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Research article

Научная статья



Technology for recycling still residues from dehalogenation to produce commercial zinc compounds

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Abstract: The study describes a method for recycling the still residue from the synthesis of hexafluoro-1,3-butadiene (HFBD) to produce zinc phosphate in the form of $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, which is used as a component in anti-corrosion pigment materials. The still residue ("heavy liquid") is preliminarily subjected to deep vacuum distillation (residual pressure 30 Pa, final temperature 160 °C) to recover volatile solvents—namely, isopropanol and dimethylformamide (DMF). The remaining residue is a concentrated solution of ZnCl_2 (about 70 wt. %) containing approximately 10 g/dm³ of iron in the form of Fe(II) and Fe(III), as well as colored organic impurities of unidentified composition. According to the proposed process, the vacuum distillation residue is diluted with water at a ratio of 1 : 2, filtered to remove suspended solids, acidified to pH 2 by the addition of concentrated HCl, and treated oxidatively with H_2O_2 at 70 °C. Fe(III) is removed by extraction with a 30 % solution of Cyanex 272 in an aliphatic diluent, and the colored impurities are removed by adsorption onto BAU-1 grade activated carbon. An alternative method for removing Fe(III) and part of the colored impurities involves precipitating zinc in the form of $(\text{ZnOH})_2\text{CO}_3$ using a 10 % Na_2CO_3 solution. Final clarification is also carried out using BAU-1 activated carbon. The purified, clear ZnCl_2 solution is then subjected to a two-step precipitation process to obtain zinc phosphate. The resulting precipitate is filtered, thoroughly washed with water, dried, and ground. The study showed that after drying at 100–105 °C, the resulting powder corresponds to the composition $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The content of regulated impurities falls within acceptable limits, and the properties of the material meet the requirements for pigment-grade substances. A comparison of the obtained zinc phosphate with a commercially available sample of pigment-grade zinc phosphate was conducted. It was established that the proposed technology yields 580 g of zinc phosphate dihydrate per 1 kg of initial raw material.

Key words: waste, hexafluoro-1,3-butadiene, heavy liquid, zinc chloride, zinc phosphate, refining.

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Технология утилизации кубовых остатков дегалогенирования с получением товарных соединений цинка

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Аннотация: В работе описан способ утилизации кубового остатка синтеза гексафтор-1,3-бутадиена (ГФБД) с получением фосфата цинка в форме $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, применяемого в качестве компонента антикоррозионных пигментных материалов. Кубовый

остаток («тяжелая жидкость») предложено предварительно подвергнуть глубокой вакуумной дистилляции (остаточное давление 30 Па, температура окончания процесса 160 °С) для извлечения летучих растворителей, изопропанола и диметилформамида (ДМФА). Остаток представляет собой концентрированный раствор ZnCl_2 (около 70 мас. %), содержит около 10 г/дм³ железа в форме Fe(II) и Fe(III), а также окрашенные органические примеси неуставленного состава. По разработанной технологии остаток вакуумной дистилляции предложено разбавить водой в соотношении 1 : 2, отфильтровать от взвешенных частиц, скорректировать pH до 2 введением концентрированной HCl, провести окислительную обработку H_2O_2 при температуре 70 °С. Железо (III) из раствора предложено отделять экстракцией 30 %-ным раствором Суапекс 272 в алифатическом разбавителе, а окрашенные примеси – сорбцией на активном угле марки БАУ-1. Альтернативным способом удаления Fe(III) и части других окрашенных примесей является осаждение цинка в форме $(\text{ZnOH})_2\text{CO}_3$ обработкой 10 %-ным раствором Na_2CO_3 . Окончательное осветление раствора также происходит на активном угле марки БАУ-1. Очищенный прозрачный раствор ZnCl_2 подается на двухступенчатое осаждение фосфата цинка, полученный осадок фильтруется, тщательно промывается водой, высушивается и измельчается. В ходе исследования установлено, что после высушивания при температуре 100–105 °С полученный порошок отвечает составу $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, содержание посторонних регламентируемых примесей находится в рамках допуска, а свойства материала удовлетворяют требованиям, предъявляемым к материалу пигментного класса. Проведено сравнение характеристик полученного фосфата цинка и коммерчески доступного образца пигментного фосфата цинка. Определено, что с использованием предложенной технологии из 1 кг исходного сырья может быть получено 580 г двуводного фосфата цинка.

