

Study of the neutralization process of organoaluminum compounds

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Abstract. Methods for cleaning and neutralizing liquid production wastes are largely determined by the specifics of the enterprise and the physicochemical properties of the circulating substances. Wastes from organic synthesis enterprises containing benzene, toluene, xylene and similar substances are as a rule subjected to mechanical and physicochemical methods of purification. Wastewater containing difficult-to-oxidize impurities undergoes a multi-stage biological treatment, which can sufficiently oxidize the alcohols and carboxylic acids contained in the wastewater. In some cases, after complete biological treatment, to reduce color and destroy difficult-to-oxidize components, methods of deeper purification are used: coagulation, filtration, ion exchange, ozonation, etc. However, the presence of aromatic hydrocarbons in liquid waste reduces the effectiveness of biological methods and leads to the need for additional use of mechanical, chemical and physicochemical methods (sorption, distillation, ion exchange) or their combinations for complex purification and utilization.

1 Introduction

To neutralize organoelement impurities in liquid wastes, rectification or the method of liquid-phase oxidation (“wet” combustion) is used, the essence of which is the oxidation of the organic part of the sludge at a temperature of 150-350 °C and pressures from 2 to 28 MPa.

Given the variety of chemical compounds in wastewater from chemical and petrochemical enterprises, the organization of the treatment process for the latter should provide for the preliminary separation of wastewater depending on the impurities they contain [1-3]. Individual treatment is necessary for the correct choice of wastewater treatment methods based on the composition of the effluent and the level of contamination.

Today, one of the main environmental pollutants is hydrocarbon-containing wastewater generated during the transportation, storage of crude oil and its products, and the greatest variety of impurities is observed in wastewater from oil refineries (refineries). The main components of catalytic complexes used in various fields of chemistry and petrochemical industries have an exceptionally high reactivity with respect to various compounds, including water and oxygen. For example, as a catalyst for polymerization reactions of ethylene,

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propylene and butadiene, organometallic compounds such as trialkylaluminum (Ziegler catalyst) are widely used. By themselves, aluminum alkyls and their derivatives do not detonate, however, in the case of uncontrolled oxidation, self-ignition of the substances formed as a result of chemical transformations occurs [3].

The risk of self-ignition can be significantly reduced by diluting with suitable organic solvents (benzene, hexane, heptane). In turn, spilled solutions of aluminum alkyls are dangerous due to the accelerated evaporation of the solvent due to the heat released during the interaction of aluminum alkyls with atmospheric oxygen. As a result of heat release, aluminum alkyls thermally decompose to finely dispersed aluminum, hydrogen, and a mixture of hydrocarbon gases. The pressure generated during thermal decomposition in closed vessels creates an explosion hazard. An even greater probability of an explosion occurs in open vessels due to the formation of local concentrations of an explosive mixture of gases. In addition, with increasing temperature, organoaluminum compounds decompose with the release of olefins, which increases the risk of their explosion not only during self-ignition, but even when heated.

Thus, taking into account the specific properties of organoaluminum compounds in reactions with hydrogen, ethylene, isobutene, ethyl chloride, sodium and aluminum (finely dispersed and active, which can spontaneously ignite in air), the production of organoaluminum compounds should be considered one of the most flammable and explosive in the chemical industry. Waste organoaluminum compounds are also dangerous, as they contain active aluminum, organic solvents and residues of organoaluminum compounds [4].

Various methods are known for the deactivation of aluminum alkyls: from oiling and burning in special furnaces to the treatment of liquid waste with aqueous solutions of mineral acids or bases [5].

By incineration, it is best to destroy a small amount of aluminum alkyls, first diluting these substances with kerosene or mineral oil, or decomposing these solutions with some higher alcohol at low temperatures. After the end of decomposition, it is necessary to add a certain amount of water and heat the reaction mixture for the final decomposition of these substances.

