

PROBLEM OF DISPOSAL OF ORGANOCHLORINE WASTE
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Abstract. The sources of organochlorine waste formation, its toxicity, and environmental impact are analyzed, and methods of its disposal are considered. The composition of insoluble compounds in the stillage residues of the dichloroethane rectification stage before incineration is determined, and the method of their extraction is proposed. It is established that the use of oxalic and hydrochloric acids as extractants significantly reduces the iron content in the stillage residues of the rectification column, which allows increasing the duration of operation of the organochlorine waste incineration equipment.

Key words: organochlorine waste, toxicity, neutralization, combustion, stillage residues, insoluble compounds, extraction.

1. Introduction

The organochlorine industry is one of the leading chemical industries of derivatives of organic hydrocarbons since organochlorine products are widely used in various areas of the national economy – electronic, metalworking, and pharmaceutical industries; production of plastics and synthetic resins, household chemicals; agriculture and many others. In particular, these are chlorine-containing monomers such as vinyl chloride, epichlorohydrin, chloroprene, chloroparaffins, chloroolefins, organol chlorides, the production of which is accompanied by generating a large amount of waste. On a global scale, in the process of synthesis of organochlorine products, about 1.2–1.5 million tons of chlorinated organic waste (COW) is generated per year [1]. The largest amount is

produced at the stage of obtaining chloroform, 1,2-dichloroethane (1,2-DCE), vinyl chloride (VC) that enter the environment. Organochlorine waste is extremely toxic, since the addition of chlorine atoms to the hydrocarbon base increases their solubility in the fatty tissues of the human body, significantly increasing the toxicity of these compounds, and also forms a “protective screen” that gives them a special resistance to the effects of chemical, physical and biological factors causing many serious diseases. For example, during the combustion of COW in the production of 1,2-dichloroethane, besides the reaction of complete combustion, a significant number of adverse processes that result in the formation of substances belonging to the 1st and 2nd class of hazard are taking place, in particular, free chlorine, phosgene, polychlorinated dioxins and dibenzo-p-dioxins which are very dangerous poisons. Entering the environment, these substances accumulate in it [2].

It is crucial that organochlorine waste does not have a permanent chemical composition. Its composition is mainly influenced by raw materials, technological parameters of processes and operating modes of equipment. Neutralization of organochlorine waste is difficult because of its high chemical resistance and toxicity, as well as an acute shortage of corrosion-resistant materials and equipment for the installation of utilization plants. Therefore, the cost of its utilization is much higher than the disposal of conventional organic waste. The cost of waste utilization equipment in the production of organochlorine synthesis, depending on the volume, properties, and method of disposal, is from 5 to 10 % of the total cost of production [1].

2. Theoretical part

The methods that are used to process organochlorine waste include regeneration, oxidation, thermal decontamination (combustion), plasma chemical recycling, electrocracking, hydrogenation, and landfilling [2].

The method of regeneration of the most valuable components of organochlorine waste is especially promising and ecological. However, this process can be used only for the extraction of easy-boiling organochlorine solvents (trichlorethylene, tetrachlorethylene, etc.) from the treated mixtures. This method is not used for the utilization of organochlorine waste from DCE and VC because of the low content of the abovementioned compounds.

The decontamination of organochlorine waste by means of oxidation is carried out using catalysts, which lower the temperature of the process [3]. The compounds containing 3- and 6-valent chromium [4] and also $(\text{Ce}, \text{Cr}) \times \text{O}_2$ / HZSM-5 (with different mass ratios $(\text{Ce}, \text{Cr}) \times \text{O}_2$ to zeolite HZSM-5) are used as catalysts [5]. In addition, the process can be carried out in a pseudo-boiling layer of a catalyst using air or oxygen as an oxidizer [6].

The final oxidation products of COW are chloride hydrogen, carbon dioxide, trichlorethylene, perchlorethylene, and polychlorinated ethane, the content of which in the gas is up to 60%. However, catalytic oxidation of COW can only be used for gaseous waste or volatile waste which is substantially diluted with air to prevent thermal decontamination of catalysts. Moreover, in the process of organochlorine waste oxidation, mixtures of chlorine and hydrogen chloride are formed, the concentration or neutralization of which is cost-ineffective.