Ключевые слова: отходы, гексафтор-1,3-бутадиен (ГФБД), «тяжелая жидкость», хлористый цинк, фосфат цинка, рафинирование.

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Introduction

A current research trend in the production of high-demand chemical compounds involves the recycling of accumulated and newly generated technogenic waste. The domestic paint and coatings industry has a demand for zinc-based pigments such as zinc white (zinc oxide), zinc chromate (zinc yellow), lithopone, and anti-corrosion formulations based on zinc–calcium medium or double phosphate. This entire group of zinc-containing pigments can be produced through the processing of a wide range of industrial waste materials.

The authors of [1] examined the synthesis of zinc–calcium mixed phosphate in chloride systems by precipitation with ammonium hydrogen phosphate. Studies [2–4] describe the synthesis and properties of anti-corrosion pigments based on zinc phosphate with benzotriazole (BTA) additives, while [5] demonstrates that changing the molar ratio of ZnCl_2/KOH influences the formation of $\text{KZn}_2\text{H}(\text{PO}_4)_2$ and KZnPO_4 phases. It was found that $\text{KZn}_2\text{H}(\text{PO}_4)_2$ exhibits better inhibiting properties in a 3.5 % NaCl solution compared to KZnPO_4 . In [6], zinc phosphate with a Zn/P ratio of approximately 1.5 was synthesized and characterized, with potential applications in the cosmetics industry. A method for synthesizing crystalline $\alpha\text{-Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was proposed in [7], where the morphology was controlled by adjusting the pH of the reaction medium.

Papers [8; 9] describe the synthesis and application of rose-like sheet zinc phosphate (SZP), as well as three-dimensional flower-like pigments based on micro- and nanoscale zinc phosphate (FZP) and ammonium–zinc phosphate (FNZP), used as anti-corrosion fillers in waterborne epoxy-modified acrylic resin. In [10], a comparative study was carried out between unmodified calcium zinc phosphate nanopigments (UCZP) and their methyltriethoxysilane-modified counterparts (MCZP). The potential use of dispersed hot-dip galvanizing waste as a component of zinc-rich coatings was explored in [11], while [12] examined the synthesis of zinc-containing pigment compounds from spent electroplating solutions. Patent [13] proposes a method for processing such solutions to obtain commercial-grade compounds. In [14], pigment-grade zinc oxide was obtained via alkaline treatment of solid galvanic sludge from the zinc-coating line at Signal-Nedvizhimost LLC (Russia). The feasibility of using electroplating sludge as a raw material for the production of inorganic pigments, including zinc-based ones, was further investigated in [15; 16].

In [17], the catalytic properties of zinc and iron phosphates in methanol conversion were investigated, with particular attention to the hydrothermal synthesis of a mixed phosphate in the $\text{R-ZnO}(\text{Fe}_2\text{O}_3)\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ system (where R is an organic or inorganic base).

Novel core—shell nanostructures of zinc phosphate/hydroxyapatite nanorods (ZPh/HPA_{NRS}) were synthesized and characterized as a modified form of hydroxyapatite with enhanced adsorption capacity for Ni²⁺ and Co²⁺ ions [18]. The application of zinc phosphate with various binders as electrode material for supercapacitors was explored in [19].

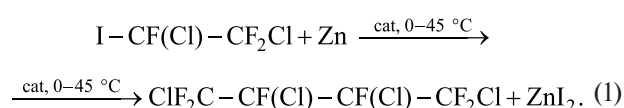
A method for producing zinc-free phosphate pigments containing strontium, calcium, and aluminum is presented in [20], along with their chemical composition, physicochemical, and anti-corrosion properties. This approach is relevant in view of environmental concerns and regulatory restrictions on the use of zinc-based anti-corrosion pigments in the European Union. The rapid and extensive release of Zn²⁺ ions from commercial lithopone pigment under solar light exposure was reported in [21], where approximately 41 % of the total Zn content was released after 24 h of simulated solar exposure.