The so-called "water" methods are based on the interaction of aluminum alkyls in solutions (for example, in benzene or ether) with water with the release of a hydrocarbon and the formation of aluminum hydroxide. Preliminary separation of the mixture of hydrocarbons and water obtained as a result of neutralization with aluminum hydroxide can be carried out by decanting.

Alkaline or acid deactivation of the catalyst requires the use of large amounts of acid or alkali, which leads to the need to neutralize a significant amount of wastewater, while the residual aluminum must be previously precipitated by neutralization and separated after settling and flotation. The difficulties of processing such wastewater include a high content of suspended solids, for the purification of which it becomes necessary to use various coagulants [6-9].

Sludge from the neutralization process (watered aluminum hydroxide) is allowed to be taken to the industrial waste landfill, however, liquid waste must be dehydrated and transferred to a pasty state with a moisture content above 85% before entering the landfill. However, the dehydration of the sludge is complicated by the fact that the aluminum hydroxide obtained as a result of the neutralization of alkyls is a white gelatinous suspension in water with a low settling rate.

Thus, it seems relevant to solve problems with liquid and solid wastes from the process of neutralization of organoaluminum substances by "water" methods [10-13]. At the same time, it is necessary to take into account the efficiency of liquid phase separation, compliance with COD standards when disposing of liquid waste, as well as the degree of dehydration and preventing the sludge from sticking together for unloading to the landfill.

2 Materials and methods

To solve these problems, experimental studies were carried out in several stages. At the first stage, the degree of separation of the initial mixture (into hydrocarbons, water and aluminum hydroxide) was compared during settling:

- 1) naturally without any additives,
- 2) in the presence of a flocculant (AN 923 SH),
- 3) in the presence of sodium aluminate.

At the second stage, a comparison was made between the stratification of the mixture and the caking of the sludge samples to be discharged from the decanter after cooling by various methods.

3 Results and discussions

The studies of the obtained samples at the first stage showed that the initial mixture after unloading from the apparatus (D-6504) remains chemically active for a long time, as evidenced by the release of heat due to the continuation of exothermic reactions of the previous stages of processing. This assumption is confirmed by excess pressure and temperature in the containers with the samples under study for five hours. These circumstances allow us to conclude that during the specified time, organoaluminum compounds form a physicochemical bond with aluminum hydroxide, and form a homogeneous solid mass (the precipitate clumps). Since the formed conglomerates do not collapse even when an external force is applied, it causes difficulty in removing the neutralization process sludge from the vessel. Results of the first stage of research:

1) with prolonged natural settling at room temperature (during the day), after mixing, the sludge crumbles and forms a suspension, which again stratifies within 30 minutes, which may indicate the final completion of the process of neutralization of organoaluminum compounds and, as a result, a change in the adhesion properties of particles $\text{Al}(\text{OH})_3$.

2) When flocculant AN 923 SH is added, a jelly-like structure is formed that binds fine particles of aluminum hydroxide, as a result of which the separated water is more transparent when the flocculant is added than without it.

3) Sodium aluminate, on the contrary, increases the volume of the sediment, reducing its density, and also does not lead to any noticeable positive effects.

As the first stage of research showed, after intensive cooling of the initial mixture, the precipitation of aluminum hydroxide occurs faster and in the form of fine particles (compared to natural cooling), which solves the problem of unloading. Hence, it was assumed that the sludge from the process of neutralization of waste products from the production of organoaluminum compounds and alpha-olefins in D-6504 must be intensively cooled with stirring to prevent the formation of a "plug" in the conical part of the apparatus, which was confirmed at the second stage of the experiment.

The objectives of the study at the second stage were to compare the stratification of the mixture and the caking of watered aluminum hydroxide precipitated with different cooling methods.

Experimental studies were carried out in a room located in close proximity to the waste neutralization plant for the production of aluminum-organic compounds and alpha-olefins at an ambient temperature of 14°C. Cooling was carried out in three independent ways: a) in a natural way, without forced heat removal; b) bubbling the mixture with air at a temperature of 10-12 °C; c) immersion of the container with the initial mixture in water, the temperature of which was maintained in the range of 20-22 °C.

