

Obtaining New Aluminium Water Clarification Coagulant from Spent Catalyst

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ABSTRACT

The viability of obtaining aluminium coagulant from the solid vinyl chloride production waste (spent catalyst) was studied. The new coagulant $Al_6(OH)_{13}Cl_5$ was established to be effective for clarifying water with high levels of suspended substances. The consumption of the new coagulant is significantly lower than that of conventional aluminium sulphate. The application of the new coagulant, aluminium chlorohydrate, makes it possible to enhance the properties of the purified water, in particular, its hardness. The method for obtaining the new coagulant and its use for water conditioning and purification was proved viable. The process flow sheet diagram for the coagulant production was suggested

Keywords: aluminium coagulant, water purification, catalyst recycling, water conditioning and purification, spent catalyst

INTRODUCTION

The principal emphasis today is on the increasingly important issues of environment protection and sustainable, evidence-based use of natural resources, including land resources, flora and fauna, water. The intensive development of industry, power engineering, agriculture and municipal engineering results in a steady, significant increase in the water consumption. The water quality requirements are also growing stricter.

Surface water (rivers, lakes) is usually hardly suitable for domestic purposes and drinking because of its turbidity, colour index and high microbial contamination. Therefore, to ensure the compliance with the water quality requirements, a special physico-chemical water treatment, conditioning, is applied. This usually includes clarification (removal of suspended and colloidal particles), colour removal and disinfection of natural

water. One of the most efficacious methods of water purification is coagulation. This process consists in destabilizing colloidal particles by adding coagulants [Yakymenko and Solodovnik 2018, Shablii 2012, Shablii 2013]. The most widely used coagulants are aluminium and iron salts.

Iron salts as coagulants can be used at low temperatures; they operate in a wide range of optimal pH and are able to remove unwanted taste and odour caused by hydrogen sulphide. During hydrolysis they form dense flocs, due to which hydrolysis proceeds fast. However, the bulk of large flocs settle rapidly, while small ones remain suspended in the solution for a long time, thereby deteriorating the water quality. The drawback of iron coagulants is their ability to form coloured complexes with certain organic compounds. During the hydrolysis, these coagulants cause significant acidification of water and, consequently, corrosion of the equipment, etc. Therefore, aluminium

salts are more widely used [Zawawi et al. 2020, Solodovnik 2019, Fouad et al. 2016, Zinoveev et al. 2021, Astrelin and Ratnaviry 2015].

Usually, aluminium sulphate and aluminium chlorohydrate are used for water conditioning and purification. Aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is obtained by treating bauxites, nephelines or clays with sulphuric acid. It is water-soluble and is relatively inexpensive. It is used as powder and 23–25% solution. When using the solution, there is no need to install special coagulant-dissolving equipment at water treatment stations. At coagulation, aluminium sulphate interacts with calcium salts (hydrocarbonates) and magnesium salts dissolved in water with forming flocs of aluminium hydroxide and gypsum.

Despite the considerable benefits, aluminium sulphate has certain drawbacks. It is effective in a small range of pH – 5–7.5. When using it at low temperatures, coagulation (flocs formation and sedimentation) proceeds slowly. The purified water contains excessive amounts of aluminium compounds, and this poses the risk of excessive aluminium getting into the purified water and flocs formation after the water has been supplied to the consumers [Nowacka et al. 2014, Liqing Li 2021].

Aluminium chlorohydrate salts $\text{Al}_m(\text{OH})_n\text{Cl}_{3m-n}$ (Oxa) offer significant benefits as compared to most widely used aluminium sulphate. When using them, the water salt content increases not so significantly as in case of adding aluminium sulphate. They are effective in a wider range of pH (6–9). Due to the high level of water-soluble aluminium, the duration of flocs formation drops significantly and the rate of their sedimentation increases. They effectively perform at low temperatures. Lower doses of the reagents used for water clarification result in low residual aluminium levels, increased filter run, improved water stability index, increased disinfecting power due to deeper coagulation of impurities [Homelia et al. 2017].

Besides, aluminium chlorohydrates, in comparison with aluminium sulphate, less strongly reduce water alkalinity, which makes it possible to use them for water purification with a low alkalinity without prior alkalization [Radovenchik et al. 2014, Homelia et al. 2017].

Aluminium chlorohydrates are still obtained using expansive metal aluminium or freshly precipitated aluminium hydroxide. This method needs sophisticated equipment for carrying out

the processes at an elevated pressure and temperature. It should be noted that there are practically no aluminium deposits in Ukraine and almost all of this metal is imported. The operating production facilities do not meet the demand for them created by water supply stations, let alone wastewater treatment stations and water conditioning and purification stations. In other words, such coagulants are expensive albeit effective.