The application of zinc phosphates as micronutrient fertilizers and feed additives in agriculture was studied in [22], while [23] examined the synthesis of ZnO nanoparticles and their use as nano-fertilizers in original form or as ferrite or zinc phosphate composites.

Russia is one of the few global producers of hexafluoro-1,3-butadiene (HFBD) and hexafluorobenzene, which are electronic gases used in plasma etching of silicon thin films during the manufacturing of micro-electronic devices with 15–25 nm design standards, for creating grooves and vias. HFBD is considered one of the most ozone-safe gases for plasma etching applications. In 2016, new production facilities with an annual capacity of up to 72 tons of HFBD were commissioned in Perm, Russia.

The commercial HFBD production technology used in Russia is described in patents [24–27]. Patent [28] proposes using alternative precursors to obtain a purer product without additional purification steps.

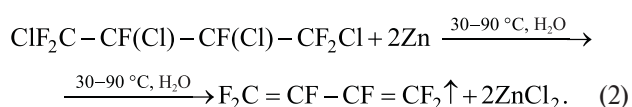
According to [24], a method was proposed for synthesizing 1,2,3,4-tetrachlorohexafluorobutane, which serves as a precursor for the production of hexafluoro-1,3-butadiene (HFBD). The process involves the reaction of 1-iodo-1,2,2-trifluoro-1,2-dichloroethane with zinc in the presence of an organic oxygen-containing complexing agent (cat), in accordance with the following equation:



The process is carried out by introducing an organic oxygen-containing complexing agent (cat) into the

mixture of starting reagents at a temperature of 0–45 °C. After completion of the reaction, 1,2,3,4-tetrachlorohexafluorobutane is isolated by rectification.

According to the method described in [25], hexafluoro-1,3-butadiene (HFBD) is synthesized by reacting 1,2,3,4-tetrachlorohexafluorobutane with granular zinc in a water—alcohol medium at 30–90 °C. The synthesis is performed by gradually dosing 1,2,3,4-tetrachlorohexafluorobutane into a reagent mixture containing metallic zinc and water, while simultaneously distilling off the target product, in accordance with the following equation:



Upon completion of dosing, the reaction mixture is heated to boiling to ensure full dechlorination.