The initial mixture, when extracted from a two-section container D-6504, was divided into 4 samples of equal volume, placed in identical containers. One of the samples was cooled

naturally without preheating (tNACH 1=28.5 °C) - was taken as a control sample, the rest were heated before the start of the experiment (tNACH 2,3,4=50 °C). The results of two identical experiments (lasting one hour) showed satisfactory convergence. Table 1 shows the dynamics of cooling of various samples during one experiment.

Table 1. Experiment results

Time from the beginning of the experiment, (min)	Temperature of sample 1, naturally cooled (control sample)	The temperature of a preheated mixture of olefins, aluminum hydroxide and water cooled in the following ways: (°C)		
		Temperature of sample 2, naturally cooled	Temperature of sample 3 cooled by air bubbling	Temperature of sample 4 placed in water
0	28.5	50.0	50.0	50.0
10	27.5	45.5	38.0	44.0
20	27.1	43.1	32.2	34.0
30	26.2	42.0	28.1	32.0
40	25.9	39.8	24.8	30.0
50	25.5	38.1	22.8	26.6
60	24.9	35.3	21.0	26.0

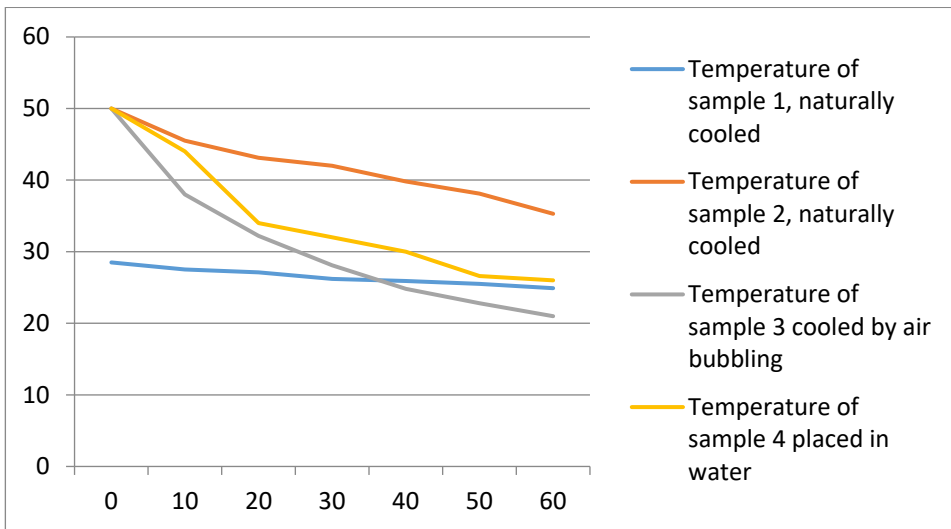


Fig. 1. Dynamics of sample temperature change under different cooling options.

A visual comparison of the samples after the end of the experiment and sedimentation of the sludge showed that the liquid phase from sample No. 3 is the most transparent in comparison with the control sample, which was not subjected to heating. The degree of separation of solid particles (aluminum hydroxide) and the liquid phase in sample No. 4 turned out to be higher than in sample No. 2. The content of suspended particles of aluminum hydroxide in the liquid phase of the control sample is maximum compared to the rest.

As a result of unloading the sludge after sedimentation of the samples, it was found that:

- the smallest amount of sediment on the inner surface of the container remains during bubbling cooling (sample No. 3);
- less intensive cooling (samples No. 2 and No. 4) leads to an increase in the amount of sticky solid phase;

- the largest amount of sediment in the tank remains after unloading the control sample (No. 1), the sludge of which is more prone to sticking than others.

