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EXTRACTION OF IRON-CONTAINING CATALYST FROM CHLORORGANIC WASTES GENERATED BY ETHYLENE CHLORINATION

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Розглянуто технології вилучення залізовмісного каталізатора з технологічних потоків прямого хлорування етилену, а також способи утилізації хлорорганічних відходів виробництва вінілхлориду. Проблеми, що виникають при термічній утилізації відходів, спричинили необхідність досліджень екстракції сполук Заліза з хлорорганічних побічних продуктів процесу хлорування етилену. Рентгено-флюоресцентним аналізом встановлено, що до складу шламу спалювання, як основні елементи, входять Залізо – 33,52 % та Хлор – 32,69 %. Досліджено екстракцію сполук Заліза водним та водно-кислотними середовищами за механічного перемішування. Показано, що додавання хлоридної кислоти до розчину не сприяє збільшенню ступеня вилучення сполук Заліза. Встановлено, що збільшення тривалості екстракції та температури здійснення цього процесу забезпечує ступінь вилучення сполук Заліза понад 80 %. Досліджено процес розділення водно-органічної емульсії, яка утворюється під час екстракції, відстоюванням, фільтруванням та центрифугуванням. Встановлено, що за температури близько 80 °С відбувається ефективне й швидке розділення водної та органічної фаз внаслідок відстоювання. На основі отриманих експериментальних результатів дослідження екстракції запропоновано функціональну схему вилучення залізовмісного каталізатора, а також шляхи вирішення технологічних та екологічних проблем, що виникають при спалюванні хлорорганічних відходів виробництва вінілхлориду. Схемою передбачене використання теплоти гарячих хлорорганічних відходів для здійснення екстракції сполук Заліза технічною водою. Окрім того, передбачене використання теплоти газів, що утворюються під час спалювання хлорорганічних відходів, для нагрівання повітря, яким віддувають низькокиплячі компоненти з цих відходів. Надалі це повітря використовують для спалювання очищених від сполук Заліза хлорорганічних відходів

Ключові слова: хлорорганічні відходи, вінілхлорид, спалювання органічних відходів, шлам від спалювання, вилучення залізовмісного каталізатора, екстракція

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1. Introduction

The production and consumption of vinyl chloride (VC) in the world is about 30 million tons [1]. The main part of VC (98–99 %) is used for the production of polyvinyl chloride (PVC), and approximately 1 % VC is used in the preparation of copolymers with vinyl acetate and other monomers. VC production consists of two main stages:

1) obtaining dichloroethane (DCE) by direct and oxidative chlorination of ethylene using iron (III) chloride and copper (II) chloride as catalysts;

2) high-temperature cleavage of hydrogen chloride from DCE with the formation of VC.

In the system of distillation columns, raw DCE is dehydrated and cleaned of “light” and “heavy” organochlorine by-products called organochlorine waste (OCW – organochlorine waste). Thermal disposal of distillation bottoms is an important stage for environmental protection in the treatment of wastes from VC production. During the thermal destruction of "light" and "heavy" organochlorine by-products, hydrochloric acid is regenerated and thermal energy is utilized by producing process water vapor using a steam generator.

2. Literature review and problem statement

It is known [2] that OCWs are formed in the production of vinyl chloride, as well as propylene oxide by the chlorohydrin method. According to the works [2–4], which are somewhat different from each other, the OCW composition formed during the rectification of DCE includes two main components: DCE – 18–30 % and 1,1,2-trichloroethane – 30–40 % and in smaller amounts of 1,1-dichloroethane – 7–10 %; perchlorethylene – 3–5 %; 1,2-dichloroethylene – 2–3 %; benzene – up to 0.5 %, as well as other organochlorine compounds. The content of the main components in various flows of OCW from the distillation process is given in [2].

OCWs are of course utilised of by burning or destructive oxidation in the case of wastewater, however, the economic efficiency of these utilisation methods is low, since valuable chemical products are lost [2, 3]. In addition, it was noted in [2–4] that hazardous compounds such as dioxins can be formed during the OCW combustion.