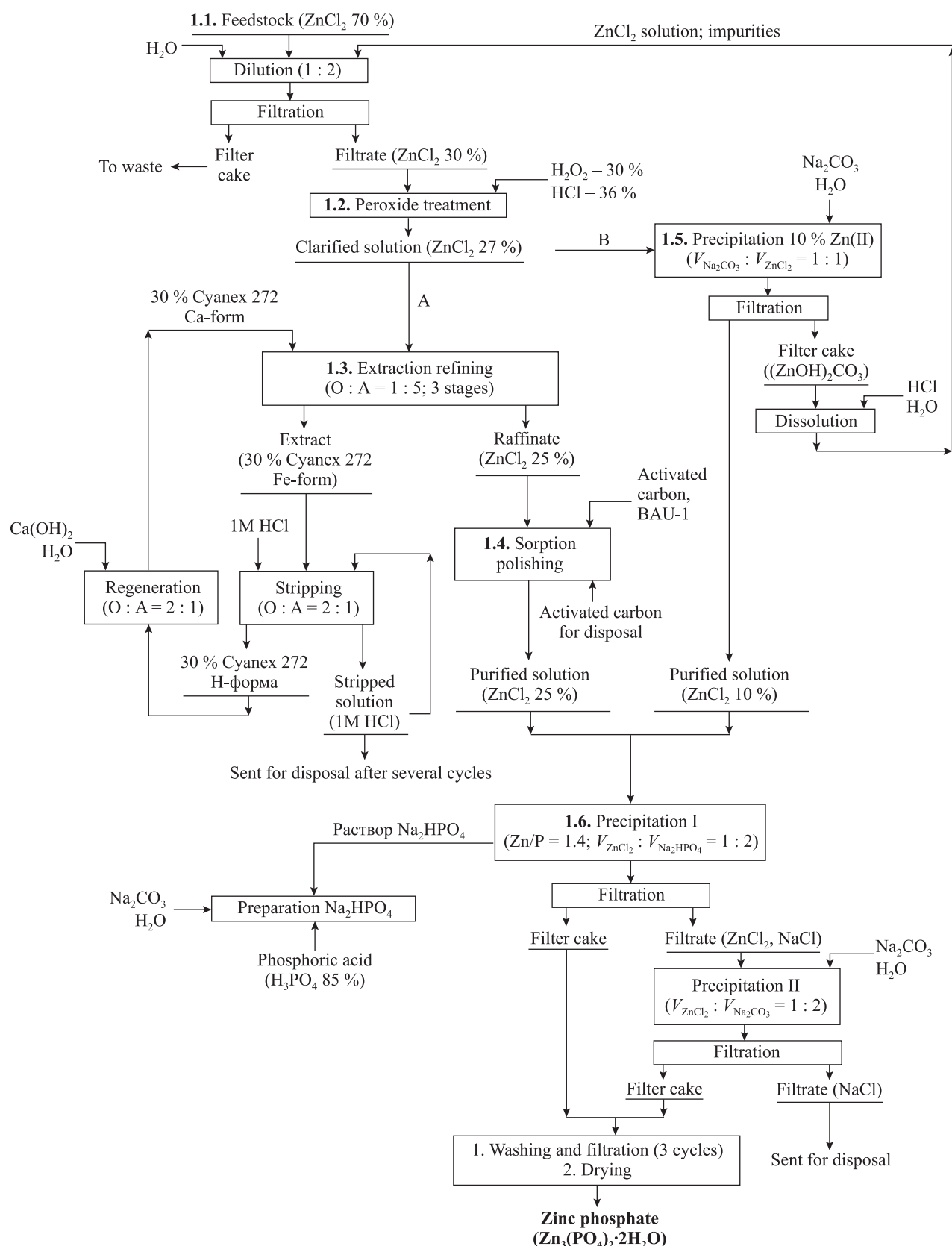
In [29], the mechanism of Fe(III) extraction by Cyanex 272 (bis(2,2,4-trimethylpentyl)phosphinic acid) was studied using a combination of methods, including ¹H NMR spectroscopy, mass spectrometry, and others. The extraction of Fe(III) from technical-grade phosphoric acid solutions using a related cation-exchange extractant, Cyanex 572, was described in [30]. The use of cation-exchange Cyanex extractants for the removal of Fe(III) from leach solutions of nickel ores was reported in [31]. The authors of [32] noted the challenges of Fe(III) stripping and proposed strategies to improve the regeneration efficiency of cation-exchange Cyanex extractants. Previously, we studied the extraction of Fe(III) from HCl solutions using 1-undecanol [33].

The application of cation-exchange extractants, including Cyanex 272, for the purification of zinc-containing solutions was discussed in [34]. The use of liquid—liquid extraction with Aliquat 336 to recover non-ferrous metals, including Zn(II), from process solutions generated during electronic waste recycling was described in [35]. In [36], the authors proposed a polyethylene glycol—sodium sulfate system (PEG-1500—Na₂SO₄) as an extractant for processing Zn-containing solutions.

The aim of the present study was to develop an efficient process scheme for recycling the still residue from the dehalogenation of 1,2,3,4-tetrachloroperfluorobutane, with the recovery of zinc orthophosphate as the target product.

1. Processing technology

The figure shows a flow diagram of the process used to treat the feedstock — the still residue from vacuum distillation of dehalogenation waste.



Flow diagram of the processing of the still residue from deep vacuum distillation of “heavy liquid” to produce commercial-grade zinc phosphate

Схема переработки кубового остатка глубокой вакуумной дистилляции «тяжелой жидкости» с получением товарного фосфата цинка

1.1. Feedstock

The so-called “heavy liquid” represents a combined discharge of liquid waste generated at all stages of HFBD production, as well as from the synthesis of precursor compounds. The synthesis of 1000 kg of hexafluoro-1,3-butadiene (HFBD) yields approximately 120 kg of waste (“heavy liquid”), consisting of the following: products of partial dehalogenation of 1,2,3,4-tetrachlorohexafluorobutane (TCHFBD); products of partial reduction of HFBD by zinc; chlorinated hydrocarbons; zinc chloride (ZnCl_2) in solution in either isopropanol (IPA) or dimethylformamide (DMF). Zinc chloride is also formed via the chlorine conversion of ZnI_2 , which is produced during the synthesis of 1,2,3,4-tetrachlorohexafluorobutane [24].

