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# Production of chromium concentrate from press-filtration residue by means of heat treatment

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# Одержання концентрату хрому з прес-фільтраційного залишку за допомогою термічної обробки

***Abstract.*** *The production of leather goods is an important industry that generates significant amounts of waste, including solid residues containing chromium compounds. Solid residues of leather production containing chromium are a valuable source for the production of chromium alloys, in particular chromium-based alloys used in metallurgy, as well as in various industries to create stainless steels and corrosion-resistant materials. The goal is to integrate the process of industrial waste recycling into production, which will reduce not only the environmental footprint but also create materials with high technological properties for further use in various industries. The methodology for producing chromium alloys from the solid residue of leather goods production is a complex and multi-stage process that includes preparation, heat treatment, chromium recovery, alloy manufacturing, and waste disposal. This approach not only reduces the environmental footprint, but also allows for the efficient use of secondary resources to produce high-quality metals and alloys. As a result of such production, significant environmental and economic benefits can be achieved, which will not only reduce costs but also ensure sustainable industrial development with minimal environmental impact. The scientific novelty of this methodology is the integration of modern technologies for processing leather waste to produce high-quality metal alloys that meet the requirements of modern industrial development. The practical significance of this method for the production of chromium alloys from the solid residue of leather products production is to save natural resources, improve the environmental situation, increase economic efficiency and promote sustainable development of both the metallurgical and leather industries. This allows us to make a significant contribution to sustainable economic growth with minimal environmental impact.*
***Key words:*** *filter cake, heat treatment, diffractography, chromium oxide, halite.*

***Анотація.*** *Виробництво шкіряних виробів є важливою галуззю промисловості, що супроводжується утворенням значних обсягів відходів, зокрема твердої фракції, яка включає залишки, що містять хромові сполуки. Тверді залишки виробництва шкіри, що містять хром, є цінним джерелом для одержання хромових сплавів, зокрема сплавів на основі хрому, які використовуються в металургії, а також в різних галузях для створення нержавіючих сталей та корозійностійких матеріалів. Мета роботи полягає в інтеграції процесу переробки промислових відходів у виробництво, що дозволить знизити не тільки екологічний слід, а також одночасно створювати матеріали з високими технологічними властивостями для подальшого використання в різних галузях. Методика виробництва сплавів хрому з твердого залишку виробництва шкіряних виробів є складним і багатоступеневим процесом, що включає підготовку, термічну обробку, відновлення хрому, виготовлення сплавів та утилізацію відходів. В результаті такого підходу можна не лише зменшити екологічне навантаження на навколишнє середовище, а й ефективно використовувати вторинні ресурси для виробництва високоякісних металів і сплавів. В результаті такого виробництва можна досягнути значних екологічних та економічних переваг, що дозволить не лише знижувати витрати, а й забезпечувати сталий розвиток промисловості з мінімальним впливом на навколишнє середовище. Наукова новизна даної методики полягає в інтеграції сучасних технологій переробки шкіряних відходів для виробництва високоякісних металевих сплавів, що відповідають вимогам сучасного розвитку промисловості. Практична значущість даного методу виробництва сплавів хрому з твердого залишку виробництва шкіряних виробів полягає в економії природних ресурсів, покращенні екологічної ситуації, підвищенні економічної ефективності та сприянні сталому розвитку як металургійної, так і шкіряної промисловості. Це дозволяє зробити значний внесок у забезпечення сталого економічного росту з мінімальним впливом на довкілля.*
***Ключові слова:*** *фільтрокек, термічна обробка, дифрактографія, оксид хрому, галіт.*

**Introduction.** Chromium is an important metal used to make alloys that have high corrosion resistance, strength and heat resistance. The most common applications for chromium alloys are in the steel, chemical, automotive and aerospace industries. Since chromium is a scarce metal, the production of chromium alloys containing waste from other industries, such as leather goods, is becoming a promising area in metallurgy. Recycling of leather waste, especially those containing chromium, is an important issue for the leather industry, as improper waste management can lead to serious environmental pollution. Waste from leather production includes leather residues, trimmings, leather scraps, as well as waste containing

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chromium compounds (as part of the tanning process), which can be toxic. Therefore, the development and implementation of efficient recycling methods is not only economically important, but also environmentally necessary.