In [4], the ways of chemical waste utilisation are proposed, which are alternative to incineration. In particular, they considered [3, 4] a method for the disposal of OCW by polymerization and copolymerization with an unsaturated fraction of C_5–C_9 monomers. This method of OCW disposal allows to get inexpensive and non-toxic polymer products that can be used as anti-corrosion waterproofing coatings. At the same time, the amount of OCW subject to thermal neutralization is reduced by 15 %.

In addition, the possibility of using polymerization for the simultaneous utilization of sulphide-alkaline waste and OCW [4, 5] is being discussed. Upon receipt of a sulfur-containing polymer with a yield of 26–50 %, the OCW conversion is 55–98 %. These sulfur-containing polymers when used as modifiers of asphalt-bitumen compositions increase the frost resistance of the road paving.

To reduce the OCW by a factor of 2–5, it is recommended [6] to use alkaline dehydrochlorination for a mixture of 1,2-dichloroethane and 1,1,2-trichloroethane to obtain a mixture of monomers $CH_2{=}CH{-}Cl$ and $CH_2{=}CCl_2$ with yields of 28 % and 70 %, respectively.

For disposal of organochlorine production wastes, it was proposed in [7] to use the process of OCW catalytic amination with a concentrated aqueous solution of ammonium hydroxide to obtain a mixture of amines. In addition to amination, it is proposed [8, 9] for utilization to condense OCW with hydrolysis of lignin in the presence of sodium polysulfide, and the resulting product can be used in asphalt mixtures for the upper layers of the road paving.

In [10], the conditions of chlorination of vinyl chloride wastes were studied with the aim of using these products as raw materials in the production of carbon tetrachloride and perchlorethylene. In [11], the possibility of OCW utilization by quaternization into quaternary ammonium salts (QAS) was examined using the example of OCW from the production of allyl chloride. These OCWs containing 1,3-dichloropropenes, 1,2-dichloropropane, 1,2,3-trichloropropane were treated with industrial monochloralcanes C_{12}–C_{15} and an aqueous solution of dimethyl or diethylamine. As a result, QAS was obtained with a yield of 96.8–98.3 %, which are used as cationic surfactants.

With a large number of studies on the development of processes for the OCW raw materials use in the industry, a significant part of the OCW is utilized according to the WtE scheme, i. e., the conversion of waste into energy. However, a number of factors that did not allow considering incineration to be the proper way of OCW processing were previously considered [12]. At the same time, a significant part of industrial plants for the combustion of OCWs operate according to simplified WtE (waste-to-energy) schemes without the use of low-temperature catalytic processes. During the operation of WtE circuits, significant problems arise, one of which, for example, is the clogging of gas pipelines between the incinerator and the steam generator, sometimes even to a state of practical obstruction. So, the solution to this problem is relevant.

The following methods are proposed for extracting metal-containing catalysts from homogeneous reaction mixtures, high-boiling wastes, oil and heavy fractions of its processing:

1) burning waste and extracting metals from the resulting ash;
2) ion exchange processes for reaction mixtures
3) extraction of metals from petroleum coke;
4) extraction of organic metal complexes from oil or from processing fractions.

The possibilities and problems of methods for extracting metals from mixtures of organic liquids are described in many works, for example [13, 14].

The review paper [15] deals with the problem of heavy metal impurities in pharmaceutical preparations and, in particular, various methods for the removal of Palladium impurities from organic pharmaceutical compounds that are synthesized by catalysis by palladium compounds.

In [16], functionalized resins based on silicon-containing polymers and polyamines in non-polar solvents, in particular cyclohexane, were proposed for the extraction of Palladium from reaction mixtures. The problem of Palladium recovery in the synthesis of pharmaceuticals was thoroughly investigated in the 1990s [17], both using ion-exchange resins and conventional precipitation using 2,4,6-trimer-S-triazine.

To extract metals such as Vanadium, Cadmium, Copper, Nickel, Zinc, and Iron from oil ash, tissue for ion exchange in the H^+ form was studied in [13]. When directly filtering oil ash through an ion-exchange tissue, Vanadium removal was 12 %. The high viscosity of the oil ash caused a low filtration rate and poor ion exchange. When oil ash was mixed with hexane or acetone in a ratio of 1 gram of ash, viscosity decreased to 1 ml of solvent, and ion exchange improved.