To recover isopropanol, the “heavy liquid” undergoes deep vacuum distillation in a Formeco unit (Italy) at a residual pressure of approximately 30 Pa and up to a final temperature of 160 °C. The resulting feedstock is a viscous, opaque, syrup-like oily liquid with an ether-like odor, containing suspended impurities.

The density of the solutions was measured using ~5 mL pycnometers on an analytical balance with a precision of ± 0.0001 g. The density measurement accuracy was ± 0.001 g/cm³.

The Fe(III) concentration was determined by the thiocyanate spectrophotometric method according to [37], using a calibration curve. Fe(II) in the samples was oxidized to Fe(III) by adding an excess of potassium peroxodisulfate.

The Zn(II) concentration was determined by direct complexometric titration using eriochrome black T as an indicator in accordance with [38]. The concentration was found to be 9.0 ± 0.1 mol/dm³.

The key parameters of the initial feedstock are listed below:

ZnCl ₂ concentration, g/dm ³	1340 ± 15
Total iron content, g/dm ³	5.8 ± 0.1
Feedstock density, g/cm ³	1.910 ± 0.001

1.2. Peroxide treatment

Preliminary experiments showed that the initial feedstock contained Fe(II) and Fe(III) compounds as colored impurities, as well as unidentified organic contaminants. The feedstock was diluted with water at a volume ratio of 1 : 2. The resulting solution was filtered through a pre-coated sand layer using a Büchner funnel. Exposure to concentrated zinc chloride solutions leads to the dissolution of paper and fabric, causing traditional filter membranes to fail rapidly.

To oxidize iron into the Fe(III) state and to promote the oxidative degradation of organic impurities, the filtrate was sequentially treated with concentrated HCl and H₂O₂ as follows: 100 mL of the filtrate was placed in a beaker and heated in a water bath for 30 min. Then, every 10 min, 1 cm³ of H₂O₂ and 1 cm³ of concentrated HCl were alternately added to the hot solution under stirring, for a total of four additions. Each addition of H₂O₂ and HCl caused the solution to foam, followed by clarification, indicating the oxidation of organic impurities and the decomposition of colored Fe(III) complexes. The oxidation process was carried out for 1.5 h, and by the end of the treatment, the pH of the solution had decreased to 2.

1.3. Solvent extraction of iron (III)

Cyanex 272 (bis(2,2,4-trimethylpentyl)phosphinic acid), a commercial weakly acidic organophosphorus extractant, was selected as the extractant. Its selection was based on its low acidity, which facilitates the stripping of Fe(III) — a highly extractable ion with strong affinity for cation-exchange extractants. A 30 % solution of Cyanex 272 in a mixture of Isopar-L and tributyl phosphate (in a volume ratio of 9 : 1) was used as the diluent. The Cyanex 272 concentration, determined by potentiometric titration, was 0.73 ± 0.01 mol/dm³. The extractant was first converted into the Ca-form (30 %) by mixing with dilute water containing slaked lime, and then into the Zn-form by contacting with a zinc chloride solution.

To extract Fe(III), the filtered and oxidized solution was treated with three portions of the extractant at an extractant-to-aqueous phase volume ratio of 1 : 5.

The residual Fe(III) concentration in the aqueous phase, determined by spectrophotometry, was approximately 40 mg/dm³.

1.4. Sorption polishing of the raffinate

Following extraction, a yellowish transparent raffinate was obtained. To remove the residual yellow tint, sorption polishing was applied. Prior to that, the effectiveness of several sorbents — Purolite MN200, Purolite XDA1, and BAU-1 activated carbon—was assessed. For the test, 15 g of each sorbent was added to 50 cm³ of raffinate.

During static sorption treatment, BAU-1 activated carbon demonstrated the best performance: the solution became clear and colorless, with no visible yellow tint. The solutions treated with resins retained a noticeable yellow coloration. Based on these results, BAU-1 acti-

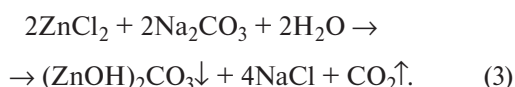
vated carbon was selected as the sorbent for the sorption polishing stage.