The process of organochlorine waste utilization by hydrogenation depends on the conditions, in which it is conducted, the composition of the COW, and the catalyst nature [7]. The key advantage of this method is the preservation of the hydrocarbon component of waste which is the most valuable. However, this method of utilization is recommended for processing COW obtained at the pyrolysis stage of DCE under reduced pressure, in the absence of chlorinated derivatives of aromatic hydrocarbons in waste. In general, COW practically always contains chlorinated arenes.

The non-oxygen method of organochlorine waste disposal is based on its restoration by gas ammonia at a temperature of 500–600 °C. The advantages of this method are the possibility of processing a wide range of organochlorine compounds (poisonous chemicals, fighting poisonous substances), and lower capital and operating costs than by using the hydrogenation method. Concerning the disadvantages of this method

of neutralizing COW, they are similar to hydrogenation [3].

The plasma chemical method is mainly used for basic organochlorine production with permanent chemical composition waste since changes in the composition of waste negatively affect the work of plasma chemical reactor and the quality of the formed products [3]. The disadvantages of this method of COW utilization are the work of plasma torches and plasma chemical reactors, the multi-stage process, the complexity of pyrolysis product fractionation and the requirement of a constant waste composition.

Another effective method of organochlorine waste disposal is to neutralize and utilize it by biological degradation. The proposed method provides the biological decomposition of polychlorinated aromatic compounds in the soil by the cellular slime mold, from which bacteria are obtained in the nutritional medium [8]. It is proposed to clean the ventilation air with the help of settled microorganisms of bio-filters able to convert harmful substances (chlorinated, including aromatic hydrocarbons) into carbon dioxide, water, and salt. The authors found that the rate of destruction of harmful substances in such filters can reach 30–40 g/m per year, and decomposition exceeds 90 %. In addition, [9] shows the use of nanomaterials, especially iron and palladium, that are used to restore soils and eliminate their toxicity by soil microorganisms. It explores the feasibility of integrating with other recovery technologies, including bioremediation. Biological methods can clean the air, sewage, and soils from COW pollution in small amounts, but they are not able to solve the problem of utilization of tens of thousands of tons of concentrated organochlorine waste, and, most importantly, the valuable components of COW are lost.

As the amount of organochlorine synthesis waste is increasing today, and equipment for its utilization is rather expensive, organochlorine waste is sometimes buried in landfill [12]. In the case of solid insoluble in water waste, this happens in conventional shielded chambers. However, liquid waste landfilling should be carried out in specially equipped chambers with continuous monitoring of their condition. The creation of such landfills is a technically difficult task and costs much more than thermal decontamination.

The utilization of organochlorine waste by combustion is used in the production of vinyl chloride at the “Karpatnaftokhim” Ltd. Solid and liquid COW are formed at the stages of 1,2-dichloroethane and vinyl chloride production because of incomplete main and secondary processes, and impurities in the raw materials. Solid residues of COW, which are formed during the

periodic cleaning of filter, rectification columns, heat exchangers, pyrolysis furnaces, reservoirs, and after centrifugation at the wastewater treatment stage, are taken to landfills and buried. Liquid COW is formed at

the stages of direct and oxidative chlorination of ethylene and 1,2-dichloroethane pyrolysis, at the stages of rectification, dehydration, and cleaning and makes up about 85 % of all industrial waste (Fig. 1).

