added, it is 1.97 ml/g.

The analogous researches were carried out for the sulfide-bearing sludge. For the research, there was simulated the model of the sulfide waste containing sodium sulfide. The concentration of the solution in the amount of 6.5 g/dm³ was chosen assuming the worst conditions of the leather production wastewater coming.

The density of the sludge made up 1.11 g/cm³, specific resistance - 34.7•10¹⁰ cm/g. The sludge moisture made up 96.3 %, moisture of the cake  91.7%.

The necessary quantity of sulfuric acid per gram of the treated sample was determined; so for the sulfide-bearing sludge, this amount is 0.29 ml/g, for the dried sulfide-bearing sludge, it is 13.38 ml/g, for the cake of the sulfide-bearing sludge, it is 33.15 ml/g, for the frozen sulfide-bearing sludge, it is 0.61 ml/g, for the frozen sulfide-bearing sludge with the flocculant added, it is 1.18 ml/g.

3. Results
The obtained experimental results allowed to make a conclusion that for transforming into a concentrate any chromium- and sulfide-bearing sludges can be appropriate in the natural condition, after drying, after freezing and after preliminary processing by flocculants and freezing.

In the suggested technology, there were used reactors, ceramic filters, belt thickeners, and cylindrical mesh filters. It is also suggested to organize two lines of water treatment and sludge refining and unite by flows for the local usage. Unifying the flows is necessary in case of using the treatment equipment just for one type of flow chromium or sulfide in case of maximum productivity approximately twofold. The local work consists in the possible simultaneous neutralization of chromium- and sulfide-bearing wastes. For the treatment of wastes by this technology, it is possible to
organize the one unit for refining and treating the sludges by sulfuric acid. As a result, we obtain the concentrated solution, which later can be used for obtaining the reagents for the leather production.

The suggested technology presupposes the use of equipment of the Russian production [16,17], for example, a gravity belt thickener a continuous -action device working on the principle of filtering under the influence of gravity forces.

While choosing the technology of sludge accumulation in the areas, there are accepted the areas of storage or freezing. According to [18], the gullies, the depleted pits or the special areas organized on the natural foundation not less than 2 meters deep and banked up by soil can be used as an accumulator of sludges. The calculated period of the sludge coming to an accumulator should be considered as not less than five years.

4. Conclusion

The developed technology is recommended for the reconstruction and erection of new treatment plants. Due to the different solutions, there can be chosen an optimal variant for the concrete production with an account of local conditions. For this, it is necessary to select the most appropriate modern facilities and carry out the engineering and economical comparison, and an ecological assessment. An advantage of this technology is the possibility of obtaining a by-product concentrates out of the chromium- and sulfide-bearing sludges in the natural state, after being dried and frozen in the natural conditions. The application of the technology of neutralization and disposal of the chromium- and sulfide-bearing sludges will allow passing to almost waste-free production process at the leather-making enterprise what complies with the modern requirements of environment protection [19].

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