In [18], biocatalytic extraction of Nickel and Vanadium from petroporphyrins and asphaltenes were studied both in an aqueous buffer solution and in mixtures of organic solvents with water.

Let's note that when washing mixtures of organic substances (for example, oil and heavy fractions of its processing) with water, stable emulsions are formed, which must be separated. To accelerate the destruction of emulsions in industry, the phenomenon of coalescence is used [19–21].

In [22], membrane separation was studied by ultrafiltration through polyacrylonitrile (PAN) membranes of an oil-water emulsion with an oil concentration of 10 % vol., which had chemical oxygen demand (COD) of 77,000 mg O_2/dm^3.

When separating such an emulsion for PAN membranes (pore sizes of 3, 10, and 30 nm), the COD of the filtrate was 2,250, 2,320, 6,570 mg O_2/dm^3, that is, the degree of oil recovery was 97.1; 97.0 and 91.5 %, respectively.

For emulsions of oil with water, mainly non-ionic type demulsifiers are used, the flow rate of which is 5–150 g/t of oil or a trapped product [23–26].

For example, in [26] it was found that for the separation of water (salinity 3.5 g/dm^3) from oil emulsions of the "water in oil" type with a water concentration of 30 % vol. It was optimal to use a mixture (1:1) of polyethylene glycol grade PG62 (M=1500, HLB=0.443) and polypropylene glycol grade PG35 (M=2700, HLB=0.248). A dosage of 100 g/t and 55 °C ensured the efficiency of water separation (WSE – Water Separation Efficiency) in 100 minutes for medium grade KD1 oil – WSE=99 % and for heavy grade DGH2 oil (asphaltene content – 6.0 % wt.) – WSE=94 %.

To extract the organic phase from a 1 % oil-in-water emulsion, which is used as a cutting fluid in metal processing, a hybrid process was studied [27]. This process consists of two stages:

1) coagulation of the destabilization of the emulsion using calcium chloride, followed by centrifugation;

2) ultrafiltration using tubular multichannel ZrO_2 ceramic membranes (300 kDa).

By the method of planning the experiment, the optimal conditions for each stage of the hybrid process were determined [27], in which a decrease in COD to 97.4 % was achieved. In particular, for the ultrafiltration stage, these conditions were: transmembrane pressure – P=2 Bar, T=60 °C, inlet stream – Q=800 l/h, concentration of salt coagulant C=0.20 mol/dm^3).

Centrifugation for the separation of water-oil emulsions and the processing of oil ash in industry is often carried out using equipment from ALFA LAVAL – decanter centrifuges (https://www.alfalaval.ua/products/separation/centrifugal-separators/decanters/). The study of emulsions under centrifugation is ongoing [28–30].

A certain standardized approach to solving the problem has already been proposed for the extraction of metals from aqueous media. In contrast, for the extraction of metals from mixtures of organic substances, it is necessary to choose a method taking into account its effectiveness, productivity and economic feasibility for each specific case.

However, in the literature [2–30], the results of studies regarding the seizure of Iron with XOO were not found. Iron must be removed from the OCW, since the presence of Iron compounds in the OCW complicates further technological processes. OCW utilisation by the WtE scheme generates ash. One of the components of this ash is a compound of iron, which is part of the catalytic system of direct chlorination of ethylene to 1,2-DCE. This ash during deposition on gas pipelines and heat exchange elements of the steam generator causes a violation of the normal process and leads to emergency stops.

One way to solve this problem could be to remove the Iron-containing catalyst from the OCW direct chlorination of ethylene to 1,2-DCE. Thus, the study of the extraction of the Iron-containing catalyst with OcW and technologically rational proposals for the practical implementation of this extraction process are promising.

3. The aim and objectives of research

The aim of research is determination of the possibilities of extracting Iron compounds from solid ash resulting from the combustion of organochlorine wastes. This will significantly reduce the formation of solid ash, which is deposited on gas pipelines and heat exchange elements of the steam generator.

