Development of national standards for the needs of the water industry on the examples of the aluminium polyoxychloride

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Abstract. An important stage in conditioning of water before its supply is the use of coagulants, with polyaluminium chloride being one of such agents. Active application of this coagulant began late last century, and its global output has been consistently growing since. The purpose of the work was to create a new standard because of the need to ensure a uniform assessment of the quality of the proposed coagulants. The necessity of unification in the field of quality control processes of coagulants is shown. General requirements for quality control of aluminum polyoxychloride are formulated. In particular, the standard contains universal methods to determine impurities and main quality parameters (basic capacity, contents of aluminium oxide and chloride ions) in polyaluminium chloride; regulate pH, residual aluminium, chlorides and heavy metal ions for the whole concentration range of the active ingredient in the agent (i.e. the standard covers both dry and liquid products); avoid use of low-quality raw materials (including aluminium scrap) in the production of polyaluminium chloride; characterise high- and low-basic products (given a non-linear change in properties at different concentrations); regulate frequency of and conditions for checking polyaluminium chloride against declared parameters.

1. Introduction

Providing the population of Russia with high-quality drinking water that meets sanitary and hygienic requirements, the strategic importance of drinking water supply, as one of the factors of life safety, the need to comply with the requirements of sanitary legislation, make very serious demands on water treatment technologies, both in terms of the quality of the process and parts of used materials and reagents.

The activities of water supply and sewage enterprises (WSS) in terms of meeting performance targets (Federal Law of December 7, 2011 N 416-FZ “On Water Supply and Sanitation”) are aimed at ensuring the proper quality of drinking water, and reagent costs are an integral part of the water supply tariff, which is approved once for a year or for a longer period (long-term tariff), taking into account the marginal index of a possible tariff increase (Decree N 400 "On the formation of indexes of changes in the size of fees of citizens for utilities in the Russian Federation"). Thus, water utilities have the
opportunity to plan the cost of water supply, and consumers of services are practically insured against a sharp increase in prices.

2. Methods

According to our estimates, surface water sources are used for water supply of the population of 65% of large cities (Moscow, St. Petersburg, Nizhny Novgorod, Yekaterinburg, Perm, Volgograd, Omsk, Rostov-on-Don, Yaroslavl, Vladivostok, Novosibirsk, etc.). The prevailing sanitary-chemical indicators of pollution of surface water sources of water supply for cities of over 1 million people are general mineralization, turbidity, and hardness. In Russia as a whole, this type of pollution is present in 21.2% of sources, and in the overwhelming majority in certain regions. The task of providing the population of Russia with high-quality drinking water that meets sanitary and hygienic requirements, the strategic importance of drinking water supply, as one of the factors of life safety, determine serious requirements both for the water treatment process itself and for the materials and reagents used.

The quality of surface water sources, unfortunately, is not improving, therefore, the use of solutions that ensure the quality of drinking water of centralized water supply in accordance with the requirements of the relevant hygiene rules (Decree N 400 "On the formation of indexes of changes in the size of fees of citizens for utilities in the Russian Federation") is objectively based on maximum optimization, and more often, on the cost of the water treatment process. In the preparation of drinking water for surface water sources, the practically universally used stage of the technological process is clarification, the basis of which is coagulation, which is implemented by introducing the appropriate water treatment reagents - coagulants. Qualitatively carried out clarification allows to reduce further chemicalization of water and reduce production costs in the process of water treatment ([1], [2], [3]).

According to the assessment, in 2018, out of 6996 enterprises, 2685 enterprises (38.4%) operate with losses, the amount of losses for the reporting period amounted to 11.7 billion rubles. In this regard, water utilities enterprises reasonably have questions of optimizing the process, as well as accounting for purchased reagents in the cost of water when setting the tariff for water supply. The need to optimize the consumption of coagulants naturally forces water utilities to pay attention to the price of products. The price of a product, in turn, depends on the cost of the feedstock and the cost of technological operations for its conversion into a final product. Considering the fact that today products can be manufactured on the basis of the technical conditions of a particular manufacturer, the question arises - how do consumers - water utilities - ensure uniformity in assessing the quality of the proposed coagulants. If we consider aluminum sulfate, you should pay attention to the fact that this type of product exists (State Standard GOST 12966-85. Technical purified aluminium sulphate. Specifications), and an aqueous solution of aluminum sulfate is produced on the basis of indicators of the same standard. The presence of the standard allows for uniform procedures for assessing the quality of the reagent and significantly facilitates the water utilities enterprises to formulate testing programs and control residual concentrations of potential impurities in the water. The situation is different with coagulants of the aluminum polyoxychloride group. Of course, there are requirements for the control of water extracts from products for water treatment, which are necessarily controlled, but already in prepared drinking water (SanPiN 2.1.4.1074-01 Drinking water. Hygienic requirements for water quality of centralized drinking water supply systems. Quality control. Hygienic requirements for ensuring the safety of hot water systems, Decision of the Commission of the Customs Union of 05.28.2010 N 299 On the application of sanitary measures in the customs union) and are included in the production quality control program for water. But this control does not show the presence of other potential impurities in the product - a coagulant for drinking purposes, when it comes to incoming quality control of the coagulant itself. The production of aluminum-based coagulants as part of technical conditions of production does not regulate the requirements for the feedstock, which, in turn, makes controversial issues regarding the input control of coagulants by the consumer and potential comparison of products from different manufacturers.
3. Results and Discussion
Coagulants based on aluminum polyoxychloride are more expensive due to the high technology of the production process than coagulants based on aluminum sulfate [4]. This leads to a number of consequences, the main of which are as follows:

