Research of the component of the hybrid aluminosilicic reagent
-aluminum sulfate in the process of water treatment

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Abstract. The work is devoted to theoretical and experimental studies of the process of
hydrolysis of an aluminum salt in an aqueous solution. Quantitative dependences of secondary
contamination by aluminum ions in the process of hydrolysis of aluminum sulfate on the initial
salt concentration and pH of the solution are derived, and the range of pH values at which the
largest number of uncharged aluminum hydroxide complexes are formed is determined.
Experimental studies have confirmed the theoretical dependence of the pH value of the solution
on the amount of aluminum sulfate dissolved in water.

1. Introduction
At present, one of the urgent tasks is to obtain clean drinking water. One of the most popular methods
of water purification is a reagent method based on the processes of coagulation and flocculation, in
particular, using aluminum-containing reagents. The use of such reagents can lead to an increase in the
concentration of residual aluminum, which leads to secondary contamination of the water being purified
by aluminum ions. However, when using a hybrid aluminosilicic coagulant-flocculant FC - 9, the
residual aluminum concentration is significantly reduced due to the implementation of the sorption
mechanism in self-assembled mesoporous aluminosilic structures [1].

The method of obtaining the FCS - 9 reagent is based on the treatment with sulfuric acid of the
aluminosilicate raw material and is described in. The mechanism of water purification by the FCS - 9
reagent includes the process of formation of aluminum hydroxide. In this paper, a numerical study of
the mathematical model of the process of hydrolysis of a given component of a reagent is conducted,
whose behavior is similar to the process of hydrolysis of aluminum sulfate [2, 3]. Consequently, the
subject of this study is Al₂(SO₄)₃.

A comparison is also made between the theoretical change in the pH of the solution, depending on
the amount of aluminum sulfate dissolved in the aqueous solution and experimental. Confirmation of
the correctness of the mathematical model allows us to use numerical studies to determine the optimal
dose of the reagent in the process of water purification.

2. Experiment
In the aluminum sulfate solution, stepwise hydrolysis takes place along a multiply charged cation:
\[ 2Al_2(SO_4)_3 + 4H_2O \rightleftharpoons 4AlOHSO_4 + 2H_2SO_4 \]  
(1)

\[ 2AlOHSO_4 + 2H_2O \rightleftharpoons (Al(OH)_2)_2SO_4 + 2H_2SO_4 \]  
(2)

\[ (Al(OH)_2)_2SO_4 + 2H_2O \rightleftharpoons 2Al(OH)_3 + H_2SO_4 \]  
(3)

In the process of hydrolysis, concentration of uncharged compounds \( Al(OH)_3 \), which have a strong coagulating ability, arise [2]. In this case, the total aluminum concentration \( Al_\Sigma \) as monomers will be determined by the sum of all the concentrations of various aluminum hydro complexes [4]:

\[ Al_\Sigma = [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3] + [Al(OH)_4^-] \]  
(4)

When using the general equilibrium equations of chemical reactions to describe real solutions, it is necessary to use the ion activity method, according to which certain numbers are introduced into these equations, instead of the concentration to take into account the interaction of solution ions. In accordance with this, we rewrite equation (4) taking into account the activities of the components of the hydrolysis process, where in parentheses we denote the activities of the corresponding substances:

\[
Al_\Sigma = (Al^{3+}) \times \left\{ \frac{1}{y_{Al^{3+}}} + \frac{K_1}{(H^+)y_{Al(OH)^{2+}}} + \frac{K_2}{(H^+)^2y_{Al(OH)_2^+}} + \frac{K_3}{(H^+)^3y_{Al(OH)_3^-}} + \frac{K_4}{(H^+)^4y_{Al(OH)_4^-}} \right\},
\]

(5)

where \( y_i \) – coefficient of activity \( i \) – th solution component \( \log(y_i) = -Az_i^2\sqrt{T}, I_c = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \), \( A = -0.511 \) – a constant that does not depend on the charge of the ion and the ionic strength of the solution, but depends on the dielectric constant of the solvent and the temperature, \( z_i \) – ion charge \( i \) – th solution component, \( I \) – ionic strength of solution, \( c_i \) – molar concentration [5], and the corresponding equilibrium constants: \( \log_{10}(K_1) = -5.02, \log_{10}(K_2) = -9.3, \log_{10}(K_3) = -15, \log_{10}(K_4) = -23.57 \).

Using the equilibrium constants and equation (5), one can determine the concentrations of the hydrolysis products by the general formula:

\[
\left( Al_m(OH)_n \right)^{3m-n} = \frac{K_{mn} \times (Al^{3+})^m}{(H^+)^n \times y_{Al_m(OH)_n}^{3m-n}},
\]

(6)

where the constant \( K_{mn} \) corresponds to \( K_4 \) for \( m = 1, n = 1 \). In a similar way, correspondence with the remaining equilibrium constants is carried out.

