



## Aluminum Oxychloride For Coagulation More Effective Coagulant For Water Purification

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### ABSTRACT

The article presents the data of water coagulation tests with the use of aluminum oxychlorides in three types of lightmetal also with optimal alkalization. The results obtained allowed us to determine the best way to obtain high-quality water, even in the absence of alkalization. Use of aluminum oxychloride instead of aluminum sulfate

### KEYWORDS

Aluminum sulfate, water, oxychloride, current, chemical formula

### INTRODUCTION

The quality of the coolant, which determines the reliable operation of the TPP equipment, largely depends on the efficiency of removing

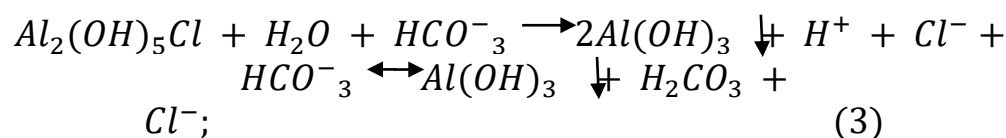
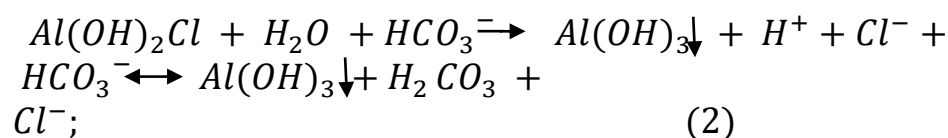
organic impurities at the stage of coagulation of the source water. Currently, the improvement of the coagulation process is

carried out by the reconstruction of clarifiers and the replacement of  $Al_2(SO_4)_3$  coagulants such as aluminum dihydroxysulfate or aluminum oxychlorides (OCHA). The latter are synthesized with a different content of OH groups in the molecules, and their basicity is characterized by basicity or acidity modules, i.e., the molar ratio of  $OH/(OH+Cl)$  or  $HCl/Al_2O_3$ . The industry produces OHA with modules of basicity  $1/3 [Al(OH)Cl_2]$ ,  $2/3 [Al(OH)_2Cl]$  and  $5/6 [Al_2(OH)_5Cl]$ , as well as their mixtures with the content of the main product  $Al_2O_3$  from 7 to 30 %. These coagulants are widely used in drinking water supply installations [1] and are gradually being introduced in water treatment plants (VPS) of power plants [3].

The source water of the Pskov Hydroelectric Power Station (Shelon River) is characterized by a high content of organic impurities: permanganate oxidizability is 25..... 45  $MgO/dm^3$ , chromaticity is 225..... 425 deg. At the same time, the alkalinity is usually equal to

about 1  $mg-eq/dm^3$ , and in flood periods (spring and autumn) it decreases to 0.6  $mg-eq/dm^3$ . The coagulation of such water proceeds effectively only at high doses of aluminum sulfate with preliminary alkalization at almost "zero" alkalinity. This mode leads to the production of clarified water with low pH values (5.0...5.3), an increase in salt content, an increase in aggressiveness and the load on the ion exchange filters of the VPU.

To improve the mode of operation of clarifiers and the quality of clarified water, studies of coagulation by aluminum oxychlorides with different basicity modules were conducted. The process of hydrolysis of OX is multi-stage; in this case, hydroxo-complexes, hard-to-grow basic salts and partially polymeric aluminum hydroxides are formed. Simplistically, this process, depending on the modules of the basicity of the OHA, can be represented as follows:



In accordance with reactions (1)—(3), dosing of 1  $mg-eq/dm^3$  of OX with basicity modules  $1/3$ ,  $2/3$  or  $5/6$  (in the presence of an alkaline "reserve"), in contrast to aluminum sulfate, will lead to a decrease and an increase in the concentration of chloride ions for

coagulants without NaCl or  $CaCl_2$  impurities, respectively, only by  $2/3$ ;  $1/3$  and  $1/6$   $mg-eq/dm^3$ . This shows that the influence of the basicity modulus of OHA will significantly affect the quality of clarified water, especially when using high-base coagulants.