Water conditioning and purification can also be based on a mixed iron-aluminium coagulant, which is prepared using solutions of aluminium sulphate and ferric chloride at a ratio of 1:1 by weight. The recommended proportion can be changed depending on the specific operating factors. Water treated with mixed coagulant does not cause hard deposits even at low temperatures. Flocs formation and sedimentation proceed quite rapidly. The formed flocs settle uniformly. The application of the mixed coagulant allows a significant reduction in the consumption of the reagents [Yakymenko and Solodovnik 2018, Shablii 2012]. However, using these two coagulants entails serious complication of the purification technology and causes an increased salt content in the purified water. Each of the above-described coagulants has its benefits and disadvantages. Therefore, we carried out the study aimed at obtaining new coagulants that would meet most of the listed requirements.

The aim of the study was: (i) to analyse the raw materials available at Karpatnaftokhim and select suitable ones for obtaining the coagulant, (ii) to determine the optimal technological conditions for the coagulant synthesis, and (iii) to develop the process flow sheet for the coagulant synthesis.

MATERIALS AND METHODS

At different stages of the production, Karpatnaftokhim uses various catalysts. Mostly, those are supported catalysts, in which the active agent is affixed to the support, usually inert. For instance, in the vinyl chloride production, at the oxychlorination stage, the reaction occurs in the fluidized bed of the catalyst. Copper chloride applied on aluminium oxide is used as a catalyst. This catalyst has a highly developed porous structure and, correspondingly, high specific surface area and contact surface area. The CuCl_2 mass fraction is 4.5–5.5% and the rest is aluminium

oxide. In the process of using the catalyst, only the CuCl_2 mass fraction decreases, and Al_2O_3 stays unchanged. This aroused the interest in using this spent catalyst for synthesizing aluminium chlorohydrates. The first stage of the study was aimed at developing the technique for obtaining aluminium chlorohydrate from the spent aluminium-containing oxychlorination catalyst.

Hydrochloric acid (6 mol/dm^3) was added in small portions of 20 cm^3 to the weighed quantity of the catalyst. The catalyst was taken in excess. The reaction mixture was heated in the water bath to speed up the process. To achieve better dissolution, the mixture was allowed to stay for two days. After that, the solution was poured off and the precipitate was dried and weighed. Based on the difference in the weights of the catalyst before and after the reaction, the amount of the substance that had reacted (dissolved) was evaluated. This made it possible to calculate the degree of recovery, which amounted to 47%.

By analysing the results, we can state that using spent oxychlorination catalyst as a recyclable material for producing the coagulant allows obtaining a partial solution to the problem of the disposal of the solid waste containing mostly aluminium compounds and small amounts of copper chloride. The amount of solid waste is respectively reduced by 47%, which is economically and environmentally beneficial for Karpatnaftokhim.

The solution obtained after the contact of the acid with the catalyst contained the compounds of aluminium and copper. To separate this mixture, the displacement reaction of copper with more active aluminium ($\Delta E = +0.34 - (-1.66) = 2 \text{ V}$) was used. Scrap aluminium wire was added to the solution. To achieve a complete displacement of copper from the solution, aluminium was added in excess. The reaction proceeded violently with a release of the gas and formation of a highly dispersed phase – elemental copper powder, which gradually settled down on the flask bottom. The contents of the flask were filtrated. No copper ions were detected in the filtrate, and the percentages of aluminium and chlorides are presented in Table 1. Based on the outcomes and calculations, the formula of the obtained substance was

determined to be $\text{Al}_6(\text{OH})_{13}\text{Cl}_5$. To verify the viability of using it for water purification, experimental studies were carried out.

RESULTS AND DISCUSSION

It is known that the effect of coagulation depends on the content of the active agent in the reagents that forms flocs of metal hydroxides in the water. To compare the obtained substance with other conventional coagulants, the aluminium content was expressed as that of Al_2O_3 . According to the calculation, the Al_2O_3 content in the solution of the obtained coagulant is 30.74% and, calculated with reference to the dried substance, it is 54.59%. By way of comparison, in purified aluminium sulphate (state standard GOST 12966–85), the Al_2O_3 content is to be no less than 13.5%, and in aluminium chlorohydrate $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 6\text{H}_2\text{O}$ it is to be 40–44%. Therefore, the obtained $\text{Al}_6(\text{OH})_{13}\text{Cl}_5$ has a high content of the main substance, which allows achieving maximum coagulation at a lower consumption of the reagent as compared to other coagulants.

