Use of aluminosilicic reagent for water purification

S N Tikhonov¹, I M Kurchatov¹, V A Byrkin¹, D Y Feklistov² and N I Laguntsov¹

¹ National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe highway 31, Moscow, 115409, Russia
² JSC Aquaservice, Kashirskoe sh. 31, Moscow, 115409 Russian

E-mail: tisenik@mail.ru

Abstract. Workability of the hybrid reagent based on aluminium salts and the use of active silicic acid for the purposes of water treatment was investigated in this paper. The research of the residual aluminium concentration in the water was conducted after the introduction of the reagent into the model solution. The optimum concentration ASFC and the pH value was determined at which the coagulation process is intensified. The approaches of the interaction of the dispersed particles, specified method for calculating the interaction potential of the dispersed particles in the circumstance were described.

1. Introduction

Currently, complex reagents are widely applied in water purification systems and perform the function of coagulant, flocculant, precipitant and adsorbent. This allows using the benefits and advantages of the individual components. In this work a reactant hybrid aluminosilicic reagent based on materials containing aluminium sulphate and an active silicic acid was used. The main task of the reagent is a dispersion system destabilization [1].

During the hydrolysis the aluminium compound coagulates with particles formation, sedimented with pollutants. The coagulating effect of active silicic acid is based on the mutual coagulation of oppositely charged particles, wherein the silicic acid molecules are the centres of the coagulation system. Under certain conditions, these centres form a cell as a result of their continued engagement. Next, the structure becomes larger due to the coalescence of these links. As a result, the self-organization process produces complex spatial three-dimensional structure in which the flocculation ability is increased cause of the ability to absorb pollutants in the cavity between the units. High efficiency of aluminosilicic reagents is conditioned, on the one hand, as an additive reagent coagulant properties of components and on the other hand, the formation of mesoporous aluminosilicic structures, leading to flocculation.

2. Chemical processes

ASFC are prepared from raw materials containing nepheline by treating it with sulphuric acid, what is not a great technical problem in manufacturing. Such rocks have a greater concentration of the necessary components SiO₂ and Al₂O₃.
Table 1. The chemical composition of nepheline raw materials

| Element          | SiO$_2$ | Al$_2$O$_3$ | Na$_2$O + K$_2$O | Fe$_2$O$_3$ |
|------------------|---------|-------------|------------------|-------------|
| Concentration, % | 44      | 28          | 19               | 2.3         |

The main stage of the destabilization of the colloidal system is the hydrolysis of aluminium salts and precipitation Al(OH)$_3$. Chemical reaction scheme:

$$\text{Al}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \leftrightarrow 2\text{AlOHHSO}_4 + \text{H}_2\text{SO}_4 \leftrightarrow \text{AlOH}^{3+} + \text{H}^+ + 2\text{AlOH}_2^2+ + \text{H}_2\text{SO}_4 \leftrightarrow [\text{Al(OH)}_2]^+ \text{H}^+ + [\text{Al(OH)}_2]^+ \text{SO}_4 + 2\text{H}_2\text{O} \leftrightarrow$$

$$2\text{Al(OH)}_3 \downarrow + \text{H}_2\text{SO}_4 + \text{[Al(OH)}_2]^+ + \text{H}_2\text{O}$$

Formed protons H$^+$ connects with HCO$_3^-$ of natural water. This reaction can be represented by the stoichiometric equation:

$$\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca(HCO}_3)\_2 \leftrightarrow 2\text{Al(OH)}_3 \downarrow + 3\text{CaSO}_4 + 6\text{CO}_2 \uparrow$$

Under addition of alumsilicic flocculant with pH = 6 - 7 takes place an allocation of aluminium ions, which are included in the exchange reaction with the cation impurity diffusion layer hydrophobic particles. This diffusion layer is compressed reducing the stability of the system, resulted in coagulation of the medium particles. Silicic acid is a flocculant, forming a bridge structure "particle – micro ion - multiply charged counter ion – micro ion - particle", passed through the coagulation stage.

The presence of free aluminium is an important indicator of water quality treatment, as aluminium is toxic and carcinogenic, is not oxidized and is not excreted from the body. In accordance with WHO recommendations, the EU and the standards of developed countries [2] content of residual aluminium in water should not exceed 0.2 mg/l. Residual aluminium problem exists for any aluminium-containing reagents (aluminium sulphate, ASFC oxychloride aluminium Al$_2$(OH)$_3$Cl∙6H$_2$O etc.)

Table 2. Doses ASFC

| ASFC dose (per litre of treated water), ml/l | pH model solution | Residual aluminium, mg/l |
|--------------------------------------------|------------------|--------------------------|
| 0                                          | 7,3              | <0,04                    |
| 0,5 ml/l                                   | 6,4              | <0,04                    |
| 1 ml/l                                     | 6,2              | <0,04                    |
| 2 ml/l                                     | 5,5              | 0,13 ± 0,05              |
| 3 ml/l                                     | 4,5              | 0,31 ± 0,05              |
| 4 ml/l                                     | 4,1              | > 0,4                    |

The results show that the aluminium content of the water is primarily dependent on the pH of the aqueous circumstance, which in turn is related to the concentration of hydrogen ions and the acidity of the initial water solution introduced ASFC.