**Table 1. Composition of the coagulants used**

| Коагулянт                            | Chemical formula  | Al <sub>2</sub> O <sub>3</sub> , % | Basicity Module | pH         | Density, g / cm <sup>3</sup> |
|--------------------------------------|---|------------------------------------|-----------------|------------|------------------------------|
| Aluminum sulfate                     | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>             | 16,7                               | -               | -          | -                            |
| OXA [1/3 (50%) + 2/3 (50%)]*         | Al(OH)Cl <sub>2</sub> +Al(OH) <sub>2</sub> Cl               | 10,35                              | 1/3+2/3         | 2,2... 2,3 | 1,220                        |
| Aurat OXA [1/3 (50%) + 2/3 (50 %)]** | Al(OH)Cl <sub>2</sub> +Al(OH) <sub>2</sub> Cl               | 10,02                              | 1/3+2/3         | 2,48       | 1,228                        |
| OHA [2/3 (100%)]*                    | Al(OH) <sub>2</sub> Cl                                      | 15,84                              | 2/3             | 2,7        | 1,309                        |
| OHA [2/3 (60%) + 5/6 (40%)]*         | Al(OH) <sub>2</sub> Cl+Al <sub>2</sub> (OH) <sub>5</sub> Cl | 21,3                               | 2/3+5/6         | 3,0... 3,1 | 1,435                        |

Manufacturer of JSC "Boksitogorsky alumina".  
Manufacturer of OA "Aurat". Laboratory experiments on the water coagulation of the Pskov GRES were carried out with the dosing of OHA (table. 2).

For comparison, water was also coagulated with aluminum sulfate. The formation of flakes in all experiments was accelerated by the introduction of the cationic flocculant Praestol-650TR in an amount of 0.1 mg / dm. The doses of coagulants were calculated based on the content of Al<sub>2</sub>O<sub>3</sub> in the reagents. Water coagulation was carried out according to the generally accepted method without preliminary alkalization. The pH was determined in the settled coagulated water, and the alkalinity, oxidability (Ok), chromaticity, and concentrations of sulfates, chlorides, iron, and aluminum were determined in the filtered clarified water

The experiments have shown that the decrease in Alp for the coagulation of OX is proportional to the dose and basicity modulus in accordance with equations (1) – (3), and for the coagulation of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> — is equivalent to the dose. Figure 1 shows, for example, the results of pH changes in the coagulation of water with an initial Sh = 0.93 mg-eq/dm and an oxidizability of 27.3 MgO/dm<sup>3</sup>, depending on the dose of Dk of the coagulants used. The pH value strongly depends on the DK when coagulated with aluminum sulfate, and when treated with aluminum oxychlorides, the pH is also determined by the basicity modules. The higher the basicity modulus of the OCA, the smaller the decrease in the pH of clarified water with equal doses of coagulants. Moreover, the absolute decrease in alkalinity and pH increases in accordance with a number of:

$\text{OHA} [2/3(60\%) + 5/6(40\%)] < \text{OHA} [2/3(100\%)] < \text{OHA} [1/3(50\%) + 2/3(50\%)] < \text{Al}_2(\text{SO}_4)_3$ .