To induce coagulation of colloidal particles, it is necessary to reduce their ζ -potential to the critical value. One of the methods to reduce the ζ -potential of a colloidal system is raising in the water the concentration of electrolytes, which are coagulants [Kulskiy 1983]. Hence, the coagulation rate and efficiency are proportional to the metal cation concentration, i.e. the higher the concentration of the coagulant, the more effectively the process of floc formation proceeds. However, it should be taken into account that as the amount of the coagulating agent increases, a charge reversal can occur, increasing the water turbidity to the initial value. As it was mentioned above, the aluminium content in the obtained coagulant is quite high. Therefore, a little amount of aluminium-containing coagulants is needed for effective coagulation.

The second stage was the experimental study of the efficiency of the obtained coagulant, namely the selection of its concentration and dose. Therefore, to study the properties of $\text{Al}_6(\text{OH})_{13}\text{Cl}_5$, its 1%, 2% and 5% solutions were prepared. Using the optimal dose of the coagulant ensures the maximum removal of contaminants from the water and the minimum residual levels of aluminium in the water (state standard GOST 2874–54) [6, 12–14]. The optimal concentration of the

Table 1. Coagulant composition

Item number	Composition	Value
1	Aluminium, % by weight	16.27
2	Chlorides, % by weight	18.34

coagulant was evaluated in the following way. For the study, water with a high content of suspended particles (1600 mg/dm^3) was taken. The water was poured into three cylinders, 1000 cm^3 into each. Then 10 cm^3 of 1%, 2% and 5% solutions of $\text{Al}_6(\text{OH})_{13}\text{C}_{15}$ was added into the cylinders, respectively. After adding the coagulant, the water was intensively stirred for 2 min., after which it was allowed to settle. In the purified water the amount of suspended substances was determined gravimetrically in 30 min, 2 hours, 5 hours and 24 hours after adding the coagulant.

It should be noted that after adding the coagulant into the system, pH of the water under study decreases. This is due to the formation of acidic compounds as a result of the coagulant hydrolysis. This is a fully expected result because as the weight percent of the aluminium-containing substances increases, the amount of the hydrolysis products also increases. The results of the analyses are presented in Figure 1.

It should be noted that as soon as several minutes after adding the 1% coagulant solution, the water went turbid and then the flocs formed intensively and the precipitate settled down. Figure 1 shows that in the case of using 1% solution, within the first 30 min. after adding the coagulant an abrupt reduction in the concentration of suspended substances was observed. For instance, in 30 min. after adding the reagent the amount of suspended substances decreased by 89.4% as compared to the initial amount. When 5% and 2% solutions were used, the clarification process occurred less intensively. For instance, in 30 min. after adding the coagulant the colloidal particles

concentration dropped by 21.3% for 5% solution and by 34.6% for 2% solution.

The results of the analysis reveal that the best performance of the clarification process is achieved when adding 1% coagulant solution to the water since in 24 hours almost complete clarification was observed. When adding 2% and 5% solutions, the amount of suspended substances was reduced by 94.6% and 85.3% compared to the initial value, respectively. In case of these solutions, the incomplete clarification can be put down to the charge reversal of some colloidal substances due to the high concentration of the coagulant. Therefore, it was decided to use 1% solution of the obtained coagulant.

The coagulation process is significantly impacted by the coagulant dose. The optimal dose is the lowest one that ensures the best clarification result. The value of the coagulant dose depends on the quality of the water being treated and the degree of its contamination with colloidal and suspended particles. Therefore, the optimal amount (dose) of the coagulant for specific water is usually estimated experimentally. To determine the optimal dose of the coagulant to be added to the water containing 1600 mg/dm^3 of suspended substances, different volumes of the 1% $\text{Al}_6(\text{OH})_{13}\text{C}_{15}$ solution were added. After that the water was intensively stirred. In 30 min. the purified water was analysed for the concentration of suspended particles. The changes in the hardness and chloride levels in the water treated with the coagulant were evaluated (Table 2).