A volume of 160 cm³ of raffinate was transferred to a beaker and 15 g of activated carbon was added. The sorption process was carried out under periodic stirring for 2 days. During this time, the original zinc chloride solution became fully decolorized. The zinc concentration, determined by titrimetric analysis, was found to be 3.6 ± 0.1 mol/dm³.

1.5. Clarification of the peroxide-treated solution via zinc carbonate precipitation

To remove Fe(III) from the zinc chloride solution, it was proposed to co-precipitate 10 % of the zinc in the form of zinc hydroxycarbonate, (ZnOH)₂CO₃. This method allows the extraction stage for Fe(III) removal to be omitted, while the peroxide oxidation step can be carried out using a lower amount of peroxide — just enough to oxidize Fe(II) to Fe(III). As a result of co-precipitation of Fe(III) and adsorbed organic impurities on amorphous zinc hydroxide, the solution can be clarified more effectively.

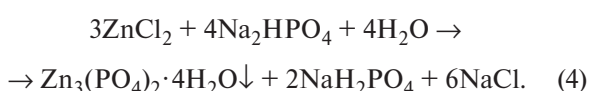
Zinc precipitation with sodium carbonate occurs in the form of zinc hydroxycarbonate according to the following reaction:



To precipitate 10 % of the zinc from the initial solution, a weighed portion of sodium carbonate was dissolved in an equal volume of water and slowly added to the zinc chloride solution under vigorous stirring over 30 min. The resulting suspension was then filtered through a “blue ribbon” filter to obtain a clear, colorless filtrate. The resulting contaminated filter cake can be dissolved in hydrochloric acid and reintroduced into the main solution during its dilution.

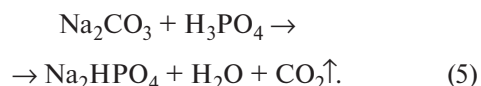
1.6. Precipitation of zinc phosphate

According to the standard procedure [39], sodium hydrogen phosphate is used for the precipitation of zinc orthophosphate. The precipitation occurs according to the following reaction:



The purified zinc chloride solution and the sodium hydrogen phosphate solution were mixed so that the molar ratio Zn : P was maintained at 1.4.

Sodium hydrogen phosphate (Na₂HPO₄) was prepared by mixing solutions of sodium carbonate and orthophosphoric acid in stoichiometric amounts according to the reaction:

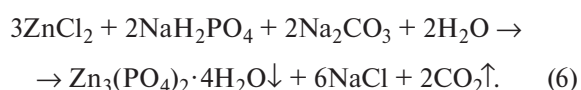


The weights of the reagents were calculated based on the Zn(II) concentration in the feed solution, which ranged from 3 to 4 M.

To prepare the sodium hydrogen phosphate solution, 26.7 g of sodium carbonate was dissolved in 100 cm³ of water and added to an 85 % orthophosphoric acid solution (29.0 g) previously dissolved in 250 cm³ of water. After neutralization, the prepared sodium hydrogen phosphate solution was used to precipitate zinc orthophosphate by adding it to 150 mL of the purified zinc chloride solution, in accordance with reaction (4). Thus, the volume ratio Zn²⁺/HPO₄²⁻ was approximately 1 : 2. During precipitation, a flocculent precipitate formed. After stirring the reaction mixture for 10 min, the zinc phosphate precipitate was filtered through a Büchner funnel using a “blue ribbon” filter, and the filtrate was returned to the reactor for further precipitation of zinc phosphate. The precipitate was washed twice by repulping with water at a solid-to-liquid ratio of 1 : 10, followed by an additional washing step directly on the filter using heated water (also at a 1 : 10 ratio). The resulting zinc orthophosphate was then dried at 100 °C and subsequently calcined at 250 °C.

Since, as indicated by reaction (6), half of the sodium hydrogen phosphate is converted to sodium dihydrogen phosphate, incomplete precipitation of zinc occurs. The solution becomes increasingly acidic, and equilibrium is established at pH = 2. To ensure complete precipitation of zinc as zinc phosphate and full consumption of the orthophosphoric acid, it was proposed to carry out an additional precipitation step by neutralizing the excess acidity with sodium carbonate.

