ISNN 3030-3907

2026/4
VOLUME 8

DEVELOPMENT OF SCIENCE

ILMIY JURNAL



Development of science

Ilmiy jurnal

2026/4 VOLUME 8

ISSN 3030 -3907

Ilmiy jurnal OAK rayosatining 2024 yil 27 sentabrdagi 361-son qaroriga asosan 02.00.00 kimyo fanlari hamda 2025 yil 12 fevral 367- son qaroriga asosan 05.00.00 texnika fanlari bo‘yicha falsafa doktori (PhD) va fan doktori (DSc) ilmiy darajasiga talabgorlarning dissertatsiya ishlari yuzasidan dissertatsiyalari asosiy ilmiy natijalarini chop etish tavsiya etilgan milliy ilmiy nashrlar ro‘yxatiga kiritilgan.

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ISSN 3030-3907

Development of science ilmiy jurnali 2024 yil 15 aprel kuni №256445 sonli guvohnoma bilan Davlat ro‘yxatidan o‘tgan.

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ISSN 3030-3907

VARIETIES OF ALUMINUM COAGULANTS AND THEIR FUNCTIONAL CHARACTERISTICS

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Annotation. Today, various coagulants are used in the world to purify various industrial waters produced in the oil and gas processing industry. This leads to an increased demand for coagulants. This article provides detailed instructions on how to obtain modern coagulants with preserved aluminum, their main characteristics and types.

Keywords: oil, gas, technical waters, coagulant, aluminum, aluminum sulfate, aluminum oxide

Аннотация. Сегодня в мире используются различные коагулянты для очистки различных промышленных вод, образующихся в нефтегазоперерабатывающей промышленности. Это приводит к увеличению спроса на коагулянты. В этой статье приведены подробные инструкции по получению современных коагулянтов с сохранением алюминия, их основные характеристики и виды.

Ключевые слова: нефть, газ, технические воды, коагулянт, алюминий, сульфат алюминия, оксид алюминия

Annotatsiya. Bugungi kunda dunyoda neft va gazni qayta ishlash sanoatida ishlab chiqariladigan turli sanoat suvlarini tozalash uchun turli koagulyantlar qo‘llanilmoqda. Bu koagulyantlarga bo‘lgan talabning oshishiga olib keladi. Ushbu maqolada alyuminiy saqlangan zamonaviy koagulyantlarni olish, ularning asosiy xususiyatlari va turlari haqida batafsil ko‘rsatmalar berilgan.

Kalit so‘zlar: neft, gaz, texnik suvlar, koagulyant, alyuminiy, alyuminiy sulfat, alyuminiy oksidi

INTRODUCTION.

Aluminum – containing coagulant – $Al_2(SO_4)$ is widely used in the process of water purification. To a lesser extent, aluminum chloride is used, as well as sodium aluminate.

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Currently, purified aluminum sulfate in production conditions is mainly obtained from aluminum hydroxide. This method is the simplest and most rational, it allows you to obtain a high-quality product with a low content of iron oxide.

Aluminum hydroxide is an intermediate product in the production of alumina, which is obtained by the Bayer alkaline method mainly from high-quality bauxite. Alumina is produced in smaller quantities from nephelines by sintering them with limestone, as well as from alunites by an alkaline reduction method [Halilov S.H., 2022, 601-604].

The production of aluminum sulfate consists of two main technological stages – decomposition of hydroxide with sulfuric acid and crystallization of the resulting product. The interaction of aluminum hydroxide with sulfuric acid is described by the reaction:

$$2Al(OH)_3 + 3H_2SO_4 + Q_q = Al_2(SO_4)_3 + 6H_2O + Q_q$$

In [Edelstein A.S., 1998, 3-565], the solubility of aluminum hydroxide freshly deposited and obtained at alumina plants in dilute sulfuric acid solutions was studied, depending on particle size, impurity content, storage time, and methods for preparing hydroxides. It was found that fine-grained aluminum hydroxide is better soluble in sulfuric acid than coarse-grained. Long-term storage of hydroxide reduces the rate of its dissolution in sulfuric acid. Amorphous hydroxide dissolves faster than crystalline hydroxide.

