Intensification of Wastewater Treatment Processes During Coal Enrichment Using Modified Polyacrylamide Flocculants

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Abstract.
The interaction with modifying substances of flocculants on the basis of polyacrylamide has been investigated. The main characteristics of the modified flocculants were studied. Their advantage over unmodified flocculants in the process of cleaning flotation tailings is shown. According to the results of the research, the molecular weight of the modified polymer was 25 times more than the initial matrix sample. The volume characteristics of macromolecules such as the average distance between the ends of the molecules and the hydrodynamic volume occupied by the unit mass of the macromolecule were studied. The possibility of using modified flocculants for cleaning flotation tailings during coal enrichment has been studied.

1. Introduction
Nowadays the protection of nature from pollution is an important problem. In this country much attention is paid to it. In this regard, the problem of purification of natural water and wastewater is of particular importance as it is closely connected with the protection of water resources. Most methods of purification of natural and industrial wastewater as well as methods of compaction and dewatering of sediments of various types are based on the use of reagents.

Kuzbass is one of the richest regions of Russia in terms of mineral reserves. Intensive extraction and processing of raw materials at local enterprises led to pollution of both surface and ground water. Under the current conditions of a complex environmental situation in the region and the country as a whole the problem of protecting water resources from pollution by untreated sewage of the coal industry acquires a special role. Coal-mining enterprises discharge large volumes of wastewater. There is an acute problem of the purification and use of technical water supply in connection with the growing shortage of fresh water and an increase in the amount of industrial wastewater.

Flocculants on the basis of polyacrylamide are widely used for various stages of coal enrichment and wastewater treatment in the coal industry.

Flocculants are water-soluble high-molecular compounds. When they introduce into disperse systems they adsorb or chemically bind to the surface of the particles of the dispersed phase and combine the particles into agglomerates (floccules), contributing to their rapid precipitation. The history of using high-molecular substances for the purification of liquids from suspended impurities has its roots in deep antiquity. So, even in 2000 BC in India extracts of some plants containing natural polymers were used to purify water and in ancient Greece a natural polymer such as egg white was used to clarify wines. In
the XVIII-XIX centuries, natural polymers such as gelatin and starch were used to clean fruit juices. Despite such a long history the practical application of floculation in industrial processes began in the period between the 30s and 50s of the 20th century. Floculants were used to clean mine waters from coal and clay particles, isolate and dehydrate phosphorus slags in the preparation of uranium salts and intensify the treatment of industrial wastewater. Since the mid-50s floculants have been widely used due to the need to clean up increasing volumes of wastewater and modernize technological processes associated with the separation of solid and liquid phases. When the increased demand for floculants could no longer be satisfied with natural polymers the introduction of organic artificial (starch and cellulose derivatives) and more often synthetic polymers began. The group of polyacrylamide floculants (PF) has received the greatest distribution and application among synthetic polymers.

On the domestic market of these substances, floculants of foreign firms (manufactured in England, Germany, USA, France) are available in the form of solid bulk forms. They are similar in their composition, but in our opinion, the most high-quality products are floculants of the type «Magnaflok» made by the English firm Alleds Kolloids. Jyb. These polyelectrolytes are more homogeneous in composition and molecular weight (MW). Their MW fluctuates within 10 - 25 million a. u. m. However, in order to increase the efficiency of coal enrichment processes (sedimentation and filtration of flotation tailings) a higher MW is required but the degree of polymerization is limited by the currently existing technical capabilities of the synthesis. Thus, objective prerequisites have emerged for the search for other ways of obtaining polyacrylamide with a higher MW, i.e. ultrahigh molecular weight samples of floculants. Our proposed method of preparation is based on the chemical treatment of typical granular samples of the floculant by chemical intermediaries capable of entering into chemical reactions with the reactive functional groups of the polyacrylamide macromolecules.