On the basis of equation (6), the ratios of various products of hydrolysis of aluminum in solution relative to the total amount of dissolved aluminum are plotted as a function of the equilibrium \( pH \).
Figure 1. Molar fractions of dissolved hydrolysis products of mononuclear aluminum hydroxides in equilibrium with amorphous hydroxides; \( C1 \) corresponds to the concentration of aluminum ions \( \text{Al}^{3+} \), \( C11 \) – concentration of \( \text{Al(OH)}^2^+ \), \( C12 \) – concentration of \( \text{Al(OH)}_2^{+} \), \( C13 \) – \( \text{Al(OH)}_3^{0} \), \( C14 \) – concentration of \( \text{Al(OH)}_4^- \).

As can be seen from figure 1, at \( pH < 4 \), aluminum in solution is predominantly in the form of a highly hydrated aluminum ion, the \( \text{Al(H}_2\text{O)}_6^{3+} \) aqua complex, and in the range of \( pH \) values from 9 to 10, practically all of the aluminum in the solution is aluminate ion \( \text{Al(OH)}_4^- \). Under neutral conditions, the predominant aluminum compounds in solution are uncharged molecules of \( \text{Al(OH)}_3^{0} \).

Using the equation of equilibrium of the hydrolysis process and equation (6), graphs of the distribution of aluminum hydrolysis products are plotted as a function of the equilibrium \( pH \) and the amount of dissolved aluminum salt (figures 3 a, b, c) from which the quantitative effect of the \( \text{Al}_2(\text{SO}_4)_3 \) salt on the solution can be determined.

Figure 2 a, b The graph of the distribution of aluminum hydrolysis products as a function of the equilibrium \( pH \) and the amount of dissolved aluminum salt; \( C0 \) is the concentration of aluminum salt,
blue – $C1$ corresponds to the concentration of aluminum ions $Al^{3+}$, red – $C11$ is the concentration $AlOH^{2+}$, black – $C12$ is the concentration $Al(OH)^{2+}$, green – $C14$ - concentration $Al(OH)^{4-}$.

**Figure 3.** The graph of the distribution of aluminum hydrolysis products as a function of the equilibrium $pH$ and the amount of dissolved aluminum salt; $C0$ is the concentration of aluminum salt, $C1$ corresponds to the concentration of aluminum ions $Al^{3+}$, $C11$ is the concentration $AlOH^{2+}$, $C12$ is the concentration $Al(OH)^{2+}$, $C13$ - $Al(OH)^{3}$, $C14$ - concentration $Al(OH)^{4-}$.

It can be seen from figures 2 a, 2 b and 3 that the character of the molar concentration dependence at low concentrations of $C0$ corresponds to the dependence shown in figure 1.

The most interesting is the dependence of the amount of formed uncharged $Al(OH)_3$ molecules on the initial $pH_0$ of the medium and on the $C0$ concentration of the aluminum salt $Al_2(SO_4)_3$ in solution, shown in figure 3. This product of hydrolysis - colloidal particles, is an active component of the coagulation process and affects the aggregative stability of the solution.

As a result of the stepwise reactions described by equations (1 – 3), monomeric aluminum compounds are formed, a proton is released, and the $pH$ of the solution decreases. Each subsequent stepwise reaction shifts the $pH$ of the solution to the acid zone. In view of this, it is possible to describe the change in the $pH$ of the medium from the amount of dissolved aluminum salt. Figure 3 shows the theoretical and experimental plot of the $pH$ of the solution as a function of the aluminum salt concentration $C(Al_2(SO_4)_3)$ in the solution. The error of the experimental results does not exceed 5% of the theoretical results.

**Figure 4.** The graph of the $pH$ of the solution as a function of the concentration of the aluminum salt $C(Al_2(SO_4)_3)$ in solution.
The first experimental point was obtained in a solution with $7.5 \times 10^{-4}$ kg of aluminum sulphate per m$^3$, after which it was diluted 2 times to obtain a solution with an aluminum sulfate content of $3.75 \times 10^{-4}$ kg / m$^3$. The process was repeated until the $Al_3(SO_4)_3$ content reached $0.12 \times 10^{-4}$ kg / m$^3$.

3. Conclusions
According to the numerical studies of the mathematical model of the process of hydrolysis of an aluminum salt in an aqueous solution, a theoretical dependence of the amount of hydrolysis products on the equilibrium $pH$ of the solution and the amount of dissolved aluminum sulfate, which was experimentally confirmed, was constructed. The obtained data allow to determine the range of $pH$ at which the largest amount of uncharged aluminum hydroxide molecules - $Al(OH)_3(H_2O)_3$ complexes - is formed and the water purification process is intensified.

Experimental studies on the $pH$ of the solution on the amount of aluminum sulfate dissolved in aqueous solution are consistent with numerical studies of the mathematical model of the hydrolysis process, which allows determining the optimal dose of the reagent for various initial concentrations of contaminants and increasing the efficiency of the reagent under study.

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