To achieve this aim, the following objectives are solved:

– to determine the macro composition of solid ash and identify the reasons for its formation;

– to study the extraction of the iron-containing catalyst with OCW direct chlorination of ethylene to 1,2-DCE and choose the optimal conditions for its implementation;

– to propose a functional scheme for the treatment of bottoms of 1,2-DCE rectification from iron compounds.

4. Materials and research methods for the extraction of Iron compounds from organochlorine wastes

4. 1. The investigated materials and equipment used in the experiment

The objects of the study were the OCW of rectification bottom of the reaction mixture of catalytic chlorination of ethylene – the so-called "heavy" residue, as well as solid ash that pollutes the gas pipeline between the furnace for burning the "heavy" residue and the steam generator.

4. 2. Methodology for the study of the solid ash macrostructure

To determine the qualitative and approximate quantitative macro composition of the ash, X-ray fluorescence spectral analysis (XRA) was used using an energy dispersive X-ray fluorescence spectrometer (XRS) ElvaX Plus Light. This XRS was equipped with an X-ray tube with an Rh anode at a voltage of 50 kV and a Fast SSD detector and provided a resolution of <140 eV for the $K\alpha$ manganese line. XRS operating conditions: purge with helium; sample with a diameter of 20 mm; determination duration – 30 s.

When studying the extraction of an iron-containing catalyst with OCW, the analysis of the aqueous phase for the content of Iron compounds was carried out photometrically with 1,10-phenanthroline according to DSTU 6332-2003 using a KFK-3 model at a light wavelength of 510 nm.

4. 3. Methodology for the study of the extraction of iron compounds from organochlorine wastes

The content of iron (III) chloride ions from the "heavy" residue was carried out by decylase extraction with distilled water from a volume ratio of organic phase: water=1:1. Extraction was carried out by vigorous stirring in a turbulent mode to ensure the greatest possible contact area between the aqueous and organic phases, since these phases are mixed with each other to a limited extent, forming a heterogeneous system. After stirring for 30 minutes the resulting suspension was kept for 24 hours to separate the aqueous and organic phases.

The completeness of separation was controlled by the volume of the aqueous phase, which should have been equal to the volume of water used for washing at a certain extraction stage. If the deviation of the volumes of the aqueous phase exceeded 5 % of the initial volume, which was taken for extraction, the duration of exposure was increased. The content of Iron (III) ions in the extract was determined photometrically using a KFK-3 photometer.

The study of the extraction of iron compounds from the heavy fraction was carried out with an aqueous solution of hydrochloric acid (20 %, 10 %, 6 %) and water. The ratio between the organic and aqueous phases was from 2:1 to 1:2; temperature ranging from 20 to 80 °C.

5. The results of studies of the insoluble ash composition and the extraction of iron compounds from organochlorine wastes

5. 1. The results of studies of the ash macro composition

In appearance, the ash resulting from the OCW thermal utilization of the bottoms of VC production is a brown powder, similar to iron (III) oxide. Previously, using the XRA method, it was found that the following basic macro elements (except for light than Sodium) are included in the sample of the ash studied: Iron (33.52 %); Chlorine (32.69 %); Sodium (9.87 %); Magnesium (4.44 %); Sulfur (0.89 %) and Calcium (0.32 %).

5. 2. The results of studies of the extraction of Iron compounds from organochlorine wastes

100 cm^3 of the "heavy" residue was taken for extraction. The results of the extraction of Iron (III) ions from the "heavy" residue are given in Table 1.

Table 1

The results of the extraction of Iron ions from the "heavy" residue with distilled water

Extraction ratio	Water volume, dm^3	Concentration of Fe3$^+$ ions in the extract, mg/dm^3	Mass of Fe3$^+$ ions in the extract, mg
1	0.15	76.0	11.40
2	0.10	13.8	1.38
3	0.10	5.6	0.56
4	0.10	0.7	0.07
Total	0.45	–	13.41

So, in 100 cm^3 of the "heavy" residue, 13.41 mg of iron (III) ions are contained together. Then the Fe^{3+} content in the "heavy" residue is 134.1 mg/dm^3 (g/m^3). The density of the "heavy" residue is 1.320 g/cm^3. The Fe^{3+} content in the "heavy" residue in the sample provided for research is 101.6 mg/kg.