Comparison of the dynamics of cooling and the degree of transparency of the liquid phase after settling showed that intensive cooling of heated samples contributes to better separation and sedimentation of the precipitate. In the control sample, which was not subjected to heating, there is no clear stratification in the liquid phase during settling, and the settled solid phase sticks to the vessel walls during unloading.

Results of analysis of samples of slime water.

Analysis of sludge water samples taken from the top, bottom and after bubbling of the tank pos. D-6504 of shop No. 6715 was carried out by employees of the Scientific and Technical Center of PJSC Nizhnekamskneftekhim. The research results are presented below in the form of reports.

Sludge water samples were delivered to the wastewater research laboratory. The water sample is a yellow liquid. The water sample (lower sampling) is a milky liquid with a small amount of sediment. Both samples had a specific odor.

pH (MI 8) and XAC (MI 25-A) were determined in sludge water samples.

Table 2. Results of the study of sludge water.

Selection point	pH, pcs	XAC, mgO ₂ /dm ³
Slurry water from tank (top)	-	-
Slurry water from tank (bottom)	10.15	384

In the sample (top) from the tank, it is impossible to determine the parameters under study, because the sample practically consists of hydrocarbons.

According to s/l 79169 dated 10/16/2018 on the analysis of sludge water.

According to S/L No. 79169 dated October 16, 2018, the STC analyzed samples of sludge water taken from the top, bottom, and after bubbling the tank pos. D-6504 c. No. 6715. The results of the analyzes are presented in Tables 1, 2 and 3.

Table 3. Sludge water results (bottom of tank pos. D-6504).

Component	Component concentration	
	% mass	mg/dm ³
Propylene trimers	0.02046	204.62
Propanol	0.00013	1.29
Isobutanol	0.00676	67.63
N-butanol	0.00003	0.34
Olefin C ₁₁ -C ₂₂	0.00632	63.34
Undefined component	0.002	20.01
pH, pcs pH	10.15	
XAC, mgO ₂ /dm ³	384	

Table 4. Sludge water results (without bubbling pos. D-6504).

Component	Component concentration	
	% mass	% mass
Acetaldehyde	0.00008	0.78
Olefin C ₁₁ -C ₂₂	0.00175	17.52
pH, pcs pH	10.15	
XAC, mgO ₂ /dm ³	384	

Table 5. The results of the hydrocarbon layer (top of the tank pos. D-6504).

Component	Component concentration, % mass
C ₁ +C ₆	0.022
C ₈	88.125
C ₁₀	9.979
C ₁₂	0.447
C ₁₄	0.389
C ₁₆	0.348
C ₁₈	0.325
C ₂₀	0.314
C ₂₂	0.028
C ₂₄	0.012
C ₂₆	0.012

3.1 Selection of brand and dosage of flocculant

The optimal choice of the brand and dosage of the flocculant is based on the study of the following characteristics:

- for the liquid phase: determination of density, XAC.
- for the solid phase: sludge structure, bulk density, liquid phase content in the sludge.
- for the filtration process: total filtration time, thickness of the resulting sediment.

During the work, the following samples of flocculants were tested, which, according to passport data, are effective when used in strongly alkaline media:

- anionic Flopam AN 923 VHM, Flopam AN934, Superfloc A130;
- cationic Superfloc C498, Flopam 4440.

3.2 Determination of particle settling rate

To determine the particle settling rate, waste water with a volume of 250 or 500 ml was placed in measuring cylinders, where an aliquot of the flocculant solution was added. The resulting suspension was thoroughly mixed. Further, a gradual settling of the solid phase was observed, and for 5 hours with an interval of 15 minutes, the height of the clarified liquid column in the cylinder was measured.

The use of cationic flocculants Superfloc C498, Flopam 4440, as well as anionic Flopam AN923 (0.1%) and Superfloc A130 in various doses did not show an increase in the settling rate relative to a blank experiment [14].

The results of testing the flocculant Flopam AN934 at different dosages are listed in Table 5. Based on the data obtained, graphs were constructed showing the dependence of the degree of particle settling on time (Fig. 2).

