Use of waste sludges from chemical enterprises as secondary metallurgical raw materials

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Abstract. The characteristics of dump zinc-containing sludges from chemical enterprises producing artificial fibers are given. The analysis of quantitative, chemical and phase compositions of sludge fields is carried out. The possibility of pyro- and gyrometallurgical processing of these materials was established. The need for preliminary preparation of sludge for processing is shown. Technological recommendations for obtaining marketable sulfate and zinc oxide are formulated.

1. Introduction
Zinc belongs to the group of major non-ferrous metals in terms of production and consumption. In 2018, its production amounted to more than 13 million tonnes, second only to aluminum and copper. At the same time, zinc consumption is growing steadily from year to year. In this regard, the amount of zinc-containing waste is proportionally increasing and inevitably there are questions about their disposal. The domestic zinc industry has now mastered the processes of processing rich wastes with zinc content of more than 30%, and poorer materials are practically not used due to the high costs of their delivery and processing [1].

However, the increase in the amount of accumulated waste, the aggravation of environmental issues related to warehousing and storage, and toughening of environmental legislation brings the task of recycling to the fore. Rather high prices for basic non-ferrous metals in the world market make solution of this problem economically attractive. The initiator of active work in this direction was the flagship of the Russian zinc industry – Chelyabinsk Zinc Plant. Issues of using secondary raw materials are on the agenda due to an acute shortage of zinc concentrates conditioned by the inaccessibility of domestic raw materials associated with the redistribution of property in the extractive industries, the increased cost of zinc in the world market and logistics costs because of the rise of transportation tariffs.

As part of the “Raw Material” plant program, efforts were made to expand the ore base of zinc concentrates, the characteristics and reserves of secondary zinc represented by the waste from ferrous and non-ferrous metallurgy, as well as a number of chemical plants were attested. Research and design work was carried out to introduce new and modernize existing technological processes for recycling. Employees and students of Siberian State Industrial University were involved in these works. The studies were carried out jointly with the engineering and technical center of Chelyabinsk Zinc Plant.
2. Attestation of dump zinc-containing sludges from enterprises producing artificial fibers

To develop an effective technology for extracting zinc from waste, first of all, it is necessary to attest these materials in terms of quantity and composition. The paper summarizes information on the types, amount and chemical composition of zinc-containing sludge from wastewater treatment and waste technological solutions at domestic enterprises for the production of artificial fibers.

A comprehensive attestation of reserves, chemical and mineralogical composition of sludge from enterprises producing artificial fibers in the West Siberian region (LLC “Sibvolokno”, LLC “Krasnoyarskiye Volokna”) were carried out. The total amount of accumulated zinc-containing materials is estimated at about 1.5 million tonnes (up to 200 thousand tonnes of zinc). Table 1 summarizes information from available literature on the amount of zinc-containing sludges from various chemical plants with similar chemical and material composition [2]. The amount of zinc in the sludge is comparable to the annual programs of large zinc plants.

| Enterprises                              | Amount of zinc in the sludges, thousand tonnes | The zinc content in the sludge, % |
|------------------------------------------|-----------------------------------------------|----------------------------------|
| LLC “Sibvolokno”, Zelenogorsk, Krasnoyarsk Territory | 25.0                                         | 18.0-42.0                        |
| LLC “Krasnoyarskiye Volokna”, Krasnoyarsk                                   | 20.0                                         | 10.0-22.0                        |
| LLC “Balakovo Fiber Materials Plant”, Balakovo, Saratov Region             | 103.0                                        | 13.0-24.0                        |
| OJSC “SvetlogorskKhimvolokno”, Svetlogorsk, Republic of Belarus             | 24.0                                         | 34.0-42.0                        |
| PO “Khimvolokno”, Kalinin                                                      | 15.0                                         | 9.0-12.0                         |
| NPO “Khimvolokno, Barnaul                                                      | 2.0                                          | 24.0-26.0                        |
| AO “Azot”, Kemerovo                                                            | 0.8                                          | 24.0-34.0                        |

Zinc-containing sludge is formed during the production of artificial fibers using technology of zinc sulfate to form fibers through spinning jets. Precipitation bath is an aqueous solution containing sulfuric acid, zinc sulfate and sodium sulfate. The jets leaving the die are deposited (coagulated) due to the formation of zinc – xanthate bonds and the desolvating effect of electrolytes.