- aluminum containing waste is used to reduce costs
- manufacturers minimize product quality control to reduce costs
- during the competitive procedures (bidding), the coagulant, which is obviously inferior in quality, but cheaper in price, has an advantage.

Thus, in order to improve the quality of water, reduce its secondary pollution that comes with water products of inadequate quality, it seems very important to have requirements that uniquely determine the input quality control of coagulants on the water channel and the technical conditions for the production of coagulant.

In this regard, the Russian Water and Wastewater Association, together with the Aluminum Association, initiated the inclusion in the national standardization program of the development of the national standard GOST R “Aluminum polyoxychloride. technical conditions.” Work on this standard is carried out by the Technical Committee for Standardization (TC) 343 “Water Quality”, coordinating the standard with TC 099 “Aluminum” and TC 060 “Chemistry”. The new standard GOST R 58580-2019 takes into account relevant foreign regulations including in Europe (EN 883 1197) and Asia (MS 1454:2007, GB 15892-2009).

One of the most important prerequisites for the development of requirements for the production of coagulants was the need to minimize the chemicalization [5] of water due to water treatment reagents ([6], [7]). The determining component for this task, in our opinion, is the requirements for the feedstock and its maximum purity. The requirements formulated and further presented allow conscientious producers responsibly approaching the technological processes for the production of coagulant based on aluminum polyoxychloride to be able to sell products for the needs of the population with drinking water. At the same time, the quality control of the product (coagulant) should not be an excessive burden both for the manufacturer and for the water utility, which uses the proposed reagents for drinking water supply.

The main objectives of the standard being created are as follows:

- Prohibition of the use of secondary raw materials for the production of coagulant within the framework of the standard;
- Formation of uniform requirements in terms of product quality and requirements for residual impurities;
- Formation of product quality control programs for consumers at the acceptance stage;
- Development and presentation of methods for performing measurements of quality indicators.

The measurement procedures proposed in the standard are specially developed and certified for the purpose of standardization of aluminum polyoxychloride, which will allow evaluating the quality of aluminum polyoxychloride for drinking water supply systems on a single standardized platform. As part of the development of the standard, the following measurement procedures were applied or recertified, as applied to aluminum polyoxychloride:

- Determination of the mass fraction of polyoxychloride in terms of alumina Al2O3);
- Determination of the mass fraction of chlorides;
- Determination of the mass fraction of water-insoluble residue;
- Determination of basicity;
- Determination of the mass fraction of iron;
- Determination of lead, nickel, chromium, beryllium and cadmium by ICP-AES;
- Determination of the mass fraction of arsenic, selenium and antimony by the hydride method and mercury by the cold vapor method;
- Determination of the mass fraction of beryllium, cadmium, arsenic, nickel, lead, selenium, chromium and antimony by atomic absorption spectrometry with electro thermal atomization.

Given the number of companies producing aluminum polyoxychloride, the requirements for the quality of the final product are unified by the common concentrations of the active substance of the coagulant. The residual impurity concentrations clearly do not make it possible to use secondary raw materials and waste containing aluminum as a raw material for the coagulant [8]. In turn, for the WSS enterprises, the possibility of conducting current and expanded input control of quality indicators of coagulants of the aluminum polyoxychloride group is proposed, which can guarantee the prevention of the possibility of impurities entering the prepared drinking water. The final version of the standard takes into account all the requirements of sanitary legislation, technical regulation, safety of the production and transportation of aluminum polyoxychloride. Consider the general requirements for quality control of aluminum polyoxychloride formulated in the standard (table 1).

### Table 1. Quality indicators of coagulants of the aluminum polyoxychloride group, according to the standard.

| Requirement                                                                 | Type 1          | Type 2          | Type 3\(^b\) | Type 4          | Type 5          |
|------------------------------------------------------------------------------|-----------------|-----------------|--------------|-----------------|-----------------|
| 1. Mass fraction of alumina (Al\(_2\)O\(_3\)), %, not less than              | 10.0 ± 2.5      | 15.0 ± 2.5      | 20.0 ± 3.0   | 30.0 ± 3.0      | 45.0 ± 5.0      |
| 2. Density (at 20\(^\circ\)C), g/ml, within                                  | 1.24 ± 0.04     | 1.33 ± 0.07     | 1.24 – 1.38  | -               | -               |
| 3. Mass fraction of chlorides, % of mass                                     | 10.0 ± 5.0      | 20.0 ± 2.5      | 10.0 ± 4.5   | 33.0 ± 5.0      | 21.0 ± 7.0      |
| 4. Basicity, within %                                                        | 25 – 55         | 30 – 55         | 50 – 83      | 50 – 83         | 50 – 83         |
| 5. pH (u) of an aqueous solution, within                                     | 2.5 ± 1.5       | 2.0 ± 1.5       | 3.0 – 5.5    | 3.2 – 5.0       | 3.5 – 5.0       |
| 6. Mass fraction of water-insoluble residue, % by weight, not more than     | 0.1             | 0.1             | 0.1          | 1.0             | 1.0             |
| 7. Mass fraction of iron (Fe), % by weight, no more                          | 0.05            | 0.05            | 0.05         | 1.0             | 1.0             |