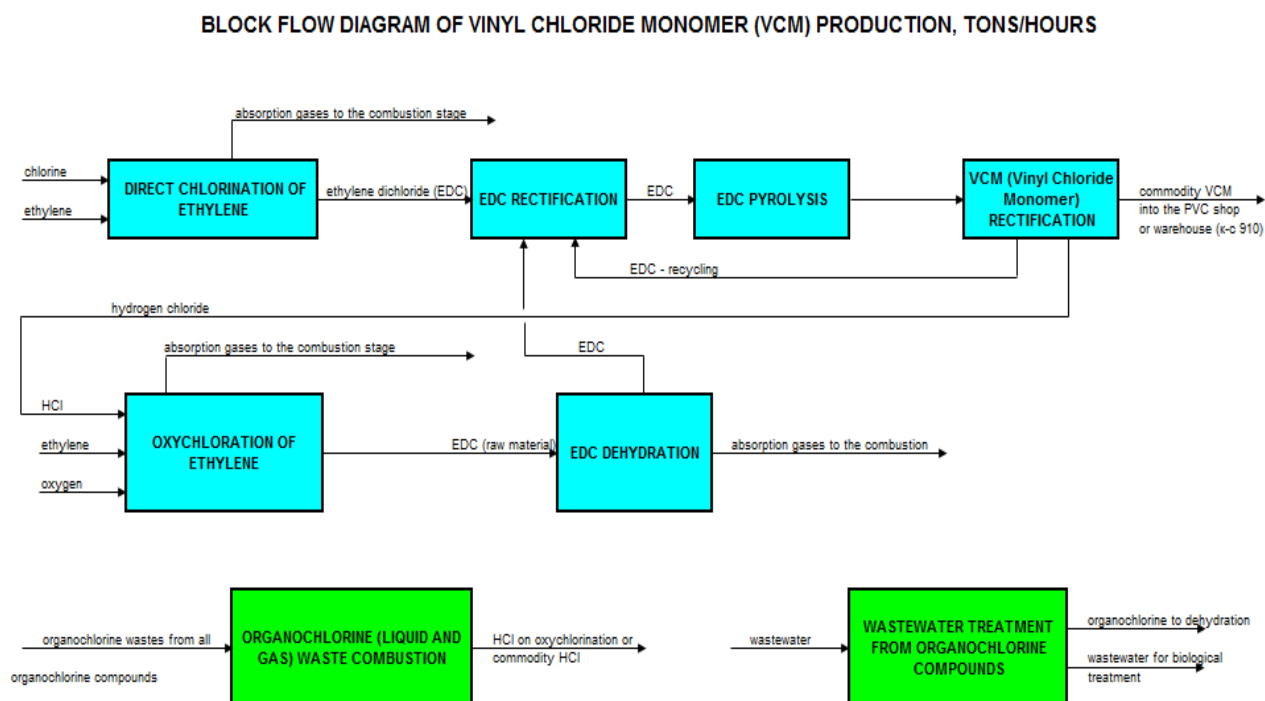


Fig. 1. Block flow diagram for the production of vinyl chloride monomer (VCM) and the formation of liquid organochlorine wastes (OCW).

This is a complex, multi-component mixture of chlorinated compounds, which cannot be effectively separated at the stage of rectification due to the formation of azeotrope. Waste is sent to the combustion stage where at a temperature of 800–1250 °C it is burned with further absorption of hydrogen chloride with water which in the form of hydrochloric acid is neutralized or enters the stage of oxychlorination. The total volume of COW formed at a maximum design production capacity of 370 thousand tons of VC per year can reach 9100 tons of COW. The amount of waste is not constant and depends directly on the equipment load, the rhythm of the operation of individual units, the quality of raw material flows, and the state of the main technological equipment.

According to the technology [13], organochlorine waste is burned with the formation of flue gases which flow through a heat exchange system (steam generator) into a quench. Due to different chemical composition of the waste (stillage residues of dichloroethane rectification stages), in the process of operation of the heat exchange systems, we can observe overgrowth of the internal surfaces of the tubes of the steam generator

with insoluble compounds. The deposition of scale on the walls worsens the conditions of heat transfer, which results in over-consumption of the water boiler. The nature of insoluble compounds deposited on the walls of the tubes of the steam generator is different. Some get to the stillage residues of rectification columns together with raw materials; others are formed in the process of production of semi-finished and finished products. Due to the overgrowth of the steam generator's pipes, frequent stops of the combustion plant occur, which leads to the violation of technological regime rules and over-consumption of energy resources. Recently, the frequency of stops has increased significantly, so the study of the content of insoluble compounds in the stillage residues would allow assessing the nature of their formation, and reducing their content becomes a priority task of technological, environmental and economic nature. Thus, the purpose of this work is to study the composition of insoluble compounds in the stillage residues at the stage of dichloroethane rectification to extract them, which will lead to reducing the frequency of stops of the combustion plant.