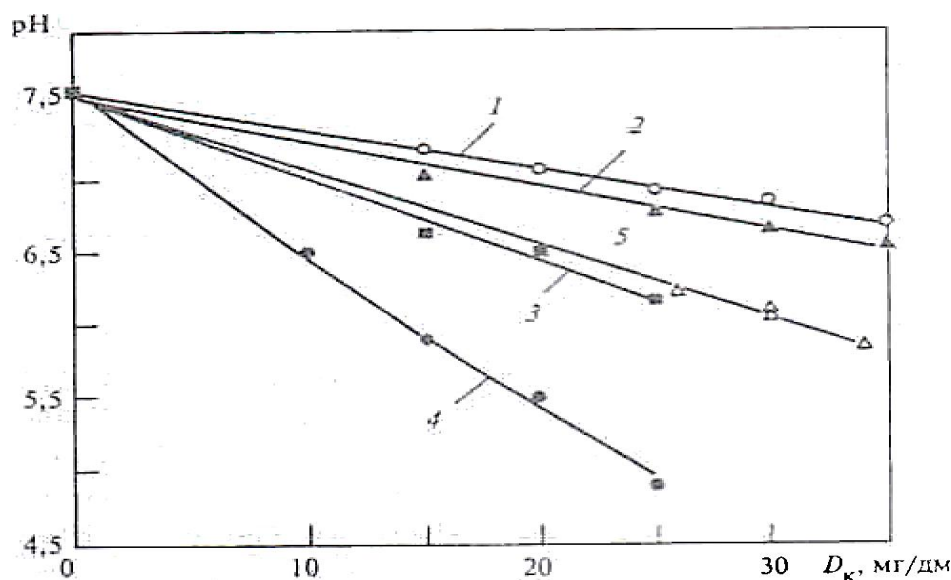


Fig.1. Change in the pH of the treated water depending on the dose of various coagulants

1 —  $\text{OXA} [2/3(60\%) + 5/6(40\%)]$ ; 2 —  $\text{OHA} [2/3(100\%)]$ ;

3 —  $\text{OXA} [1/3(50\%) + 2/3(50\%)]$ ; 4 —  $\text{Al}_2(\text{SO}_4)_3$ , 5 —  $\text{OHA} [2/3(100\%)]$ , manufacturer OAO «Aurat».  
Manufacturer of Coagulants 1—4 — OAO «Boksitogorsky alumina»

The effectiveness of reducing permanganate oxidability also depends on the basicity modulus of the OX (Fig. 2): the higher it is, the more coagulant is required to achieve the same oxidability. At equal  $D_K$ , reducing the concentration of organic impurities is more effective at lower pH, i.e., at a dosage of  $\text{Al}_2(\text{SO}_4)_3$  and OX with a low basicity modulus. However, its effect on the oxidability, in contrast to the pH value, is insignificant.

Regardless of the initial oxidizability, the decrease in the concentration of organic impurities decreases in accordance with the order:  $\text{Al}_2(\text{SO}_4)_3 > \text{OHA} [1/3(50\%) + 2/3(50\%)] > \text{OHA} [2/3(100\%)] > \text{OHA} [2/3(60\%) + 5/6(40\%)]$ .

)]. This dependence is typical only for waters with high color content. With less chroma, on the contrary, there is a high efficiency of reducing the oxidability during coagulation with high-base OHA. The dose of these coagulants is lower to achieve optimal oxidizability, and the coagulation proceeds more efficiently in a less acidic environment than with a dosage of  $\text{Al}_2(\text{SO}_4)_3$ .

For the Pskov GRES water, the following results on oxidability were obtained: the values of 4.9...5.0  $\text{MgO/dm}^3$  are reached when dosing about 20  $\text{mg/dm}^3$  of aluminum sulfate and with a slight increase in the dose of aluminum and with a slight increase in the dose (by 15...20 %) of high-base OHA. In this case, the water

content is reduced by about 0.9 when treated with  $\text{Al}_2(\text{SO}_4)_3$ , and by 0.3 mg-eq/dm when treated with OX, with a corresponding decrease in pH to about 5.3 and 7.0 with an increase in the concentration of  $\text{SO}_4$  ions by 1.2

mg-eq/dm, and chlorides — by 0.6 mg-eq/dm. If mixed OHA is used [2/3 (60 %) + 5/6 (40 %)], then the change in pH and Sch will be even smaller.