Aluminum sulfate can be obtained by decomposition of aluminum hydroxide with a stoichiometric amount of 45-50% sulfuric acid at 110-120 °C for 40 minutes. By lowering the acid dose to 95-90%, a product with a higher content of aluminum oxide is obtained with satisfactory crystallizability [Ostrovskij, 2007, 88-94].

Aluminum sulfate is produced in periodic or continuous devices with a capacity of 10-150 thousand tons of product per year.

In [Chen S., 2018, 322-328; Du, 2018, 7201-7215], the decomposition of high-iron bauxite with sulfuric acid was studied. Bauxite was characterized by the following chemical composition (in %): Al_2O_3 - 40.8; Fe_2O_3 – 27.0; SiO_2 – 8.7; TiO_2 – 2.2; CaO – 0.75; MgO – 0.2; Na_2O+K_2O – 0.5; pp.p. – 0.7. With an increase in temperature from 20 to 98 °C and the concentration of sulfuric acid from 10 to 60% extraction of aluminum and iron oxides into the solution increases, reaching 78.9 and 71%, respectively, at 98 °C and 1hour exposure. The degree of extraction of these components at boiling point depends on the duration of the process: with the decomposition of 60% H_2SO_4 bauxite, with an increase in the duration of the process from 5 to 90 minutes, the extraction of Al_2O_3 increases from 67.6 to 94%, and Fe_2O_3 – from 57.3 to 93.1%. boehmite bauxites are worse opened with sulfuric acid. Exposure to 10 n sulfuric acid for 1 hour leads to complete dissolution of

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gibbsite, partial (by 30%) – kaolinite and insignificant – boehmite. After firing at 550°C and subsequent decomposition of bauxite for 3 hours, 90% Al_2O_3 is extracted into the solution.

In [Chuang, 2007, 187-195] it is proposed to decompose bauxite with dilute sulfuric acid at 135 °C in a steel reactor lined with acid-resistant tiles.

Initially, 93% H_2SO_4 is fed into the solution, it is diluted with washing waters from sludge washing and heated to a boil, after which bauxite is introduced in small portions to avoid foaming and $Al_2(SO_4)$ is obtained.

The process of obtaining aluminum sulfate from low-quality bauxites is described. Another source of aluminum-containing coagulant is kaolin clays.

In [Mahmudov, 2023, 72-75] kaolins are difficult to open with sulfuric acid. Despite the large number of works devoted to the study of thermochemical transformations of kaolin, there is still no consensus on the mechanism of the process. Based on a complex of studies using physico-chemical methods, including X-ray phase analysis and IR spectroscopy, the mechanism of thermochemical transformations of kaolinite can be represented by the following reactions:

$$Al_2Si_2(OH)_4 \xrightarrow{450\text{-}550^oC} Al_2O_3 * 2Si_2O_2 + 2H_2O;$$

$$Al_2O_3 * 2SiO_2(OH)_4 \xrightarrow{830\text{-}850^oC} j\text{-}Al_2O_3 + 2SiO_2;$$

$$3(j\text{-}Al_2O_3) + 2SiO_2 \xrightarrow{900^oC} 3Al_2O_3 * 2SiO_2.$$

Aluminum alum is also used as coagulants, but they are used less often than aluminum sulfate, which is due to their high cost. In addition, alkali metal sulfates, which are part of aluminum alum, saline the purified water, reducing coagulating properties. Therefore, ammonium-, potassium- or sodium-aluminum alum is used, which has good coagulating properties, as well as more affordable and cheaper ones. Ammonia alum is used for the treatment of chlorinated water.

An aluminum-containing coagulant can also be obtained from nepheline. In this case, it is advantageous to obtain alum, which is a more effective coagulant.