To prepare the sodium carbonate solution for the additional precipitation, 11.8 g of sodium carbonate was dissolved in 100 cm³ of water. The resulting solution was added to the mother liquor to precipitate the remaining zinc phosphate according to the following reaction:



The procedure for precipitating zinc phosphate from the mother liquor was analogous to that described pre-

Table 1. Gravimetric determination of precipitate moisture content

Таблица 1. Результаты измерения влажности осадков

Stage	m_{100}, g	m_{250}, g	$m_{\text{H}_2\text{O}}, \text{g}$	$\omega_{\text{H}_2\text{O}}, \%$
Primary precipitation	32.9	30.0	2.9	8.8
Additional precipitation	27.1	24.9	2.2	8.1

viously. Upon addition of the sodium carbonate solution, gas evolution, foaming, and the formation of a white flocculent precipitate were observed. The reaction mixture was stirred for 10–15 min. The precipitate was filtered and dried following the same method as for the initial precipitation.

The masses of the precipitates obtained after the precipitation and additional precipitation steps were determined after drying at 100 °C (m_{100}) and 250 °C (m_{250}). The mass loss upon drying at 250 °C and the water content were calculated using the following formulas:

$$\Delta m_{\text{H}_2\text{O}} = m_{100} - m_{250}, \quad (7)$$

$$\omega_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{m_{100}} \cdot 100 \%. \quad (8)$$

The moisture content of the obtained precipitates, determined gravimetrically, is presented in Table 1. The loss of moisture upon heating from 100 °C to 250 °C corresponds to the behavior of zinc phosphate in the form of $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ after drying at 100 °C. Thus, both anhydrous and dihydrate forms of zinc phosphate can be obtained, both of which are highly sought after for use in the production of pigment materials.

2. Characterization of the synthesized zinc phosphate

2.1. Oil absorption of pigments

One of the key characteristics of technical pigment materials is their oil absorption. According to GOST 21119.8-75, oil absorption of the first kind is defined as the amount of oil (in grams) required to produce 100 g of a homogeneous pigment paste. It is determined as follows: a sample of the pigment is gradually mixed with linseed oil, grinding the mixture until a uniform paste is obtained. The amount of oil consumed in the test is then recorded and rounded to the nearest whole number [34].

In our case, 1.44 g of oil was used to wet approximately 5 g of the pigment sample. The oil absorption was calculated using the formula:

$$X = \frac{0.93V}{m} \cdot 100, \quad (9)$$

where V is the volume of linseed oil used during testing (cm^3); m is the mass of the pigment sample (g); and 0.93 is the density of linseed oil (g/cm^3).

As a result, the oil absorption of the obtained pigment was 29 $\text{g}_{\text{oil}}/100 \text{ g}_{\text{pigment}}$.

2.2. Elemental analysis of zinc phosphate

The elemental composition of the zinc phosphate samples was determined using an X -ray fluorescence analyzer integrated into the VEGA 3 SBH scanning electron microscope (TESCAN, Czech Republic) at the Engineering Center of the St. Petersburg State Institute of Technology (Technical University). Samples dried at 250 °C and prepared as a white powder were used for the analysis.

The results are presented in Table 2, based on which the contents of the main compounds in the pigment were calculated:

Zinc compounds (as Zn), wt. %50.6

Phosphorus compounds (as PO_4), wt. %49.1

Table 3 presents the specification values for a commercial-grade pigment sample used in paints (Neo-PZ, manufactured by PS Akvilon LLC), along with the properties of the zinc phosphate pigment obtained in this study after drying at 100 °C, corresponding to the composition $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

The test results confirm that the synthesized zinc phosphate dihydrate meets all standard requirements for zinc phosphate pigment materials.