**Tab 2.**

Results of laboratory experiments at  $D_K = 25 \text{ mg / dm}^3$

| Coagulant                     | rH   | W mg-<br>ekv/dm <sup>3</sup> | Cl <sup>-</sup> mg-<br>ekv/dm <sup>3</sup> | $\text{SO}_4$ mg-<br>ekv/dm <sup>3</sup> | Femkg/d<br>m <sup>3</sup> | OkmgO/<br>dm <sup>3</sup> | I <sub>st</sub> [4] |
|-------------------------------|------|------------------------------|--|--|---------------------------|---------------------------|---------------------|
| Source water                  | 7.60 | 0.93                         | 0.1  | 0.6                                      | 1075                      | 24.3                      | -0.84               |
| $\text{Al}_2(\text{SO}_4)_3$  | 4.90 | 0.06                         | 0.1  | 2.1                                      | 50                        | 3.7                       | -4.56               |
| OHA [1/3 (50 %) + 2/3 (50 %)] | 6.16 | 0.31                         | 1.0  | 0.6                                      | 19                        | 3.5                       | -2.66               |
| OHA [2/3 (100 %)]             | 6.79 | 0.60                         | 0.8  | 0.6                                      | 29                        | 4.8                       | -1.85               |
| OHA [2/3 (60 %) + 5/6 (40 %)] | 6.91 | 0.85                         | 0.6  | 0.6                                      | 25                        | 5.5                       | -1.70               |

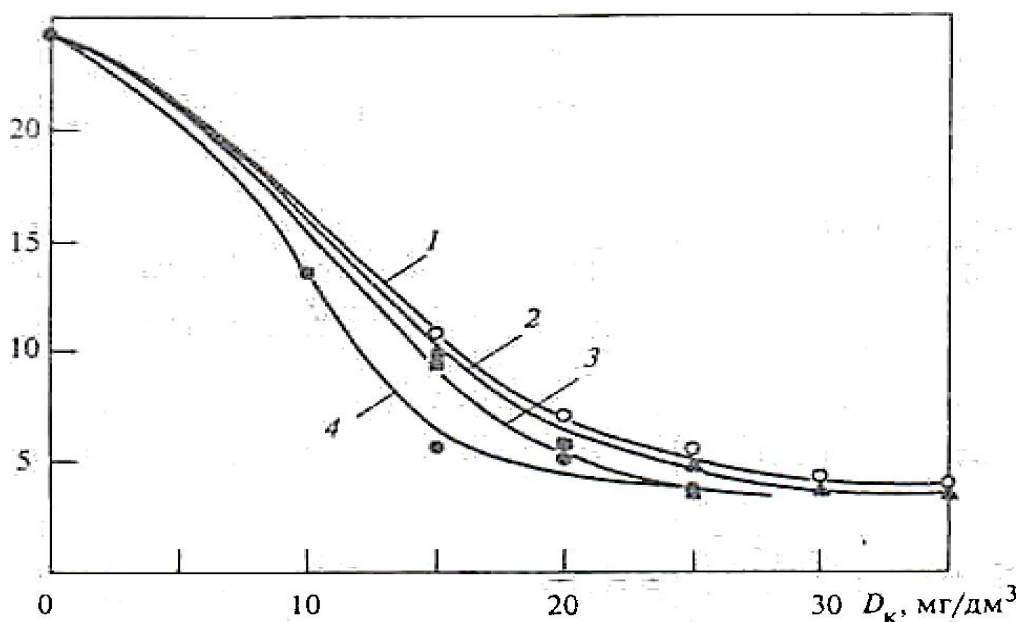


fig.2. Changes in the oxidability of treated water depending on the dose of various coagulants. 1-4 see on fig. 1

Such changes in the quality of clarified water also affect its stability. Table 2 shows the results of laboratory experiments on coagulation for the studied coagulants, as well as the calculated values of the stability index of Ist [4]. From the analysis of its data, it follows that the water treated with  $Al_2(SO_4)_3$  is characterized by low pH values, and the highest negative stability index, i.e., the water is extremely aggressive. The quality of water coagulated with OHA is characterized by higher pH values, and less aggressiveness. Differences in the quality of water clarified by OHA [2/3 (100 %)] and mixed coagulant, insignificant. Therefore, for industrial tests, a cheaper coagulant with a basicity modulus is recommended [2/3 (100 %)] produced by JSC "Boksitogorsky alumina". The main purpose of experimental and industrial tests using OCA is to test the coagulation technology in three