The waste solution is neutralized with soda ash or lime milk. As a result, a suspension of zinc carbonate is formed, which is sent to the sump. The precipitate is a pasty, slightly sticky powder of dirty gray color, insoluble in water [3].

According to the technical reports of the enterprises, it was found that the total amount of zinc in the sludge damps of “Krasnoyarskiye Voloknu” and “Sibvolokna” is about 20,000 and 25,000 tonnes of zinc, respectively, with an average zinc content of 16 to 30%. To certify the chemical, particle size and phase composition of the sludge, samples were taken from various places of the dumps using steel rods: along the perimeter of the dumps in the warm season, from the surface in winter. The depth of sampling ranged from 0.3 to 4 m.

It was found that the color of the samples depends on the content of the main impurities and varies from light gray to light brown or brown. In all samples, cellulose fiber residues are present that significantly increase the water-holding capacity of the sludge. The material is a clay-like mass with a moisture content of 40 to 80%. The particle size of the material is in the range of 0.1 – 2.5 mm. The bulk density of the samples is in the range of 0.87 – 1.25 g/cm³, and the density (true) is 1.60 – 1.68 g/cm³ [4].

The results of the samples chemical analysis are shown in table 2. For comparison, the compositions of zinc-containing sludges from the production of artificial fibers at Balakovo Fiber Materials Plant and SvetlogorskKhimvolokno (Republic of Belarus) attested in the chemical laboratory of the Chelyabinsk Zinc Plant are shown.
The analysis of the chemical and phase composition of the sludge shows that zinc in them is represented by carbonates, sulfates and sulfides. The main ballast impurities are calcium and silicon oxides. There is a large scatter of data on the chemical composition of sludge even within the same enterprise, which is determined both by changes in the parameters of the technological regimes of enterprises, and by the conditions of waste storage.

The total zinc content in the materials in question varies between 11–47%, calcium oxide – 2–10%, silicon oxide – 1–11%. The presence of sulfide sulfur in the samples of sludge, reaching, in some cases, 2%, was confirmed. It should be noted that there are residues of cellulose fiber in the sludge and, in some cases, traces of organic impurities that negatively affect the processes of direct leaching of sludge and filtering products. The moisture content of sludge in sludge collectors is 70–90%, after natural drying in air it decreases to 30–40%.

Despite the similarity of the technologies for producing synthetic fibers and wastewater treatment at these enterprises, the zinc content and mineralogical composition of the samples taken are significantly different. So, in the samples of sludge from LLC “Krasnoyarskii Volokha”, the zinc content is significantly lower than in samples taken at LLC “Sibvolokno”. In addition, the content of impurities in the first case is much higher – most likely this is determined by the fact that wastewater from all adjacent industries, including household ones, was directed to the sludge collectors. The high zinc content in the sludge of the OJSC “SvetlogorskKhimvolokno” is explained by the use of caustic soda solution to neutralize acidic effluents instead of lime milk at the other compared enterprises.

### 3. Features of zinc-containing sludge processing

A sufficiently high zinc content, phase composition and insignificant content of “critical” impurities make it possible to process these materials at existing zinc production facilities. Experience in the processing of sludge confirms the effectiveness of the Waelz process for these purposes [5]. The cost-effective zinc content in the sludge, in this case, should exceed 14%.

Due to the existing geographical structure of existing zinc plants, the distance to the nearest enterprises is more than 2000 km, which does not allow for a positive profitability of sludge delivery and zinc extraction because of the high logistics costs even at relatively high prices for zinc, currently exceeding $ 2000 per tonne. This fact necessitates the development of mobile sludge processing technologies in place.