3. Results

A method has been proposed for processing the hazardous waste currently accumulating, enabling the

Table 2. Elemental composition of zinc phosphate samples

Таблица 2. Элементный состав образцов фосфата цинка

Sample	Content, wt. % (at. %)			
	O	P	Cl	Zn
Precipitate	35.55 (64.61)	13.56 (12.73)	0.08 (0.06)	50.62 (22.51)
Mother liquor	36.69 (64.38)	13.17 (11.72)	0.06 (0.05)	47.07 (19.85)

Table 3. Test results of the zinc phosphate pigment for use in Neo-PZ paints (PS Akvilon LLC)

Таблица 3. Результаты испытаний цинкофосфатного пигмента для красок Neo-PZ предприятия ООО «ПС Аквилон»

Sample	Zinc compounds (as Zn), wt. %	Phosphorus compounds (as PO ₄), wt. %	pH of aqueous suspension	Δm_{600} , %	Particle size (residue on No. 0045 sieve), wt. %	Appearance
Specification for Neo-PZ	40–47	40–47	7–9	8–16	≤0.5	White powder
Test results for synthesized pigment	43.2	45.5	8.1	10.2	Trace	Complies

recovery of valuable solvents—isopropanol and dimethylformamide (DMF) — which are presently not produced in Russia. At the same time, the large-scale recovery of these solvents is not feasible without addressing the problem of utilizing the still residue. The processing technology for the still residue, developed within the scope of this study, comprises the following stages.

1. Dilution of the still residue from the vacuum distillation of the heavy liquid with water and subsequent filtration ($V_{\text{feedstock}} = 50 \text{ cm}^3$, $V_{\text{H}_2\text{O}} = 100 \text{ mL}$).

2. Treatment of the filtrate with a 31 % hydrogen peroxide solution and a 36 % hydrochloric acid solution under heating to 80 °C ($V_{\text{H}_2\text{O}_2} = 4 \text{ mL}$, $V_{\text{HCl}} = 4 \text{ mL}$).

3.1. Solvent extraction of Fe(III) using a 0.8 M solution of Cyanex 272 (3×20 mL, organic phase to aqueous phase ratio O : A = 1 : 5); followed by sorption purification of the raffinate ($m_{\text{BAU-1}} = 15 \text{ g}$).

3.2. Alternatively to Stage 3.1, precipitation of $(\text{ZnOH})_2\text{CO}_3$ and organic impurities by treatment with a sodium carbonate solution ($V_{\text{H}_2\text{O}} = 100 \text{ mL}$, $m_{\text{Na}_2\text{CO}_3} = 4.24 \text{ g}$).

4. Precipitation of zinc phosphate by treatment with Na_2HPO_4 ($m_{\text{Na}_2\text{CO}_3} = 26.7 \text{ g}$, $m_{\text{H}_3\text{PO}_4} = 29.0 \text{ g}$, $V_{\text{H}_2\text{O}} =$

$= 350 \text{ mL}$), followed by additional treatment with a sodium carbonate solution ($m_{\text{Na}_2\text{CO}_3} = 11.8 \text{ g}$, $V_{\text{H}_2\text{O}} = 100 \text{ mL}$).

The amount of $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ that can be obtained from 1 kg of initial feedstock is approximately 580 g.

In addition to zinc phosphate, the developed technology also allows the production of ZnCO_3 , ZnO , and a refined concentrated ZnCl_2 solution (ZnCl_2 concentration > 50 %).

Conclusion

A technological scheme has been developed for producing pigment-grade zinc phosphate from zinc chloride contaminated with impurities, a waste by-product of the dehalogenation process. The concentrations of iron and zinc chloride in the initial feedstock were determined.

Experimental results showed that treating the diluted feedstock with hydrogen peroxide in the presence of hydrochloric acid under heating promotes the decomposition of colored organic impurities, which impede the separation of iron and the complete

decolorization of the solution. Both solvent extraction and precipitation methods for achieving complete decolorization of the zinc chloride solution were proposed. As a result of the two-stage precipitation process, zinc orthophosphate was obtained as the final product. The pigment's oil absorption was determined experimentally, and its elemental composition was established.

Comparison of the synthesized product's characteristics with those of the commercial Neo-PZ zinc phosphate pigment (PS Akvilon LLC) confirmed that the properties of the synthesized material fully meet the standards for pigment-grade zinc phosphate.

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V.A. Dorozhko – determined the purpose of the study, developed the processing technology, and wrote the manuscript.

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Вклад авторов

В.А. Дорожко – определение цели работы, разработка технологии, написание текста статьи.

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