modes: with nominal alkalization of the source water [corresponds to the mode for dosing  $Al_2(SO_4)_3$ ]; with minimal alkalization and in the absence of preliminary alkalization, aluminum oxychloride with a basicity modulus of 2/3 was delivered to the Pskov GRES for coagulation instead of OCA with a basicity modulus of 2/3, as shown by the input control of the reagent [2/3 (46 %) + 1/3 (54 %)], those with less basicity than was recommended. The supply of such an OX to the clarifier with a dose of 1 mg-eq/dm should theoretically reduce the Schna of 0.48 mg-eq/dm. However, when the initial alkalinity of the water is low, due to the incompleteness of the hydrolysis process, the change in the Sc will be less. The increase in the concentration of chlorides is proportional to the dose of the coagulant and is approximately 0.6 mg-eq/dm due to the presence of NaCl impurities,

changes in the alkalinity and concentration of chlorides, as shown by laboratory studies, will be significantly greater, and the pH is lower than if the OCA with a basicity modulus of 2/3 was used. Therefore, for a given water, the indirect indicator that determines the value of  $D_K$  will be the change in the concentration of chlorides, and not the alkalinity.

During the tests, the coagulant was supplied to the source water in front of the air separator, and polyacrylamide was supplied to the cone part of the clarifier in all modes.

At the first stage of the research, the optimal dosage of OH was specified during the preliminary alkalization of the source water

and the hydraulic characteristics of the sludge were determined; at the second stage, the operating mode of the clarifier and the quality of the coagulated water with minimal alkalization were analyzed; at the third stage, the optimal and minimum doses of OH without alkalization were determined. During the tests, the operational control of the dose of the coagulant was carried out (by increasing the concentration of chlorides and the actual consumption of the coagulant solution from the measuring tank), the operating mode of the slurry filter, the quality of the source water and the main indicators of the coagulated water in the mixing zone and at the outlet of the clarifier.

**Tab.3. Quality indicators of clarified water according to the data of the day laboratory of the Pskov Hydroelectric Power Station**

| Indicator                           | Alkalization, Coagulant       |                    |             |                  |
|-------------------------------------|-------------------------------|--------------------|-------------|------------------|
|                                     | Nominal value, $Al_2(SO_4)_3$ | Nominal value, OHA | Minimum OHA | The lack of, OHA |
| J, mg-ekv/dm <sup>3</sup>           | 1.0                           | 1.04               | 1.0         | 1.0              |
| W, mg-ekv/dm <sup>3</sup>           | 0.03                          | 0.45               | 0.29        | 0.3              |
| Ok, mgO/dm <sup>3</sup>             | 5.2                           | 6.4                | 4.2         | 3.8              |
| PH                                  | 5.3                           | 6.79               | 6.2         | 6.4              |
| Concentration mkg/dm <sup>3</sup> : |                               |                    |             |                  |
| Al                                  | -                             | 100                | 20          | 85               |
| Fe                                  | 60                            | 55                 | 38          | 36.5             |



| Concentration<br>mkg/dm <sup>3</sup> : |              |               |               |               |
|--|--------------|---------------|---------------|---------------|
| Cl <sup>-</sup>                        | 2.0          | 34.8          | 36.6          | 32.0          |
| SiO <sub>2</sub>                       | 3.0          | 2.75          | 3.0           | -             |
| SO <sub>4</sub> <sup>-</sup>           | 98           | -             | 0.8           | 1.2           |
| Date                                   | 9/IX<br>2004 | 24/IX<br>2004 | 27/IX<br>2004 | 30/IX<br>2004 |

In addition, 1 a day, the main indicators of the clarified water quality were determined by the day laboratory (Table 3). The transition to aluminum oxychloride coagulation in all modes did not lead to violations of the clarifier; the sludge filter functioned stably. A comparison of the quality of clarified water during the coagulation of OH and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> shows that there are no obvious advantages in terms of such indicators as the concentration of Fe, Al, SiO<sub>2</sub> and oxidability. At the same time, when using OHA, clarified water is characterized by higher rH values, less aggressiveness and a decrease in the total salt load on ionite filters.