### Table 2. The chemical composition of zinc-containing sludges from enterprises of artificial fibers.

| Component          | Krasnoyarsk | Zelenogorsk | Balakovo | Svetlogorsk |
|--------------------|-------------|-------------|----------|-------------|
| Zinc total         | 10.8 - 22.3 | 14.2 - 29.6 | 21.2     | 46.7        |
| Zinc soluble       | n/f         | 18.6        | 13.6     | 45.7        |
| Zinc water-soluble | n/f         | 0.33        | 0.12     | 0.36        |
| Iron               | 0.80 - 1.65 | 1.92 – 2.70 | 1.5      | 1.55        |
| Lead               | 0.029       | 0.21        | 0.041    | 0.13        |
| Cadmium            | n/f         | 0.0004      | 0.005    | 0.0033      |
| Copper             | 0.022       | 0.009       | 0.011    | 0.011       |
| Nickel             | n/f         | 0.012       | 0.009    | 0.011       |
| Cobalt             | n/f         | 0.004       | 0.0031   | 0.0023      |
| Tin                | n/f         | 0.023       | 0.041    | n/f         |
| Chlorine           | n/f         | 0.071       | n/f      | 0.028       |
| Fluorine           | n/f         | 0.044       | n/f      | 0.005       |
| Aluminum           | 0.95        | 3.05        | n/f      | n/f         |
| Arsenic            | n/f         | 0.007       | 0.0026   | 0.001       |
| Antimony           | n/f         | 0.0025      | 0.0018   | 0.0048      |
| Silica             | 0.5         | 7.21        | 11.2     | 10.97       |
| Calcium oxide      | n/f         | 1.73        | 10.3     | 0.19        |
| Sulfur total       | n/f         | 16.27       | 16.9     | 1.76        |
| Magnesium oxide    | n/f         | N/f         | 0.79     | 0.24        |
Worthy of attention is the proposal for the processing of materials similar in chemical composition according to the standard scheme of carbothermal sludge recovery with coke or coal in a rotary tube furnace for expanded clay firing [6]. A significant reduction in capital costs is achieved through the use of standard equipment, and a high concentration of zinc in the resulting Waelz oxide (more than 50%) makes the processing process cost-effective. The disadvantages of the technology under consideration include the need for a bulky exhaust gas cooling system and capture of Waelz oxide, as well as high professional requirements for the personnel serving the process.

Figure 2 shows one of the possible instrumentation-technological schemes of hydrometallurgical processing of viscose slimes [7]. Direct leaching of sludge shows a low extraction of zinc, accompanied by a breakdown in the regular process. It is connected with the presence of carbonates and organic impurities in these materials, due to the presence of residues of viscose fiber and waste products of the existing biocenosis in the area where sludge collectors are located. Thus, to remove the organic component in the materials under study, it is recommended that the technological stage of oxidative burning (calcination) of sludge be introduced.

Figure 1. The hardware setup for processing viscose slurries: 1 – screw wet sludge feeder, 2 – dryer drum, 3 – ball mill, 4 – rotary kiln, 5 – chilled cinder, 6 – leach tank, 7 – tank of sulfuric acid, 8 – dispenser of sulfuric acid, 9,18,26 – filter presses, 10,19 – storage tank for solution, 11,14,22,28 – containers for cakes, 12,27 – tank for industrial water, 13 – calcining drum of plaster stone, 15 – precipitator of zinc concentrate, 16 – reactor for the preparation of soda solution, 17 – dispenser of soda solution, 22 – drying drum for zinc concentrate 23 – alkali regeneration reactor, 24 – reactor preparing lime milk, 25 – doser of milk of lime, 29 – cyclone, 30 – electric precipitator, 31 – induced draft fan, 32 – pipe.

4. Conclusion
Taking into account the specifics of the location of considered chemical enterprises, the existing on-site infrastructure, human resources and the consumption environment of possible products as the basic technology for the processing of zinc-containing sludge, in our opinion, it is currently most appropriate to consider the hydrometallurgical scheme for the extraction of zinc in the form of zinc sulfate or zinc oxide. Application of such processes makes it possible to use high-performance
standard equipment that provides high technological performance and cheap, non-deficient leaching reagents, such as sulfuric acid. High mobility, adjustability and adjustment of leaching processes, cleaning solutions and isolation of finished products provide high quality materials at low cost.

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