3. Experimental part

In the studies we used the stillage residue of dichloroethane C-403 rectification column of vinyl chloride production [13], the chemical composition of which was determined using gas chromatograph Crystal 5000 with a flame ionisation detector (Table 1):

Table 1

Chemical composition of the stillage residue of dichloroethane rectification column of vinyl chloride production

No	The name of the component	Component content, % wt
1	ethyl chloride (C ₂ H ₅ Cl)	0.006
2	1,1-dichloroethane (C ₂ H ₄ Cl ₂)	0.002
3	chloride allyl (C ₃ H ₅ Cl)	0.008
4	trans-1,2-dichlorethylene (C ₂ H ₂ Cl ₂)	0.001
5	1,1-dichloroethane (C ₂ H ₄ Cl ₂)	0.003
6	chloroprene (C ₄ H ₅ Cl)	0.187
7	1,2-dichloroethane (C ₂ H ₄ Cl ₂)	24.851
8	ethylene chlorohydrin (C ₂ H ₅ ClO)	0.119
9	benzene (C ₆ H ₆)	0.005
10	carbon tetrachloride (CCl ₄)	0.062
11	1,1,2-trichloroethylene (C ₂ HCl ₃)	0.005
12	chlorine (C ₂ HCl ₃ O)	0.964
13	1,1,2-trichloromethane (C ₂ H ₃ Cl ₃)	31.409
14	perchlorethylene (C ₂ Cl ₄)	0.02
15	1,1,2,2-tetrachloroethane (C ₂ H ₂ Cl ₄)	1.776
16	chloroform (CHCl ₃)	0.012
17	unidentified polychlorinated hydrocarbons	40.570

During the research, several series of experiments were carried out. They corresponded to the stages of stillage residue study. For this purpose, a sample of powder from the tubes of the steam generator was selected during its cleaning to study the phase and chemical composition.

Phase analysis of the powder sample was carried out on a DRON-3M diffractometer (Fe-K α radiation) using a complex of structural analysis programs CSD 2000 and a database of crystalline structures of the known compounds of CRYSMET. The results of the X-ray diffraction analysis have shown that there are two compounds in the test sample: Fe₂O₃ (spatial group Fd3m, a = 0.8377 (5) nm) and Fe₃O₄ (spatial group

R-3c, a = 0.50387 (4) nm; c = 1.3750 (8) nm) with a predominant phase content of Fe₃O₄.

To conduct a qualitative and quantitative analysis, the sample of the powder from the tubes of the steam generator was dissolved in a mixture of concentrated acids HNO₃: HCl (1:3). The dissolution occurred within 4 days under continuous mixing at a temperature of 100 °C.

The qualitative analysis of the resulting solution was carried out using the ammonia-phosphate method of cation analysis which is based on different solubility of metal phosphates in the water, ammonia solution, weak and strong acids, using known techniques. The results of the analysis show that there is a significant number of Fe³⁺ ions, minor admixtures of Ca²⁺ ions, and H₂SiO₃ methacrylic acid residue. The latter two components could enter the test solution because of contamination by the products of dissolution of the dishes (glass) since the dissolution had been carried out for a long time (4 days) at a high temperature by using a concentrated solvent. The quantitative determination of Fe³⁺ ions was carried out with the help of a spectrophotometric method using the formation of a coloured complex compound of iron (III) with sulphosalicylic acid in an acidic medium. The results of the analysis show that the test sample contains 69,8±3 % Fe³⁺.

The purpose of the second stage of the research was to extract iron from organochlorine residues. To do this, a certain amount of stillage residue was evaporated at a standard laboratory-scale plant at a temperature of 98 °C and atmospheric pressure to extract the hydrocarbon component of the abovementioned chemical composition (Table 1). The suspension after evaporation was calcined for 2 hours in a muffle furnace at a temperature of 900 °C. The resulting residue of reddish-brown colour was dissolved in hydrochloric acid with a mass fraction of 25 % under constant heating at 100 °C. In the resulting solution, Fe³⁺ content was determined. As a result of the measurement, the iron content in the solution is 0.05919 % wt.

The third series of studies was to extract iron from the stillage residue of the rectification column before combustion. Literary sources show that one of the most promising methods of decomposition and concentration is the method of liquid extraction, since, with the use of a suitable extractant, this method is suitable for the extraction of almost all elements with different concentrations [14]. The main property of the extractive reagent is its selectivity, the ability to extract one of several solution components as much as possible. Therefore, from this point of view, the best one is the extraction agent that dissolves the maximum of one