It was found that at a temperature of 25±5 °C after intensive mixing of the heavy fraction with aqueous solutions and water, a stable emulsion was formed. Almost complete separation of the organic ("heavy" fraction) and aqueous phases was achieved within 24–36 hours. Moreover, the emulsions obtained in parallel experiments sometimes differed significantly in structure (Table 2).

In all cases, the extraction degree of Iron compounds, which was estimated by the content of Fe^{3+} ions in the aqueous phase, taking into account the ratio of the heavy fraction and the aqueous solution, was not less than 65–70 % (Table 3). The extraction degree (%) of Fe^{3+} ions was calculated by the formula (1):

$$X_A=((C_{Ao}-C_A)/C_{Ao})100, \tag{1}$$

where C_{Ao} – the initial concentration of Fe^{3+}, g/dm^3.

Table 2

Characterization of extraction of Fe^{3+} ions from the "heavy" fraction at a temperature of 25±5 °C

No.	Description of extraction and characterization of emulsions
1	The mixture separates within 30–40 minutes. The phase boundary is clear; homogeneous organic phase
2	The mixture separates within 10–12 hours. The phase boundary is blurred, 2–3 mm thick; the organic phase is heterogeneous
3	The mixture separates within about 24 hours. The phase boundary is blurred with a thickness of 2–3 mm; the organic phase is heterogeneous, contains loose inclusions with sizes from 2–3 to 5 mm
4	The mixture separates within two days, the phase boundary is blurred 3–4 mm thick; the organic phase is heterogeneous, contains loose inclusions; on the surface of the aqueous phase a foam layer about 5 mm thick
5	The mixture separates within 12–14 hours. The phase boundary is blurred with a thickness of 2–4 mm; the organic phase is homogeneous.
6	The mixture separates for more than 36 hours, the phase boundary is blurred, 5–6 mm thick; the organic phase is heterogeneous.

Table 3

The results of extraction of Fe^{3+} ions from the "heavy" fraction at a temperature of (25±5) °C

No. from Table 2	Volume of organic and aqueous phases, cm^3			Extraction duration, min	The extraction degree of Fe^{3+} ions, %
	«Heavy» fraction	Water	HCl solution		
1	60	60	–	5	12
2	60	60	–	15	45
3	60	60	–	30	67
4	60	60	–	45	69
5	60	30	30	15	69
6	60	30	30	30	69

As can be seen from the Table 3, at a temperature of about 25 °C, more than 65 % of the compounds of Iron can be removed. However, at the same time, the separation of the aqueous and organic ("heavy" fractions) phases takes a very long time, which will require the use of technological equipment (sedimentation tanks) of a significant amount. Use for extraction of the aqueous phase into which 20 % hydrochloric acid was introduced (Table 3, items 5, 6) gave neither a significant increase in the extraction degree of Iron compounds, nor a decrease in the duration of separation. A solution of hydrochloric acid was used to acidify the aqueous medium in order to avoid the formation of practically insoluble iron hydroxide, which would largely remain in the volume of the "heavy" fraction.

For destruction of the "water–OCW "heavy" fraction" emulsion as surfactant a demulsifier named "PM-A" was used, which is used to separate oil from the aqueous medium [31]. Changing the dose of "PM-A" demulsifier in a wide range of values of 0.5–3 % vol. did not provide a noticeable reduction in the duration of the process of separation of the water-organic emulsion.

The "heavy" fraction and the aqueous medium moisten such materials as polyethylene, polypropylene, chlorine fabric, belting, and glass well. Therefore, a study was carried out on the possible coalescence of one of the phases on these surfaces, which could lead to their separation.

A filter surface was formed from the chlorine fabric, and other materials were used as a bulk layer. Through them passed the previously obtained emulsion (mixing time of the heavy fraction and the aqueous medium) for 30 minutes. In terms of research, this did not give a positive effect. Centrifugation of the emulsion gave unclearing results, so that these results were poorly reproduced. For example, phase separation was obtained very well with a clear interface; the volumes of the heavy and aqueous fractions were almost equal to the initial ones. In parallel experiments, the interface was blurred, and foam was formed on the surface of the aqueous phase, which contained dispersed inclusions in the form of turbidity.