**Literature review and problem statement.** The problem of utilization of chromium-containing leather goods production waste is one of the most pressing in the world. Taking into account the toxicity of chromium compounds and their ability to accumulate in ecosystems, it is necessary to develop effective and economically feasible methods for processing such waste [1], [2]. The main problems include the imperfection of existing technologies, environmental risks, economic constraints, and the need to develop innovative technologies.

The production of chromium alloys from solid tannery waste is based on the utilization of chromium components contained in tannery waste, such as chrome-plated leather trimmings or sludge from incineration. The main stages of the process include: tanning of leather waste, which involves fixing the protein structure of collagen to prevent decay and provide strength and elasticity, and obtaining filter cake after tanning, which is a dense precipitate consisting mainly of insoluble chromium complexes associated with organic residues. This precipitate can accumulate in sludge or be present as residues on the processed materials. Filter cake is characterized by a high content of Cr(III) in the form of oxides or coordination compounds, which makes it a potential raw material for further chromium recovery in production. To isolate filter cake from leather waste, mechanical methods (filtration or centrifugation) are used to separate the dense precipitate from the liquid phase containing dissolved chromium compounds. The resulting precipitate (filter cake) can be subjected to additional heat treatment (e.g., drying) to remove residual moisture and reduce organic impurities. This improves the quality of the filter cake, which contains a high percentage of Cr(III) in the form of oxides. Pure filter cake can serve as a valuable raw material for further chromium recovery, for example, it can be used to produce high-carbon ferrochromium alloys or as a component for the manufacture of other chemicals used in the tanning of new raw materials. Data on similar technologies for extracting chromium from leather waste confirm the effectiveness of thermal and chemical methods for producing filter cake [3]. Thus, the process of producing filter cake includes the preparation of waste after tanning, separation of dense precipitate and its further processing to obtain a product that can be effectively used for chromium processing and alloy production.

**Objective.** To obtain a powder, which is considered to be a chromium concentrate (yield by weight 15-18%), from press-filtration residue (filter cake) by means of heat treatment.

**Methods.** To evaluate the effectiveness of the developed technological process in terms of the yield of 8% chromium oxide by weight after firing and obtaining chromium concentrate in the form of a finely dispersed powder by heat treatment.

**Results.** The production of chromium alloys from the solid residue of leather goods production is an important component of environmentally friendly and efficient waste management in modern metallurgy. The residues generated during leather processing, particularly after tanning, contain a significant amount of chromium in the form of various chromium compounds that require processing to reduce their toxicity and efficient use in industrial production. Recycling this waste to make chromium alloys not only reduces the negative impact on the environment, but also creates additional economic opportunities, as the resulting chromium compounds can be used in metallurgy, including for the production of stainless steel.

The first stage of processing involves the collection and preparation of solid waste containing chromium, such as solid tannery residues containing tanning agent residues, as well as liquid waste with chromium salts. In this study, the press-filtration residue (filter cake) of the water purification process of the tanning cycle was selected as the basic raw material containing chromium (Fig. 1). Due to the use of the basic chromium sulfate crystallohydrate compound $Cr_2(SO4)_{(3)}$-$nH_2O$ (n = 3, 6, 9, 12, 14, 15, 17, 18) in the solution, the filtrate has a sufficiently high concentration of chromium. Table 1 shows the chemical composition (on a dry weight basis), and Table 2 shows the results of the calorific value of the filter cake.