Nepheline reacts with sulfuric acid at room temperature with the release of a large amount of heat by reaction:

$$(Na, K) / AlSiO_4 / + 2H_2SO_4 + nH_2O \rightarrow (Na, K) / Al(SO_4)_2 * 12H_2O + SiO_2 + (n-12)H_2O\uparrow$$

The sulfatization process is greatly influenced by the concentration of sulfuric acid and its dose. The higher the concentration of sulfuric acid, the higher the temperature the reaction mass is heated due to the released heat of the reaction. At the same time, more water is released into the vapor phase and alum is formed with a lower content of crystallization water. As a result, anhydrous alum can be

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formed – double sodium-potassium aluminum sulfates. The choice of the acid concentration is primarily determined by the possibility of separating the silica sludge from the sulfuric acid solution [3-4].

In [Dzhamolovich, 2024, 85-89], technologies have been developed for the production of anhydrous aluminum chloride from various aluminum-containing raw materials. The monograph by B.G. Rabovsky and A.A. Furman systematizes practical experience and theoretical knowledge in this field.

For oxide raw materials (natural aluminum-containing ores or alumina), chlorination is carried out only with a reducing agent. The reducing agent in this case is coal, clay–like reducing agents are also used – phosgene, generator gas, carbon monoxide, from solid ones – coal pitch and coke. In the presence of these reducing agents, the chlorination process proceeds at temperatures from 1000 to 1100 °C.

Some researchers, in addition to chlorine, suggest the use of carbon tetrachloride, sulfur chloride, hydrogen chloride, etc. as chlorinating agents. It is noted that alumina reacts with hydrogen chloride at a higher temperature, and the reaction itself is reversible. When a small amount of coal is added to the reaction mixture, increased formation of aluminum chloride is noted. When mixing sulfur chloride and chlorine, there is an increase in both reducing and chlorinating properties. Therefore, a lower temperature is necessary for this reaction to occur. The complete interaction of carbon tetrachloride with alumina occurs at a temperature of 390 °C, while $AlCl_3$ is formed.

For alumina, chlorinating agents in the presence of aluminum ores or carbon can also be iron, sodium and calcium chlorides.

In the monograph [Makhmudov, 2023, 63-65], several methods for aluminum chlorination are considered, in particular, chlorination in a fluidized bed (the fluidized bed is created by inert materials, for example, sand, or inert gases).

Industrial technological schemes for the production of aluminum chloride, which were developed by Soviet, German and American specialists, are also presented here.

In production conditions, the production of aluminum chloride consists of several stages. At the first stage, concentrated carbon monoxide is produced in special generators in which coal coke is gasified with oxygen. In the second stage, kaolin briquettes are prepared, dried and calcined, the main task of the second stage is the chlorination of kaolin briquettes, which is carried out in the presence of carbon monoxide with chlorine gas in a continuous shaft furnace.

Aluminum chlorides are obtained by the basic reaction:

$$Al_2O_3 + 3Cl_2 + 3CO \longrightarrow 2AlCl_3 + 3CO_2$$

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Silicon oxide also reacts with chlorine by reaction:

$$Si_2O_3 + 2Cl_2 + 2CO \rightarrow SiCl_4 + 2CO_2$$

As shown in [Mahmudov, 2021, 86-95], when aluminum and silicon oxides interact with chlorine, the phenomenon of mutual catalysis is noted, when the rate of chlorination of mixtures is higher than when chlorinating individual oxides. According to [19-20], silica and alumina are chlorinated in the temperature range from 550 to 800 °C in the same ratios as in the feedstock.

The literature provides contradictory data on the interaction of chlorine with oxides at higher temperatures. Thus, Kocharovsky [Ostrovskij, 2007, 88-94], investigating the chlorination of Polish clays, found that at temperatures above 900 °C, the yield of $AlCl_3$ decreases. Meanwhile, according to Kocharovskys data, confirmed by long-term practice, the yield of $SiCl_4$ in the temperature range from 1000 to 1200 °C reaches minimum values.

These contradictions can be explained by the fact that in [22] the results were obtained in a shaft furnace of continuous countercurrent action, that is, under conditions of a secondary reaction:

$$2Al_2O_3 + 3SiCl_4 \rightarrow 3SiO_2 + 4AlCl_3$$

In [Edelstein, 1998, 3-596], the results of a study on the chlorination of various types of aluminum-containing raw materials are presented. The authors studied the chlorination process of the North Voronezh bauxites, which was carried out in a fluidized bed. It is shown that all oxides included in the bauxite composition are chlorinated in the fluidized bed. The most easily chlorinated are iron and titanium oxides. Optimal chlorination conditions were found, at which the degree of chlorination of iron and titanium oxides reaches 98%, aluminum oxide – 65%, and silicon oxide – 20-35%.