Following studies on the extraction and separation of the aqueous-organic medium were carried out at elevated temperatures. Since the heavy fraction has a high initial temperature, and in the existing technological process there are powerful heat fluxes, the available heat can be used for extraction. The results of studies on the extraction and separation of the aqueous-organic medium at elevated temperatures are given in Tables 4, 5.

Table 4

Characterization of the extraction of Fe^{3+} ions from the “heavy” fraction at a temperature of 70–80 °C

No.	Description of extraction and characterization of emulsions
1	The mixture separates within 30–40 minutes. The phase boundary is clear; the organic phase is homogeneous; the aqueous phase is transparent, yellowish
2	The mixture separates within 1.5 hours. The phase boundary is slightly blurred with a thickness of 2–3 mm; the organic phase is homogeneous; the aqueous phase is transparent, yellowish
3	The mixture separates for about 2 hours. The phase boundary is blurred with a thickness of 2–5 mm; the organic phase is quite homogeneous, the aqueous phase is transparent, yellowish
4	The mixture separates for about 35 minutes. The phase boundary is blurred with a thickness of 2–3 mm; the organic phase is homogeneous; the aqueous phase is transparent, yellowish
5	The mixture separates for about 2 hours. The phase boundary is blurred 3–5 mm thick; the organic phase is quite homogeneous, the aqueous phase is transparent, yellowish
6	The mixture separates for about 2 hours. The phase boundary is blurred 3–5 mm thick; the organic phase is quite homogeneous, the aqueous phase is transparent, yellowish

The separation degree of the aqueous-organic mixture was determined by the ratio of the volume of the transparant layer of the aqueous phase to the initial volume. The dependence of the separation degree of the aqueous-organic mixture on time is shown in Fig. 1.

Table 5

The results of extraction of Fe^{3+} ions from the “heavy” fraction at a temperature of 70–80 °C

No. from the Table 4	Extraction condition		Extraction degree of ions Fe^{3+}, %
	Process duration, min	Temperature, °C	
1	5	70	25
2	15	70	68
3	30	70	82
4	5	80	25
5	30	80	84
6	30	90	84

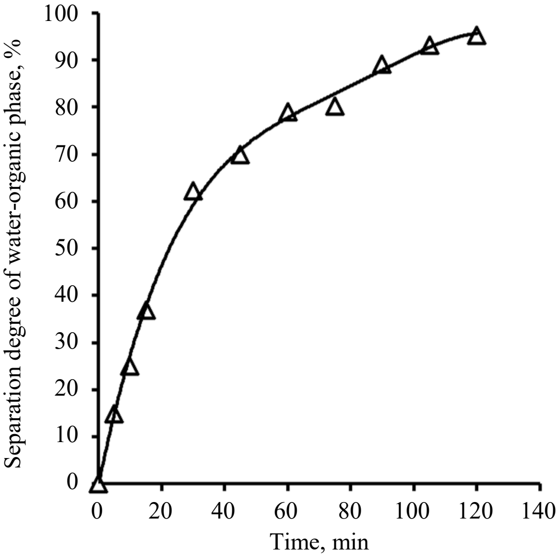

Fig. 1. Kinetics of the separation of the water-organic mixture at a temperature of 80 °C

According to the separation rate of the aqueous-organic phase (% per minute), two sections can be distinguished in Fig. 1, in the first of which, up to 30 minutes, the separation rate decreases by about 1.4 times from 2.97 to 2.07, and in the second this rate is less than 5–7 times than in the first and averages is 0.4.

5. 3. Development of a functional scheme for cleaning the “heavy” residue from Iron compounds

Based on the results obtained, a functional scheme (Fig. 2) is proposed for removing Iron compounds from the “heavy” fraction before burning.