Table 4 shows the main results of tests for the coagulation of OHA water in three modes of

operation of the clarifier, as well as with optimal alkalization during the coagulation of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. A comparison of the results obtained at almost equal doses of coagulants and alkali o<sub>sh</sub> showed that the dosing of OHA allows you to get water with less aggressiveness: the pH of clarified water is 6.69, and when using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> - 5.3. In the mode with minimal alkalization, the water

quality during the coagulation of OCHA is almost by all indicators, it is higher than with the existing technology. Complete elimination of alkalization also makes it possible to obtain high-quality water with a rH= 6.16...6.35 at doses of OHA equal to 1.7..1.2 mg-eq/dm<sup>3</sup>.

### 5. Results of oxychloride tests at the Pskov plant Hydroelectric Power Station

| Indicator | Coagulant                                       |   |
|-----------|---|---|
|           | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> | OXA [1/3(54%) + 2/3(46%)]<br>OAO<br>«Boksitogorsky alumina» |



|   |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|
| Expenditure,m <sup>3</sup> /ch          | 80    | 75    | 82    | 82    | 82    |
| Source water:                           |       |       |       |       |       |
| pH                                      | 7.35  | 7.4   | 7.33  | 7.25  | 7.3   |
| t, °C                                   | 29    | 29    | 29    | 28    | 29    |
| Sh, mg-ekv/dm <sup>3</sup>              | 0.8   | 0.7   | 0.8   | 0.8   | 0.7   |
| J, mg-ekv/dm <sup>3</sup>               | 1.0   | 1.02  | 1.0   | 1.02  | 1.02  |
| Ok, mgO/dm <sup>3</sup>                 | 21.6  | 20.0  | 21.6  | 20.8  | 21.6  |
| Cl <sup>-</sup> mg/dm <sup>3</sup>      | 1.8   | 2.0   | 1.8   | 2.0   | 2.0   |
| SiO <sub>2</sub> mg/dm <sup>3</sup>     | 3.5   | 3.3   | 3.26  | 3.3   | 3.4   |
| Offset point:                           |       |       |       |       |       |
| rH                                      | 5.2   | 6.6   | 6.01  | 6.04  | 6.32  |
| Sh, mg-ekv/dm <sup>3</sup>              | 0.02  | 0.47  | 0.22  | 0.24  | 0.36  |
| Cl <sup>-</sup> mg/dm <sup>3</sup>      | -     | 36    | 37    | 31    | 23    |
| D <sub>sh</sub> ,mg-ekv/dm <sup>3</sup> | 0.3   | 0.4   | 0.1   | 0     | 0     |
| D <sub>K</sub> ,mg-ekv/dm <sup>3</sup>  | 32    | 28    | 34    | 29    | 21    |
| Clarifier output:                       |       |       |       |       |       |
| rH                                      | 5.3   | 6.69  | 6.12  | 6.16  | 6.35  |
| SH, mg-ekv/dm <sup>3</sup>              | 0.03  | 0.46  | 0.23  | 0.23  | 0.31  |
| Ok, mgO/dm <sup>3</sup>                 | 5.2   | 5.6   | 5.2   | 5.2   | 5.8   |
| Turbidity,mg/dm <sup>3</sup>            | 0.145 | 0.145 | 0.116 | 0.319 | 0.145 |

In addition to reducing the aggressiveness of water by about 15 %, there is an increase in the duration of the filter cycle in the VPU.

Thus, the industrial tests carried out confirmed the effectiveness of OCHA and showed the advantages of mixed OCHA [ $\frac{1}{3}$  (50%) +  $\frac{2}{3}$  (50 %)] compared to  $Al_2(SO_4)_3$ . The use of aluminum oxychloride instead of aluminum sulfate reduces the aggressiveness of clarified water and its consumption for its own needs.

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