The floculation received practical application in many technological processes related to the separation of solids from liquids: for separating particles of coal and clay from mine water, in the technology for producing uranium ores, for clarifying industrial effluents in nonferrous metallurgy, in potash, pulp and paper industry, cement factories, food industry and a number of other areas in the 30s-50s. High-molecular floculants are usually divided into three groups: active silicic acid; synthetic organic polymers (polyacrylamide, polyoxyethylene, polyacrylate, polyethyleneimine, etc.); floculants based on natural substances (starch, cellulose ethers, guar gums, chitosan, etc.). Synthetic high-molecular floculants are much more widespread than natural floculants because they are more efficient, selective, cheaper and better stored. A distinctive feature of polymers, water-soluble floculants, in particular is the chain-like, linear or branched structure of macromolecules. The polymers can be homogeneous (homopolymers) and heterogeneous (copolymers). The number of monomer units can be 250-70000 and the total length of the molecular chain can reach 7.5x10 - 110x103 nm. Synthetic polymers are obtained by polymerization or polycondensation of monomers or polymerological transformations of existing polymers.

It is known that polyelectrolytes of anionic or cationic type of high molecular weight with different structures of macromolecules are widely used to intensify the separation processes of industrial disperse systems. The most common are floculants based on polyacrylamide.

The chemical properties of polyacrylamide are determined by the properties of functional groups and radicals entering the macromolecule. Polyacrylamide macromolecules during storage in solutions can lose their floculation activity due to a decrease in molecular weight during the destruction of skeletal bonds - C - C - by residual peroxide synthesis catalysts and air oxygen molecules. The chemical portrait of floculants based on polyacrylamide allows us to conclude that the macromolecules of polyelectrolytes are mobile, reactive and insufficiently resistant to destruction in time. Detailed consideration of these properties is necessary to substantiate the method of obtaining polyacrylamide macromolecules with high molecular weight.

The aim of the research was to study the possibility of using modified floculants on the basis of polyacrylamide for cleaning flotation tailings during coal enrichment.

The tasks of the research were:
1. To determine the molecular weight of the polymer.
2. To determine the volumetric characteristics of macromolecules.
3. To calculate the hydrodynamic volume.
4. To study the possibility of using modified flocculants for cleaning flotation tailings during coal enrichment.

2. Conditions, materials and research methods

Determination of polymer molecular weight. As a result of processing the initial flocculant «Magnoflok» with aliphatic low molecular weight chlorhydrins, we obtained samples of flocculants with a molecular mass of more than 25 million a. u. m. The results of viscometric tests for flocculant «Magnaflok» M - 156 (initial commodity form) and «Magnaflok» M - 156M (processed by the modifier) are presented in Figure 1. On the basis of these results the characteristic viscosity was established to determine MW of the polyelectrolyte by Mark-Houwink-Kun equation

\[ \eta = K \cdot M^a. \]  

where \( \eta \) – characteristic viscosity \( K = 0.63 \cdot 10^4, a = 0.8 \) (constant).

Determination MW for M - 156: \( \eta = 25 \) (figure 1). \( M = 10^7 = 10 \text{ mln. a. u. m.} \)

Determination MW for M - 156M: \( \eta = 125 \) (figure 1). \( M = 74.3 \text{ mln. a. u. m.} \)

![Figure 1](image.png)

**Figure 1.** Dependence of the relative viscosity of solutions of flocculants M - 156 (straight line 1) and M - 156 M (straight line 2) on their concentration.

Determination of the volumetric characteristics of macromolecules. Volumetric characteristics include specific characteristics such as:

- \( h \) - average distance between the ends of the molecules;
- \( V'_{M} \) - hydrodynamic volume occupied by a macromolecule mass unit.

The value of \( h \) characterizes the reactivity of macromolecules in the process of flocculation. The greater the \( h \), the higher the flocculating ability.

The value of \( V'_{M} \) determines the total size of the macromolecule. The higher it is, the higher the mass and volume of floccules.

The calculation of the average distance between the ends of the molecules is determined by the Fury formula:

\[ [\eta] = \frac{\Phi \cdot h^3}{M} = \frac{\Phi \beta h^3}{M}. \]
where \([h]\) – characteristic viscosity, 
\(h\) – average distance between the ends of the molecules, 
\(\Phi\) – Furry constant, 
\(M\) – polymer molecular weight, 
\(\beta\) – swelling ratio.

post-conversion calculation formula:

\[
h = \frac{[\eta] \cdot M}{2.1 \cdot 10^{21}}.
\]

For \(M\) - 156: \(h = 4.92 \cdot 10^{-5}\) cm
For \(M\) - 156M: \(h = 1.64 \cdot 10^{-4}\) cm

It follows from the data obtained that the distance between the terminal groups in the macromolecule \(M\) - 156 is 13.3 times less than in \(M\) - 156M, i.e. the end groups of the modified flocculant are more reactive during the flocculation process.