The hot “heavy” fraction passes through a heat exchanger, where process water is heated due to its heat. Subsequently, water is fed into an extractor, made as an apparatus with a stirrer, which provides a turbulent mixing mode, where intensive mixing of the “heavy” fraction and the aqueous phase takes place. If necessary, the water is acidified with a 20 % hydrochloric acid solution.

The extraction is carried out for 30 minutes at a temperature of 80±5 °C. For the total volumetric flow rate of the aqueous-organic mixture as 1.66 m^3/h and a residence time of 30 minutes the volume of the extractor is 1 m^3. After extraction the emulsion enters a heat-insulated separator-settler where phase separation occurs at a temperature of 80±5 °C. The separator volume is about 4.5 m^3. The outlet fitting of the aqueous phase should be located above the calculated level of separation of phases, taking into account the fact that the interface is not clear, but a kind of water-organic layer is formed. After separation the “heavy” fraction is fed for combustion into the furnace (pos. V-1803), as provided for in the existing technological scheme.

The aqueous phase from the extractor is removed with a pH of less than 1.5. Since the “heavy” fraction contains about 40 % dichloroethane (DCE), some of it will dissolve in the aqueous phase upon extraction. The solubility of DCE in water is 0.87 g/100 cm^3. Therefore, theoretically, after extraction, water can contain up to 7.22 kg of DCE (per 0.83 m^3). Therefore, before discharging water to a treatment plant, it must be purified from DCE. DCE blow-offs are carried out with hot air, heated due to the heat of gases generated after burning in a furnace (pos. V-1803) of a heavy fraction purified from Iron compounds. It is possible to use other heat fluxes. DCE blow-offs are carried out in packed or mesh columns. Air containing desorbed DCE is supplied from the blow-off column to the "heavy" fraction combustion furnace (pos. V-1803). Water containing Iron compounds, after the blown column, are fed to neutralize and precipitate Iron ions in the form of sparingly soluble hydroxide. To do this, a solution of sodium hydroxide, which is obtained in the workshop of caustic soda and chlorine, is dosed into water to a pH of 7...8. During studies, it was found that in the water after extraction there is Iron mainly in the form of Iron (III), but there is some the amount of Iron (II). Perhaps with increasing temperature in the environment of organic compounds, a partial reduction of Fe^{3+} to Fe^{2+} occurs. In this case, it is advisable to neutralize the water with a solution of sodium hypochlorite. Since it contains sodium hydroxide, the oxidation of Iron (II) to Iron (III) and the formation of sparingly soluble iron (III) hydroxide will occur simultaneously. The separation of $Fe(OH)_3$ is advisable to carry out on a drum vacuum filter with an alluvial layer.

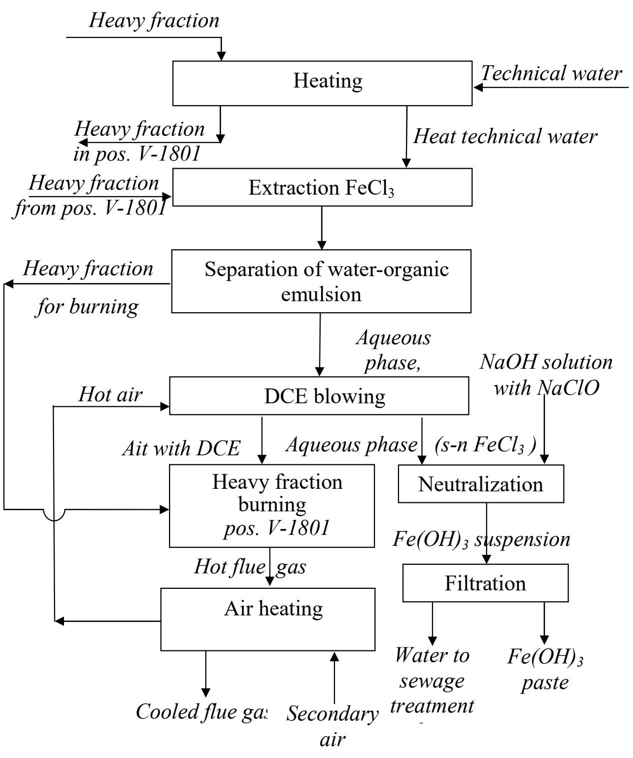

Fig. 2. Functional scheme for cleaning the "heavy" residue from compounds of Iron