In [Chen, 2018, 322-328], a technique was developed for the selective chlorination of bauxites in a fluidized bed to produce aluminum oxide in the temperature range from 800 to 900 °C with a mixture of chlorine and silicon tetrachloride. Chlorination of powdered bauxite in a fluidized bed with 1% carbon makes it possible to remove 65% of iron from it at a temperature of 800 °C, while losing 8% of aluminum (for Uglian bauxite). The chlorination of Prosyanovo kaolin of Ukhta and Severoonezhsky bauxites in the filter layer was studied.

The authors [Edelstein, 1998, 3-596] studied the process of chlorination of the mineral part of the Ekibastuz carboniferous rocks. It is shown that during chlorination of these rocks, the yield of iron and silicon oxides is 98-100%, and the yield of aluminum oxide is 91-96%. It is proposed to carry out preliminary hydrochloric acid treatment to pre-release this raw material from silica, or to

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suppress the process of chlorination of SiO_2 with silicon tetrachloride, to separate silicon and aluminum oxides.

The authors [8] present a developed method for selective low-temperature reduction of a mixture of iron and aluminum chlorides to metals. It is recommended to carry out the process in an inert gas stream containing hydrocarbons, for example, methane, as well as iron and aluminum chlorides.

The chloride reduction process is recommended to be carried out on the surface of iron, which increases the selectivity of reduction and significantly reduces the temperature of the process: $AlCl_3$ – up to 450 °C, $FeCl_3$ – up to 350 °C, the authors recommend using silicon or manganese instead of jelly, however, on their surfaces the reduction of aluminum chloride occurs at higher temperatures, 950 and 800 °C, respectively.

H. Safiev et al. [Edelstein, 1998, 3-596] studied the decomposition of nepheline syenites from the Turpi deposit of the Republic of Tajikistan by chlorination to produce oxides, and also considered the main thermodynamic characteristics of the processes occurring during chlorination of the main minerals of the nepheline syenite rock (nepheline – $Na_{0,78}K_{0,22}AlSiO_4$, albite – $NaAlSi_3O_8$, microcline – $KAlSi_3O_8$, calcite – $CaCO_3$, hematite – Fe_2O_3 and goethite is FeO(OH). This method is based on the use of coals, carbon monoxide, methane and phosgene and methane as reducing agents. The following probable ways of processes have been identified:

$$M + X + C \longleftrightarrow EX + CO_2,$$

$$M + X + CO \longleftrightarrow EX + CO_2,$$

$$M + X + COCl_2 \longleftrightarrow EX + CO_2,$$

$$M + X + CH \longleftrightarrow EX + CO_2 + H_2O.$$

where: X is chlorine gas; M is the corresponding mineral; EH is a mixture of chlorides of the corresponding elements in the composition of minerals.

Based on the comments, it can be assumed that feldspar and hematite are chlorinated more effectively when using coal as a reducing agent, and when chlorinating calcite, it is more rational to use methane as a reducing agent. Chlorination of minerals in the presence of a reducing agent – carbon monoxide in the studied temperature range is thermodynamically impossible, and when using phosgene as a reducing agent, all minerals except goethite must be chlorinated equally vigorously.

The chemical foundations of the chlorine method of processing aluminosilicate ores of Tajikistan were studied, rational conditions for the chlorine

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process were proposed, and basic technological schemes for the production of aluminum-containing coagulants were developed.

Thus, the high ability of chlorine to enter into chemical reactions, as well as the ability of chlorides to interact with other compounds, make it possible to isolate valuable components from processed raw materials, including aluminum chloride, a coagulant for water purification.

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FAOLLIGIGA TA"SIR ETUVChI OMILLARNI TADQIQ QILISh // Science and Education. – 2021. – T. 2. – №. 3. – S. 86-95.

ISSN 3030-3907