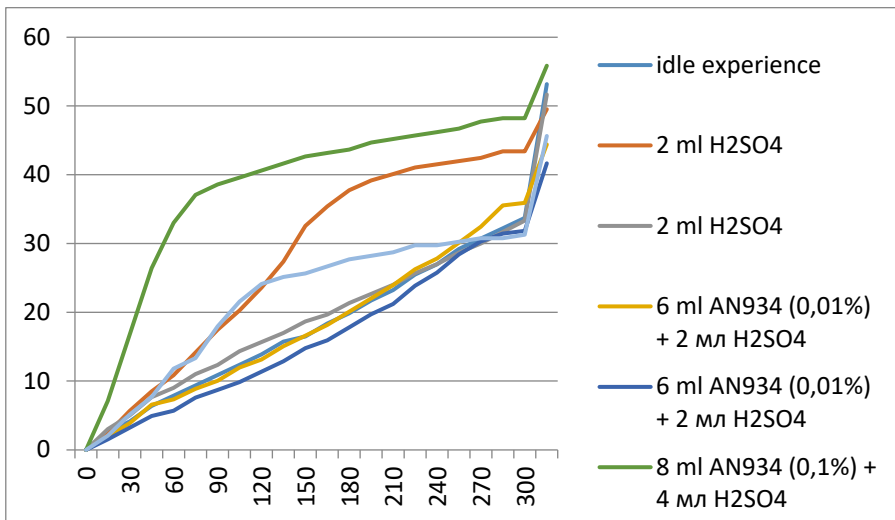


Fig. 2. Dependence of the degree of precipitation on time under different flocculation conditions (abscissa - degree of cooling in %, ordinate - experiment time).

Table 6. The degree of particle settling in samples with different doses of flocculant.

Time, min.	Settling degree, %						
	Idle experience	Dosage of flocculant and acid (based on 1000 ml of water)					
		2 ml H ₂ SO ₄	10 ml AN93 4 (0.01 %)	6 ml AN93 4 (0.01 %) + 2 ml H ₂ SO ₄	6 ml AN934 (0.01%) + 1 ml H ₂ SO ₄	8 ml AN934 (0.1%) + 4 ml H ₂ SO ₄	8 ml AN934 0.1%
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	2.62	2.36	3.00	1.93	1.52	7.11	2.05
30	4.12	5.66	5.00	3.86	3.22	16.75	5.13
45	6.37	8.49	7.67	6.56	4.92	26.40	7.69
60	7.87	10.85	9.00	7.34	5.68	32.99	11.79
75	9.36	14.15	11.00	8.88	7.58	37.06	13.33
90	10.86	17.45	12.33	10.04	8.71	38.58	17.95
105	12.36	20.28	14.33	11.97	9.85	39.59	21.54
120	13.86	23.58	15.67	13.13	11.36	40.61	24.10
135	15.73	27.36	17.00	15.06	12.88	41.62	25.13
150	16.48	32.55	18.67	16.60	14.77	42.64	25.64
165	18.35	35.38	19.67	18.15	15.91	43.15	26.67
180	19.85	37.74	21.33	20.08	17.80	43.65	27.69
195	21.72	39.15	22.67	22.01	19.70	44.67	28.21
210	23.22	40.09	24.00	23.94	21.21	45.18	28.72
225	25.47	41.04	25.67	26.25	23.86	45.69	29.74
240	26.97	41.51	27.00	27.80	25.76	46.19	29.74
255	29.21	41.98	28.67	30.12	28.41	46.70	30.26
270	30.71	42.45	30.00	32.43	30.30	47.72	30.77
285	32.21	43.40	31.67	35.52	31.44	48.22	30.77
300	33.71	43.40	33.33	35.91	31.82	48.22	31.28
1440	53.18	49.53	51.67	44.40	41.67	55.84	45.64

The data presented in Table 6 and Figure 2 showed that the dosage of AN934 flocculant at a concentration of 0.01% did not increase the settling rate of the particles. The addition of 8 ml of a 0.1% aqueous solution of the flocculant increases the settling rate in the first 4 hours of the experiment relative to the blank experience. In the interval from the 90th to the 150th minute, the values of the degrees of particle settling in this sample exceed the values for the blank experiment by approximately 10%. At the same time, according to Figure 2, the addition of 2 ml of concentrated sulfuric acid to the WW allows for a higher degree of precipitation by 5 hours.