Figure 2 shows that the coagulant dose of 1 ml/dm^3 suffices to significantly reduce the

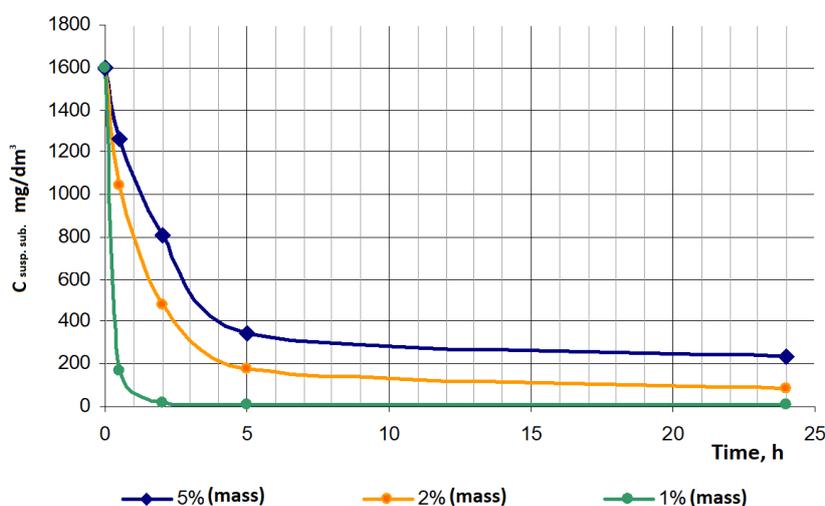


Figure 1. Effect of the coagulant concentration and clarification time on the concentration of suspended substances

concentration of the suspended substances in water. In these conditions, the water turbidity dropped by 74.2%. For the increased dose of 5 ml/dm³, the concentration of colloidal particles is 219 mg/dm³, i.e. it decreases by 86.3 % of the initial value. Further increase in the coagulant dose does not result in any considerable reduction in the concentration of suspended substances. For instance, adding 10 ml/dm³ the colloidal substances content decreases by 89.4%, while adding 20 ml/dm³ results in a 90.8% reduction.

Besides, the change of the concentration of colloidal substances in the water during the clarification was studied. As Figure 3 shows, intensive clarification takes place within 1–1.5 hours after adding the coagulant. During this time, active adsorption of most dispersed substances occurs on the highly developed specific surface area of aluminium chlorohydrate. Following that period, the clarification degree hardly changes. The coagulant dose also influences the chloride level and water hardness (Table 2).

The results show that an increase in the coagulant dose results in an increase in the chloride level in the purified water. The amount of the reagent also influences the water hardness. For instance, for 1 ml/dm³ and 5 ml/dm³, Ca²⁺ level decreases as compared to the initial value, but rises as the dose increases. This is put down to the fact that for low coagulant concentrations, the formed flocs of aluminium hydroxide partially adsorb bicarbonate salts present in the water. As the dose of the reagent increases, the amount of the acidic products of hydrolysis, which transform insoluble suspended calcium carbonate particles into soluble compounds, also grows. Based on the analysis of the obtained experimental data, it was found that the optimal dose of 1% Al₆(OH)₁₃Cl₅ solution

Table 2. Purified water composition

Item number	Coagulant dose, ml/dm ³	Cl ⁻ level, mg/dm ³	Hardness, mmol/dm ³
1	-	95	12
2	1	200	3
3	5	300	4
4	10	550	12
5	15	745	22
6	20	1305	37

is 5 ml/dm³. According to the results presented in Figure 3, it was calculated that when adding the said amount of the coagulant, 0.7 hour of clarification results in the clarification degree of 87.5% and water hardness of 4 mmol/dm³ (Table 2). It should be noted that when using the obtained coagulant, the residual aluminium level in the purified water is within the guideline range and does not exceed 0.3 mg/dm³.

The studies the results of which are discussed above and literature data analysis provided the basis for developing the process flow sheet diagram for obtaining the new coagulant, aluminium chlorohydrate (Al₆(OH)₁₃Cl₅). According to the developed flow sheet diagram, spend ethylene oxychlorination catalyst is fed into the tank 2. Hydrochloric acid is also pumped into that same tank. In two days, the obtained solution goes into the cementation reactor 3, which was first filled with aluminium scrap. The undissolved catalyst is discharged through the bottom of the tank 1 for further disposal. In the cementation reactor the solution is additionally enriched with aluminium. In two days the obtained coagulant is pumped into the tank 4, wherefrom it goes to the consumers. The copper precipitate through the bottom in the tank 3 goes for disposal.