6. Discussion of the results of a study to determine the possibilities of extracting Iron compounds from solid ash

The high content of Iron compounds (33.52 %) in the solid ash, which, due to the burning of the "heavy" residue, clearly indicates that it is formed due to iron (III) chloride. It is used as a quasi-homogeneous catalyst for the chlorination of organic compounds. After separation of the reaction mixture of iron (III) chloride is contained in the "heavy" residue. When burning such a "heavy" residue, a solid ash forms, which blocks the tubes of the heat exchanger and communications.

The results obtained in the study of the extraction of Iron compounds (Tables 3, 5) can be explained by the fact that with an increase in the duration of intensive mixing, which is necessary to create the largest possible contact area between the heavy fraction and the aqueous medium, an emulsion is formed containing less particles heterophases. Therefore, the stability of such an emulsion increases. The aqueous medium after extraction was strongly acidic (the measured pH did not exceed 1.5), since $FeCl_3$ was extracted, which hydrolyzes with the formation of hydrochloric acid, which causes a significant decrease in pH. Therefore, the introduction of HCl solution in an aqueous medium has practically no effect on the extraction degree.

So, based on the results obtained, it can be argued that it is advisable to carry out the extraction of Iron compounds at elevated temperatures for a volume ratio of the heavy fraction and water as 1:1. An increase in the extraction degree of Iron (III) ions at elevated temperatures (70–80 °C) due to a decrease in the surface tension of the liquid phase and the acceleration of diffusion. This contributes to the coalescence of heterophase particles with the formation of large agglomerates, and futher – the rapid separation of phases (Table 4). This allows a sufficiently high extraction degree of Iron compounds (more than 80 %) with an insignificant duration of the process of separation of the heavy fraction and the organic phase – about 2 hours. The presence of a fuzzy phase boundary gives necessitaty for the location of the aqueous phase outlet fitting in the apparatus for transparation must be slightly higher than calculated, and the volume of this apparatus must be slightly larger (10–15 %).

Based on the results of the studies performed, for the extraction of Iron compounds a material balance was drawn up following material flows. Initial material flows, kg/h: "heavy" fraction – 1100; water – 830. The material flows after extraction, kg/h: "heavy" fraction – 990; aqueous phase – 747; water-organic layer – 193.

The material balance is drawn up for hourly productivity following the "heavy" fraction. The calculation was based on experimental data, the interface is not clear, but blurred. The volume of this blurred layer is 10 % of the total volume of the water-organic medium. The content of the heavy fraction and water and the content of Iron compounds are distributed in it proportionally to their content in the organic and aqueous phases. It was assumed that a change in the density can be neglected for the organic and aqueous phases after extraction, since it will be within the error. The extraction degree of Iron compounds was taken as 80 %.

The proposed functional scheme covers both sequential and cross-technological connections in the form of material and heat flows. In particular, it provides for the efficient use of the heat of the exothermic process of burning organochlorine waste previously purified from Iron compounds for the extraction of iron (III) chloride and the blowing of dichloroethane from the aqueous phase.

For the development of a technological scheme, calculation and selection of technological equipment, further studies will be aimed to optimizing technological parameters for removal of Iron compounds from OCW such as temperature, hydrodynamic conditions, the ratio between the aqueous and organic phases.

7. Conclusions

1. It has been established that one of the main components of the solid residue resulting from the combustion of organochlorine wastes is sparingly soluble iron compounds. They are formed due to the high-temperature conversion of iron (III) chloride, which is used as a catalyst in the chlorination of ethylene.

2. It has been established that: the use of hydrochloric acid solutions to remove Iron compounds is not nessesary; it is enough to use industrial water; increasing the temperature to 70–80 °C allows to intensify the process of extraction and separation of the system into aqueous and organic phases.

3. A functional scheme is proposed for the extraction of Iron compounds from the bottom residue of 1,2-DCE rectification. It provides a high degree of purification of the bottom residue from Iron compounds and the efficient use of heat fluxes.

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