**Fig. 1.** Press-filter residue from the water treatment of the leather tanning process.

**Table 1 -** Chemical composition of press filter cake (filter cake).

| $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_2$ | CaO | $Cr_2O_3$ | $Fe_2O_3$ | LE* |
|---|---|---|---|---|---|---|---|---|---|
| 0.6-1.0 | 0.5-0.8 | 0.5-0.9 | 0.4-0.8 | 0.1-0.4 | 1.4-1.8 | 2.8-5.0 | 9-36 | 1.5-2.0 | 55-85 |

*The LE designation indicates the content of organic compounds and substances.
The total humidity of the filter cake is 25-30%.

Due to the presence of organic substances (animal fat residues, epithelium, tissues, etc.), filter cake has calorific properties that should be taken into account in the overall heat balance of thermal firing processes. The data on the calorific value of filter cake are given in Table 2 (the studies were conducted using a calorimetric bomb).

**Table 2 -** Results of the study of the calorific value of the cake.

| Name of the characteristic | Meaning | |
|---|---|---|
| Heat of combustion | MJ/kg | kcal/kg |
| Higher calorific value of the analytical sample | 2.21 | 527 |
| Higher calorific value in dry condition | 2.53 | 605 |
| Lower calorific value of the analytical sample | 1.27 | 302 |
| Lower calorific value in dry condition | 1.82 | 434 |

At the first stage of the process firing, the filter cake solid waste is cleaned of contaminants and foreign materials, and then crushed to a fine state, which increases the efficiency of further processing stages. Mechanical methods, such as grinding or fractionation, can be used to prepare the material for the next thermal processing process.

Rotary kilns are one of the key types of equipment for the heat treatment of solid tannery residues containing chromium compounds, which ensure efficient burning, conversion of chromium into a form suitable for metallurgical processing ($Cr_2O_3$) and removal of organic impurities (Fig. 2).

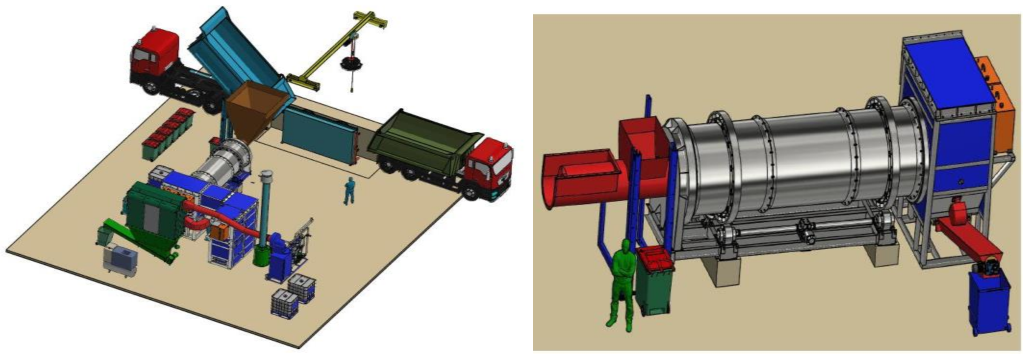

**Fig. 2.** Complex for firing leather production waste.

Table 3 shows the mode and results of laboratory firing with the determination of temperatures and specific mass loss. The resulting fired material is a crumbly powdery material of dark green color. Fig. 3 shows a photo of the appearance of the fired material, and Table 4 shows the chemical composition.

**Table 3** - Firing modes of the studied raw materials.

| Sample number | Temperature. exposure time, ºC | Crucible weight, g | | Weight loss | |
|---|---|---|---|---|---|
| | | to | after | g | % |
| 1 | 200 | 79.00 | 78.18 | 0.82 | 4.00 |
| 2 | 300 | 76.74 | 75.10 | 1.64 | 8.00 |
| 3 | 400 | 80.67 | 77.73 | 2.94 | 15.00 |
| 4 | 500 | 80.96 | 77.73 | 4.92 | 25.00 |
| 5 | 600 | 77.79 | 71.38 | 6.41 | 32.00 |
| 6 | 700 | 81.12 | 72.88 | 8.24 | 41.00 |
| 7 | 800 | 81.61 | 70.84 | 10.77 | 54.00 |
| 8 | 900 | 77.42 | 65.45 | 11.97 | 60.00 |
| 9 | 1000 | 77.34 | 64.60 | 12.74 | 64.00 |