component and the minimum of the remaining components; and the distribution factor should be at least 2. Other essential properties of the extractant include the ease of performing re-extraction, well-fluttering phases, safety during work (non-toxicity, fire safety, etc.), low cost, stability during extraction, re-extraction, storage, etc. The treatment of the solution with an extractant can be performed repeatedly, resulting in a high degree of the required substance extraction. Extracting does not require complex and expensive equipment. This process can be automated with the help of remote control, which makes it technologically and economically beneficial. Literary sources show that acid extragens are the most selective extraction reagents in the excretion of trace elements [14], so the extraction of Fe^{3+} was carried out using water soluble extractive reagents – 1–5 % of solutions of hydrochloric, nitric, acetic, sulfuric, oxalic acids and ethanol. The studies have revealed that the dissolution of the stillage residue in ethanol, nitrogen and sulfuric acids is insignificant. The solubility of the stillage residue was maximal in hydrochloric and oxalic acids. Iron extraction was carried out using 1–5 % solutions of these two acids. Extraction was carried out in a mass ratio between the stillage residue and the extractant in the range from 1: 1 to 1: 3. It has been established that the optimal ratio of the stillage residue to the selected extractants is 1: 2.5. The extraction of iron was carried out by adding a calculated amount of extractant to a certain mass of the stillage residue of the aforementioned composition, under intensive mixing of the mixture at the temperature of 98 °C for 5 minutes (per extraction), followed by separation of the phases in the separating funnel. (To speed up extraction, each time a fresh dose of extragent was added) The number of extractions was set experimentally. The filtered residue and the illuminated solution were analyzed for the iron content by a colorimetric method based on the interaction of iron ions (III) with rhodanide ions in the acidic medium and the formation of complex ions coloured in red. To determine the mass fraction of total iron $[\text{Fe}^{2+} + \text{Fe}^{3+}]$, preliminary oxidation of iron (II) to iron (III) was carried out using hydrogen peroxide.

Laboratory studies have shown that almost all the iron that was present in the stillage residue is extracted to the liquid phase of both extractants, and the multiple extraction method makes it possible to accelerate the extraction process and obtain a high degree of waste treatment, since instrumentally it is advisable to carry

out extraction using a step-counter extraction, each stage of which consists of a mixer and separator for residue decomposition.

Table 2 shows changes in the content of iron in the stillage residue C-403 [13] in 1 % aqueous solution of acids HCl and $\text{H}_2\text{C}_2\text{O}_4$.

Table 2

Changes in iron content in the analyzed sample by extraction with hydrochloric acid and oxalic acid

Extractor	Extraction Sequence	Iron content, % wt.	
		before extraction	after extraction
HCl	1	0.0592	0.0386
	2	0.0386	0.0083
	3	0.0083	0.0062
$\text{H}_2\text{C}_2\text{O}_4$	1	0.0592	0.0357
	2	0.0357	0.0051
	3	0.0051	0.0024
	4	0.0024	0.0022

4. Results and Discussion

As you can see, after three extractions the extractable agent is almost completely removed from the solution. The determination of the distribution coefficient for both extractants showed that it is 4.7 for hydrochloric acid, and 5.8 for oxalic acid. Because of extraction with hydrochloric acid, the iron content in the stillage residues decreased from 0.0592 % wt. to 0.0062 % wt., and as for extraction with oxalic acid, it decreased from 0.0592 % wt. to 0.0024 % wt. Experiments with the abovementioned reagents with concentrations of 1 % to 5 % wt. were carried out to determine the effect of the extractant concentration on iron extraction from the powder sample. Fig. 2 and 3 show the curves of the procedure and the rate of iron extraction from the stillage residue of the dichloroethane rectification column. The values of A, the iron content in the stillage residue in relation to the original content, are on the axis of the ordinate which is 100 %, or the rate of extraction; the serial number of the degree of extraction is on the abscissa axis.

Thus, with the increase in the concentration of extractants, the rate of extraction varies in a rather narrow range, regardless of the solvent nature. Analyzing the curves of iron extraction rates from the stillage residue, it is possible to note the logical reduction of the extraction rate from the first stages of extraction to the latter ones. For both extractors, the highest rates of extraction are observed at the first stages, but this rate rapidly decreases at the third stage (almost to zero).