The best results were obtained in the experiment with the simultaneous addition of 8 ml of a 0.1% flocculant solution and 4 ml of sulfuric acid, which allowed the pH to be lowered from 13 to 9-10. The most rapid process of deposition occurs in the first 90 minutes, during which the SW is clarified by 38.58%.

Thus, the optimal condition for the precipitation process is the addition of 8 ml of Flopam AN934 (0.1%) flocculant and 4 ml of sulfuric acid. Figure 3 shows comparative graphs showing the change in the degree of precipitation over time for the samples:

- with the addition of 8 ml of this flocculant solution,
- with the addition of 8 ml of flocculant solution and 4 ml of sulfuric acid,
- idle experience.

The results of determining the XAC of the liquid phase, as well as the hygroscopic moisture and the bulk density of the sediment are shown in Table 7, from which it follows that the flocculant additionally contributes to the separation of the organic phase.

Table 7. Characteristics of the obtained samples.

Value	Idle	Flocculant	Flocculant + acid
XAC bottom	-	59.2	340.4
XAC upper	-	325.6	429.2
Liquid phase density, g/cm ³	1.0106	1.006	1.0129
Bulk density of sludge, g/cm ³	1.1207	1.2207	1.1631
Sediment moisture, %	68.68	67.70	67.15
Sludge humidity after filtration, %	56.17	57.09	50.23

To carry out vacuum filtering of the precipitate, an installation was assembled, consisting of a Buchner porcelain funnel, in which a filter insert made of three layers of filter paper was placed [15]. A water jet pump was connected to the flask outlet tube. Prior to filtration, the height of the sediment layer was measured. The total filtration time and the volume of the loaded sediment are shown in table 8. After the liquid separation was completed, the height of the sediment layer and the volume of the filtrate were measured.

Table 8. Vacuum filtration results.

Value	Idle	Flocculant	Flocculant + acid
Sediment volume, ml	30	43	38
Total filtration time, s	30	60	60
Sediment layer height before filtration, mm	12	16	13

Sediment layer height after filtration stop, mm	8	11	8
Volume of filtrate, ml	10	12	15
Moisture loss, vol.%	33.33	27.91	39.47

The solid phase after settling in all samples is a loose, sticky, smearing cheesy white precipitate of an amorphous structure, the moisture content of which is close to 67-68%.

Since the moisture content of the filter cake obtained by pH reduction flocculation decreased by 27% and the moisture loss was 39.5%, it can be concluded that this sample releases water more easily during filtration.

It should also be noted that all samples are prone to cracking during filtration.

4 Conclusion

The use of Flopam AN934 flocculant accelerates sediment settling, helps to reduce its moisture content and improve filterability.

The best results are obtained by acidifying the waste water after neutralizing the organoaluminum to pH 9-10.

Optimum dosage: 8 ml of a 0.1% flocculant solution per 1000 ml of waste water with acidification of 4 ml of sulfuric acid (per 1000 ml) to reduce the pH value from 13 to 9-10.

The density of the liquid phase does not change significantly with the addition of a flocculant and in all cases is approximately 1.01 g/cm³.

Humidity of the sludge after filtration on a vacuum filter, depending on the conditions of the experiment, is reduced to 50-57%, which in all cases meets the requirements for receiving sludge to the industrial waste landfill.

Based on the results of the determination of XAC after settling with the use of a flocculant, it can be said that its addition contributes to the processes of separation and concentration of organic matter in the upper layer.

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