**Fig. 3.** Annealed chromium concentrate.

**Table 4 -** Generalized chemical composition of roasted chrome concentrate.

| $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_{(5}$ | $SO_{(2}$ | CaO | $Cr_2O_3$ | $Fe_2O_3$ | others |
|---|---|---|---|---|---|---|---|---|---|
| **2.0-3.0** | **1.5-2.5** | **1.3-1.8** | **0.5-0.9** | **0.4-0.7** | **2.5-3.5** | **6.0-9.0** | **78-83** | **2.0-3.5** | **0.1-0.5** |

The fired material was also examined to determine the list of inorganic compounds, crystalline phases detected in the bulk of the sample, by powder X-ray diffraction. The X-ray diffraction patterns were recorded in the range of 2θ=5-70° using a DRON 3M diffractometer (Burevestnik, St. Petersburg) with CuKα and CoKα radiation (λ=0.15418 nm and λ=0.1789 nm, respectively) and a Ni filter. The recorded diffractograms are shown in Figs. 4-6.

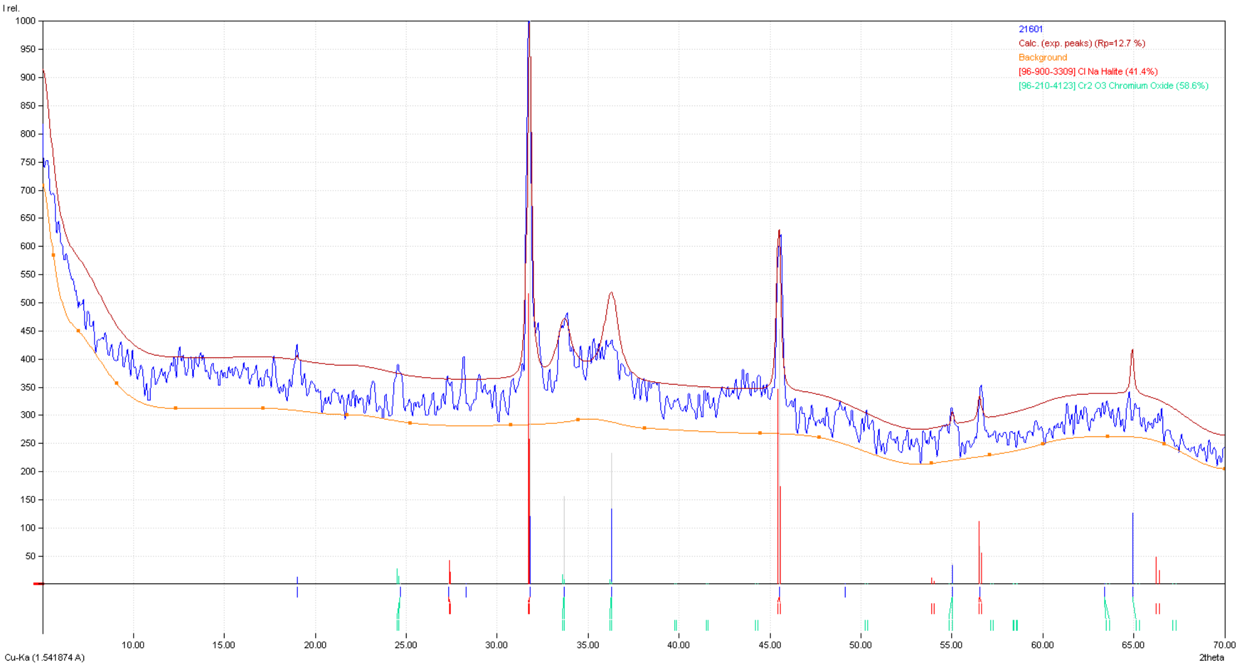


**Fig. 4.** Powder X-ray diffractogram, registered on CuKα radiation, of the main part of the sample (gray-green granules) with the results of comparison of signals with the crystallographic database.