Impurities, toxic substances\(^a\) % by weight, not more than [3]

| Requirenent                                                                 | Type 1          | Type 2          | Type 3\(^b\) | Type 4          | Type 5          |
|------------------------------------------------------------------------------|-----------------|-----------------|--------------|-----------------|-----------------|
| 8. Mass concentration, Arsenic (As)                                          | 0.001           | 0.001           | 0.001        | 0.001           | 0.001           |
| 9. Mass concentration, Cadmium (Cd)                                          | 0.001           | 0.001           | 0.001        | 0.001           | 0.001           |
| 10. Mass concentration, Chromium (Cr)                                         | 0.004           | 0.006           | 0.006        | 0.006           | 0.006           |
| 11. Mass concentration, Mercury (Hg)                                          | 0.001           | 0.001           | 0.001        | 0.001           | 0.001           |
| 12. Mass concentration, Nickel (Ni)                                           | 0.004           | 0.006           | 0.006        | 0.006           | 0.006           |
| 13. Mass concentration, Lead (Pb)                                            | 0.001           | 0.001           | 0.001        | 0.001           | 0.001           |
| 14. Mass concentration, Antimony (Sb)                                         | 0.002           | 0.003           | 0.003        | 0.003           | 0.003           |
| 15. Mass concentration, Selenium (Se)                                         | 0.002           | 0.003           | 0.003        | 0.003           | 0.003           |
| 16. Mass concentration, Beryllium (Be)                                       | 0.0005          | 0.0005          | 0.0005      | 0.0005          | 0.0005          |

\(^a\) Indicators 8-16 are determined within the framework of expanded control and at the request of consumers

\(^b\) For high-base aluminum polyoxychloride, compliance with the type 3 requirements for aluminum oxide mass fraction is required. Aluminum polyoxychloride with a lower mass fraction of the active substance, made by diluting aluminum polyoxychloride corresponding to type 3, is considered to meet the requirements of the standard. The chloride, density and pH values for high-base aluminum polyoxychloride with a lower mass fraction are determined based on the dilution of aluminum polyoxychloride with an alumina concentration corresponding
to type 3. Indicators on the mass fraction of iron, undissolved sediment and impurities (POS. 8-16 of table 4) shall not exceed the values for type 3.

4. Conclusions
Since the aluminum polyoxychloride product line is very variable [3], depending on the manufacturer, when establishing product quality indicators, product types unified by the content of the active substance (aluminum oxide) were selected. This unification allows to aluminum polyoxychloride manufacturers correctly position their products for compliance with the standard. We draw attention to the fact that we analyze the main indicators of aluminum polyoxychloride, which determine the technological regulation of its use by the consumer - this is a group of indicators 1 - 7. At the same time, it is proposed to determine the indicators of aluminum polyoxychloride, which makes it possible to determine the quality of the feedstock used in the production of the reagent, and also to guarantee that the permissible values are not exceeded according to (SanPiN 2.1.4.1074-01, Decision of the Commission of the Customs Union of 05.28.2010 N 299 On the application of sanitary measures in the customs union) the level of presence of impurities in drinking water when using aluminum polyoxychloride (group of indicators 8-16). The reliability and metrological characteristics of the results of the quality control of aluminum polyoxychloride fully meets the requirements of (Decree N 400 "On the formation of indexes of changes in the size of fees of citizens for utilities in the Russian Federation", National standard GOST R ISO 5725 “Accuracy (trueness and precision) of measurement methods and results, National standard GOST R 51672-2000 Metrological ensuring of product testing for the assurance of conformity. General principles).

Development of the national standard “Aluminum Polyoxychloride. Technical conditions” meets the urgent needs of manufacturers of the most relevant coagulant at the moment for the preparation of drinking water and its consumers - water supply and sewage enterprises. This standard was approved for use in Russia and received the number GOST 58580-2019 Aluminum Polyoxychloride. Technical conditions. The standard was approved and highly rated by the Russian Federal Agency on Technical Regulating and Metrology (Rosstandart / GOST R). Currently, an inter-governmental standard is being developed for this material for the participants of the CIS and the Eurasian Economic Union. We believe that an ISO standard for polyaluminium chloride will help create unified requirements to the quality of this product at the international level, all to improve conditioning and quality of potable water globally.

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