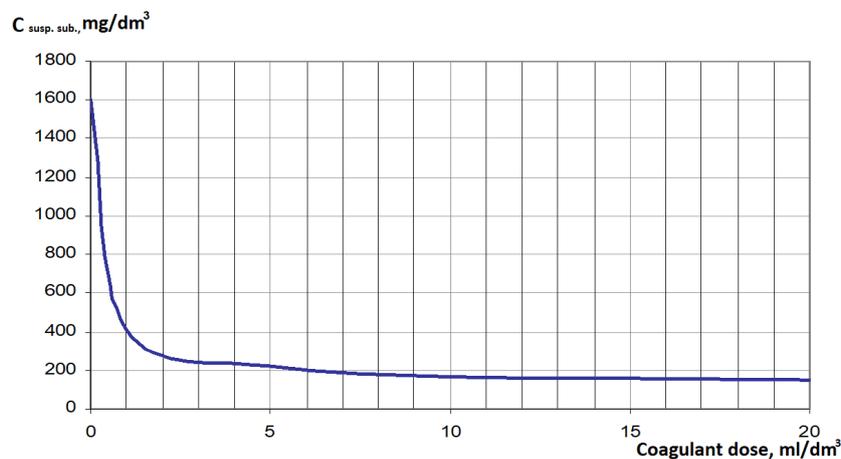


Figure 2. Effect of the coagulant dose on the concentration of suspended substances in the water

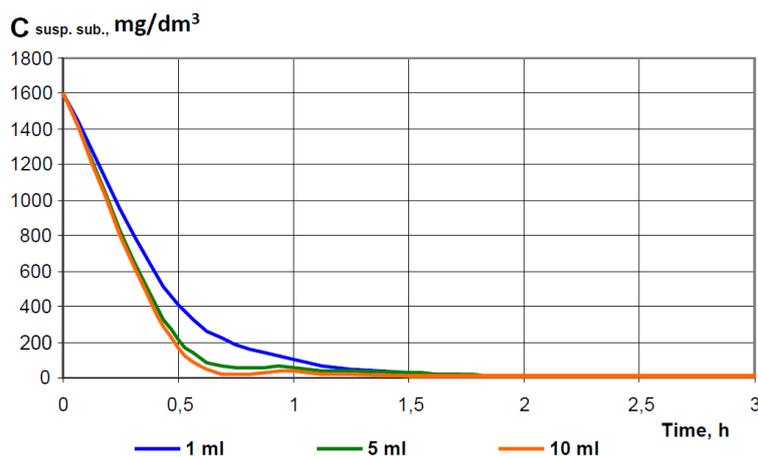


Figure 3. Effect of the coagulant dose and clarification time on the concentration of suspended substances in the water.

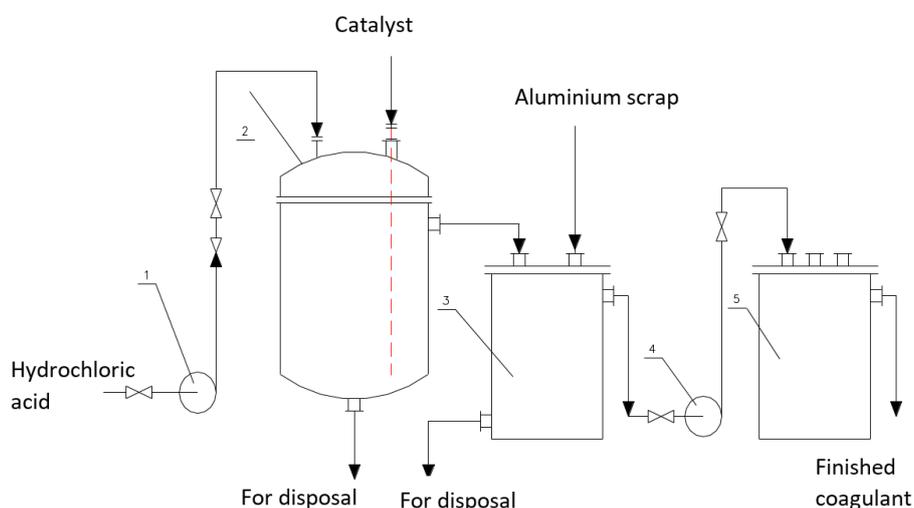


Figure 4. Flow sheet diagram for obtaining $Al_6(OH)_{13}Cl_5$:
1, 4 – pumps, 2 – reactor, 3 – cementation reactor, 5 – tanks for storing the finished product.

CONCLUSION

The method of obtaining the new aluminium chlorohydrate coagulant from spent catalysts was developed. Such coagulants can be adapted for various sources of water supply, which differ in the mineral composition and requirements to the quality of the clarified water. Obtaining the coagulant mainly relies on using industrial waste – the spent catalyst, which makes it possible to improve the ecological well-being of Karpatnaftokhim and to reduce the adverse impact of the solid waste on the environment. If necessary, a coagulant with specific properties can be obtained without significant changes to the process flow sheet diagram.

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