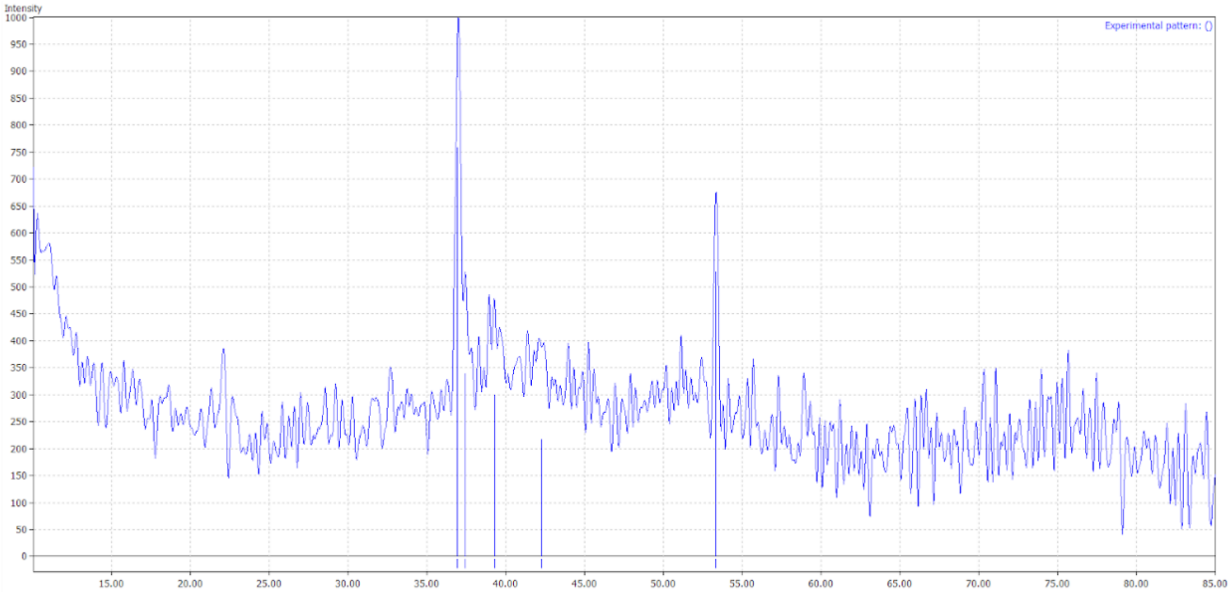


**Fig. 5.** Powder X-ray diffractogram, which is registered on CoKα radiation, of the main part of the sample (gray-green granules).

Powder X-ray diffractography revealed that the bulk of the sample consists mainly of substances that have a disordered structure or are composed of very small crystallites.

In addition, the main part of the sample contains crystalline phases of chromium oxide $Cr_2O_3$ and halite NaCl, the crystalline phase of halite is expressed by intense signals, and the crystalline phase of chromium oxide is expressed by less intense and slightly larger signals, indicating a small amount of crystalline oxide and relatively small sizes of its particles or crystallites.

**Conclusions.** In this work, the materials studied were the residues of press-filtration (filter cake) pulp from the tanning cycle in the technology of leather products production, due to the use of basic chromium sulfate, which is a valuable raw material for the isolation of chromium-containing compounds. Heat treatment is the main technological method for enriching the material in terms of chromium content. The processing temperature of the raw filter cake should be at least 700 °C. The powder yield, which can be considered a chromium oxide concentrate (COC), is in the range of 15-18% with a chromium oxide 7 $Cr_2O_3$ content of 0-80%.

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