The optimum pH value for coagulation is between 6.0 - 8.0. The coagulation process finishes in the formation of poorly soluble hydrocomplexes of aluminium. This process is accompanied by the formation of virtually no residual aluminium as goes through hydrolysis, i.e. all aluminium ions are involved in the formation of hydroxyl complexes. At lower pH values (acidic medium) is decelerating aluminium hydrolysis process. The reduced alkalinity causes hydrolysis is stopped at an intermediate stage in the appearance of the clarified water unhydrolyzed free aluminium ions with a charge of +3.
With a decrease in the pH of the contribution of this process increases, respectively, increasing the quantity of residual aluminium.

It was found that with increasing doses AS FC from 0.5 to 2 ml / l speed purification processes increases. Velocity decreases with further increase in the concentration, and at a dose of 4 ml / l brightening process is slowed dramatically. This slowdown is due to a decrease in pH and as a consequence, finishing model solution hydrolysis process.

3. Simulation method
ASFC is a colloidal particle system. The interaction of particles responds to van der Waals forces of attraction and repulsion of Coulomb forces. Coagulation centres are electrolyte ions having a negative charge. Counter ion concentration causing coagulation system is called threshold coagulation. This value is calculated according to the rule Schultz-Hardy [3], based on the structure and properties of the boundaries of the electric double layer (EDL). Driving EDL structure shown in Fig. 1.

In order to simulate the coagulation process, it is necessary to present the interaction of particles as the Coulomb force of the same or different charges. Thus the charges of the particles vary depending on the dispersed state of the system as a whole. Since pH is easily measurable parameter of the system, it will select for implicit determination of the potential on the surface of the electrical double layer $\zeta = f (pH)$. Figure 2 shows the results of the study the average zeta potential agglomerates ASFC at different pH of the medium. Measurements of $\zeta$ –potential are carried out for hybrid reagent layer 200 microns thick. The NaOH solution was added a solution of 10 l / 10 sec, to pH = 10 with external conditions: $T= 20-25^0C$, $p = 1$ atm.
In this case, besides the fact that the zeta potential $\zeta$ determines the surface charge of the particles, it is also a criterion for the stability of the dispersed system, determines the nature and extent of interaction between the particles. The colloidal theory emits the characteristic value of the zeta potential of 30 mV. [4] Above this limit the system has a stable state, and below coagulation and flocculation is possible.

The interaction of particles is determined by the potential $U(r)$, which will consist of the van der Waals attraction potential $W_-$ and the Coulomb potential repulsion or attraction $W_+$ [6].

$$W_+ = k \frac{q_i'q_j}{r_{ij}}, i \neq j$$  \hspace{1cm} (1)

$q_i'$ - micelle charge ($q_i' = \frac{\zeta N}{\sum_i}$, $N$ - the number of particles in the system)  
$q_i$ - charge of the system of ions surrounding the particles of ASFC  
$r_{ij}$ – the distance between the particles with indexes i and j

$$W_-(z,R_i, R_j) = -\frac{A}{6} \left[ \frac{2R_iR_j}{z^2-(R_i+R_j)^2} + \frac{2R_iR_j}{z^2-(R_i-R_j)^2} + \ln\left( \frac{z^2-(R_i+R_j)^2}{z^2-(R_i-R_j)^2} \right) \right],$$  \hspace{1cm} (2)

where $A$- Hamaker constant, $R_i, R_j$ - the radius of the spherical bodies, $z = R_i + R_j + r$, $r$ - the distance between the centres of the spherical bodies.

Potential interactions in which the Coulomb force is repulsion forces are described for like-charged particles. For heterogeneous systems with particles of opposite charges of the electrostatic forces would be attractive forces at all distances, caused by irreversible coagulation [7]. For pairs of particles of like charges is a potential barrier, depending on the capacity of less than the charged surface.

**Figure 2.** Dependence of $\zeta$ potential of 1-% ASFC solution from pH.
When measuring the zeta potential of the particles in the solution, only the average value in the test sample can be obtained, as well as the potential of interactions has been recorded for particle pairs, it is necessary to correlate the charge of the electric double layer with the reactant particle sizes. The surface charge of the electric double layer, to a first approximation, can be obtained from the initial distribution of the alumosilicic coagulant agglomerates cause the charge on the surface is directly proportional to the radius of the electrical double layer:

\[ q_i' = z_i N \left( \frac{r_i}{<r>} \right)^3, \]

\( r_i \)- radius of EDL, \(<r>\)- the average radius of particles in the circumstance

Experiments were performed with 1, 2, 5 and 10% solution ASFC. On the Fig. 3 particle size distribution in solution for a 1% solution is shown. The size distribution is weakly dependent on the concentration of the hybrid reagent in solution and indicates that the self-organization process is observed in the reagent solution immediately after its production, the particles are formed, which may reach sizes of 180 nm.

![Figure 3. Particle size distribution of the reagent solution.](image)

3. Conclusion
During the investigations it was established that pH parameter is implicitly affects the concentration of free aluminium in the sample. The results have the following qualitative explanation: While introducing ASFC into the water, hydrolysis of aluminium cation takes place, the hydrolysis products are polynuclear hydroxocomplexes, having coagulating properties and also, these products are the centers of the formation of primary flocs, from which floccules grow subsequently.

With the view of identifying optimal ASFC concentration, it is necessary to take into account an economic viability, and also the fact that the increase of aluminium ions concentration leads to inversion of the particles charge on the surface of the electric double layer as a result of adsorption of hydrated aluminum complexes. The result of this process is stabilizing of dispersed system and next shutdown of coagulation and flocculation [8].

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