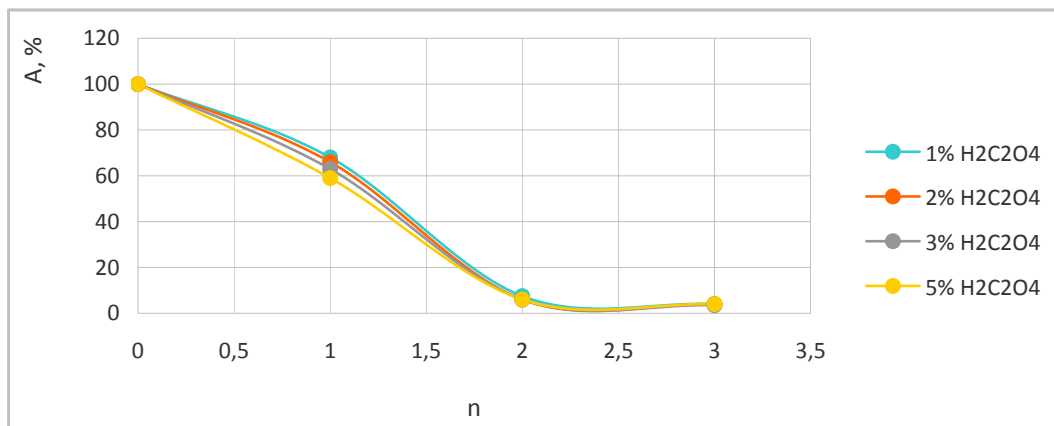


Fig. 2. The procedure and the rate of iron extraction from the stillage residue of the dichloroethane rectification column using oxalic acid.

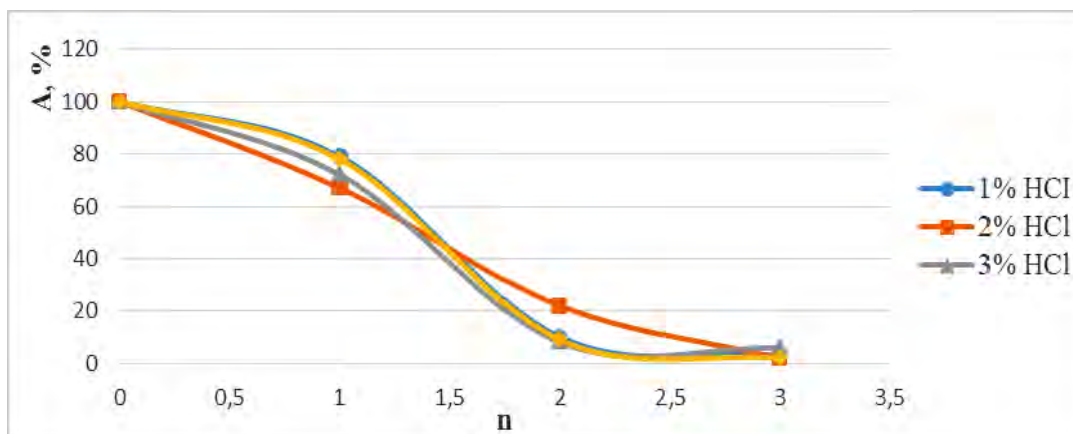


Fig. 3. The procedure and the rate of iron extraction from stillage residue of the column for the rectification of dichloroethane using hydrochloric acid

Conclusions

The research on the possibilities of iron extraction from the stillage residue of the dichloroethane production column revealed:

1. For the maximum extraction of iron from stillage residue, it is not appropriate to increase the number of successive extractions to more than 3.

2. Since the concentration of the extractant does not have a significant effect on the extraction process, taking into account the maximum iron extraction, it is appropriate to consider the 1 % concentration of the solvent to be optimal for extraction and phase separation for both the hydrochloric acid and the oxalic acid.

3. The ratio of 1: 2.5 of the phases of the stillage residue to the extractant is the most optimal.

4. Due to iron extraction in the stillage residue of the rectification column of dichloroethane production with oxalic acid, the concentration of which is equal to 1 %, in the ratio of 1: 2.5, the iron content decreases from 0.0592 to 0.0022 %, which allows increasing the

operation term of the combustion plant from 20 days to two months or more.

Since it has been found experimentally that the composition of insoluble compounds in the stillage residue of organochlorine waste contains iron compounds, the expediency of reducing their content in stillage residues combustion is a priority task. The industrial application of selective liquid extraction in this process can bring several advantages:

- increase the duration of operation of the equipment for organochlorine waste combustion;
- solve the problem of utilizing sulfur-alkali effluent of chemical production, which would be a significant contribution to the solution of the ecological problem of utilizing the sulfide-alkaline effluent from petrochemical enterprises.

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