**Calculation of hydrodynamic volume** \(V_M^f\). It is determined by the known formula:

\[
V_M^f = [\eta]^{1.54} \div [\eta]^{1.25}.
\]  (3)

For \(M\) - 156, this value was:

\[
V_M^f = 25^{1.54} \div 25^{1.25} = 3.55 \cdot 10^3 \div 1.4 \cdot 10^3, \text{ nm}^3.
\]  (4)

![Figure 2. Curves of potentiometric titration for flocculant solutions: 1 - modified, M - 156 M, 2 - unmodified, M - 156.](image)

**3. Results and discussions**

It follows from the obtained data that the hydrodynamic volume for \(M\) - 156 is lower by 80 - 100 times than the hydrodynamic volume for \(M\) - 156M, that is we obtained a more expanded and bulk macromolecule structure.
### Table 1. Kinetics of suspension clarification

| Flocculant | Volume of the turbid part, h, ml |
|------------|----------------------------------|
| M – 156 and VPK | 90  60  30  00  90  70  65  55  40  30  20  10  00 |
| M – 156M and VPK -402 | 70  30  90  40  20  10  95  80  75  70  60  55  50 |
| Clarification time, sec. | 7  5  3  2  1  0  9  08  17  26  35  44 |
| M – 156 and VPK | 85  65  60  58  55  50  49  47  43  40  39  39  39 |
| M – 156M and VPK -402 | 43  35  33  30  25  23  20  18  15  13  10  10  10 |
| Clarification time, sec. | 62  80  89  98  07  25  34  43  52  61  70  79  88 |

For M – 156M:

\[
V' \mu = 125^{2.54} \times 125^{1.25} = 2.12 \times 10^5 \div 0.52 \times 10^5 \quad nm. \tag{5}
\]

The change in the chemical properties of flocculants was determined from the results of potentiometric alkali titration of solution samples of modified and unmodified flocculants (figure 2).

It was concluded based on the test results that the number of carboxyl groups in the modified flocculant was reduced due to their interaction with the modifier.

*The use of modified flocculants for cleaning flotation tailings during coal enrichment.* The purpose of the experiment was to intensify the stages of clarification of tailing suspensions after flotation and compaction of the resulting sludge while simultaneously reducing the consumption rate of expensive flocculant M-156 and deficient VPK-402. The goal can be achieved using an ultra-high molecular weight flocculant M - 156M obtained by modifying the applied flocculant M - 156 by chemical reagents with certain functional groups.

400 ml of flotation waste was poured into one cylinder and another cylinder. The volume of each cylinder was 500 ml. Two ml of VPK-402 and 3 ml of M – 156 were added in the first cylinder. 1.6 ml of VPK-402 and 1.6 ml of M - 156M were added in the second cylinder. All was thoroughly mixed and the volume of the turbid part of the solution was measured every 9 seconds (these optimal doses were selected earlier). The results of the experiments are summarized in table 1.

According to experimental data, a plot of the height of the turbid part of the solution is plotted against the time of deposition (Figure 3).
The conclusions were made on the basis of kinetic studies:
- the time of the main clarification process at the flocculation stage for M – 156M (AB) is 100 seconds, i.e. 1.5 times less than for M – 156 (AB) – 150 seconds;
- the height of the cloudy layer for M – 156M at the point B – 170 ml, for M – 156 at the point B – 185 ml;
- sediment height after 300 seconds (at the point C) for M – 156M – 105 ml., for M – 156 – 135 ml.;
- the size of the floccules when using M – 156M is 1.5 times higher than when using M – 156.

It was established experimentally that the flow rate of the modified flocculant M – 156M is 2 – 3 times lower than the original M – 156.

4. Conclusions

According to the results of the research, the molecular weight of the modified polymer was determined. It is 25 times higher than the initial matrix sample. The volume characteristics of macromolecules such as the average distance between the ends of the molecules and the hydrodynamic volume occupied by the unit mass of the macromolecule were studied. The possibility of using modified flocculants for cleaning flotation tailings during coal enrichment has been studied. Thus, on the basis of the studies performed, it can be argued that the use of modified flocculants based on polyacrylamide for the purification of wastewater from the coal industry is feasible and cost-effective.

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