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# PURIFICATION OF CIRCULATING AND WASTE WATER IN METALLURGICAL INDUSTRY USING COMPLEX COAGULANTS

E. N. Kuzin[1], N. E. Kruchinina[1]

[1] *Mendeleyev University of Chemical Technology of Russia (Moscow, Russia)*

***E-mail: e.n.kuzin@mail.ru; krutch@muctr.ru***

AUTHOR'S INFO

**E. N. Kuzin**, Cand. Eng., Department of Environmental Engineering,
**N. E. Kruchinina**, Dr. Eng., Head of Faculty of Biotechnology and Environmental Engineering, Head of Department of Environmental Engineering

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ABSTRACT

The main goal of waste water treatment of metallurgical production is to return water to the circulating water supply system. The main pollutant of most process effluents are suspended substances, or suspensions. The key parameter for evaluating the cleaning efficiency is the residual content of suspended substances, which should not exceed 1–10 mg/l, depending on the technological purpose of the water.

The most promising reagents for physic-chemical water treatment are complex coagulants that combine salts of two or more metals. Such reagents are free from the disadvantages of traditional coagulants, and large-scale wastes from various industries can be used as raw materials for their production. Complex coagulants based on aluminum salts, when aluminium is modified by the products of hydrolysis of titanium compounds, have proven to be highly effective in treatment processes of waste water of various origins.

Testing of the complex coagulant obtained in the process of modifying of traditional aluminum sulfate by the products of hydrolysis of titanium compounds was carried out on waste water from gas cleaning plants for coal preparation, coking plants and electric arc furnaces for steelmaking. In terms of its effectiveness, the complex coagulant exceeded traditional aluminum sulfate and was as close as possible to the more expensive and modern aluminum oxychloride. The increased efficiency of the complex coagulant is due to flocculation and nucleation phenomena occurring on the surface of titanium compounds compared with aluminum sulfate. The complex coagulant was less sensitive to fluctuations in the pH of the treated water than pure aluminum sulfate. As a result of water treatment, it was possible to achieve a reduction in the content of suspended substances below 1 mg/l, which will positively affect the economy of the water treatment process. The rate of flake deposition and filtration of treated water, using complex coagulant, significantly exceeded both samples of the most common coagulants. Increased sediment density will reduce reagent costs for its dehydration, as well as the area required for its placement.

## Introduction

Metallurgical production is characterized by large volumes of water consumption [1]. Most part of water is circulated in cooling systems and is not polluted. Gas purification processes occupy the second place by amount of consumed water.

Volumes and pollution of forming waste water after gas purification processes can differ essentially for various plants [1, 2]. Insoluble mineral impurities (suspended substances) are considered as the most common polluting substances. The most part of suspensions has rather large size (more than 50 μm) and is deposited rather quickly in the primary dehydrating box under the effect of gravity force.

Purification of preliminarily enlightened water from fine-dispersed (1–10 μm) impurities is quite more complicated task. Deposition time of the particles with 5 μm diameter makes 0.01 mm/s (3.6 cm/h), and for particles with 1 μm — 0.1 cm/h, what increases significantly sizes of dehydrating boxes [3, 4]. Usage of up-to-date thin-layered dehydrating boxes allows to reduce sedimentation time by 25–30% and equipment size by 60%; however, often it is not sufficient [5, 6].

Requirements to water for its reuse differ substantially for various processes, however, increase of salt composition (above 1500 mg/l) and content of suspensions and oil products in water above 10 mg/l and 5 mg/l respectively are not desirable because it can be harmful for technological equipment.

Reagent water processing (such as coagulation/flocculation) is used most frequently for intensification of deposition processes of such articles. Compounds of Al or Fe are usually used as coagulants. These coagulants are used for a long time and displayed positive experience in the processes of purification of waste water of various origin. Despite that positive experience, these reagents are characterized by some disadvantages: Fe-containing coagulants lead to corrosion of equipment and involve secondary water pollution by Fe ions, while Al compounds can be applied only in the narrow pH range and are non-efficient at low water temperature [4].

Information about use of titanium-based coagulants in the processes of water purification has been met recently more often. Such coagulants provide sometimes more purification efficiency in smaller amounts and also have not disadvantages usual for traditional reagents [7–10]. Hydrolysis products of titanium compounds exceed in their efficiency even the most up-to-date aluminium oxychloride [11]. However, usage of pure titanium salts as coagulants is rather expensive and, consequently, is not spread widely.

Usage of complex mixed reagents is considered as prospective direction of physical-chemical purification. Traditional coagulants that are modified by titanium [12] and silicon [13] compounds displayed their high ef-

Table 1. **Chemical composition of waste water samples**

| Waste water | Total content of suspended particles, mg/l | Content of fine-dispersed particles, mg/l | pH | Size of fine-dispersed fraction, μm | Size of coarse-dispersed fraction, μm | Charge of particles, mV |
|---|---|---|---|---|---|---|
| Gas purification of coal preparation | 2563 | 98.3 | 5.34 | 2.6–3.5 | 29–103 | +(20–25) |
| Gas purification of electric arc furnace | 9341 | 58.7 | 5.23 | 5.9–7.9 | 50–270 | –(10–18) |
| Gas purification of coking | 3290 | 64.5 | 6.42 | 9.3–12.8 | 36–190 | +(26–29) |

ficiency in purification processes for waste water of various origins.

Usage of complex titanium-bearing reagents for purification of waste water of metallurgical processes seems to be the most prospective research direction, taking into account the fact that such reagents were used with positive feedbacks in purification of waste water of mining and concentration plants [14].

## Research objects and methods

The aim of this research is to evaluate possibility of usage of complex coagulants in the processes of waste water purification in metallurgical production.

The main experimental task is waste water purification to the level meeting the technical requirements of corresponding regulations for circulating water quality as well as comparison of complex coagulant with traditional reagents.

The sample of complex coagulant (CC) obtained via aluminium sulphate modification by hydrolysis products of titanium compounds was selected as the research object. Weight amounts of titanium chlorides were introduced in water solutions of aluminium sulphate; then hydrolysis reaction took place with forming of colloid particles containing of different products of hydrolysis of titanium compounds (reaction 1) [15, 16]. Content of modifying component in CC composition made 5% (mass.) (by $TiO_2$).

$$TiCl_4 \cdot 5H_2O \leftrightarrow Ti(OH)Cl_3 \cdot 4H_2O + HCl \leftrightarrow$$

$$\leftrightarrow Ti(OH)_2Cl_2 \cdot 3H_2O + HCl \leftrightarrow Ti(OH)_3Cl \cdot 2H_2O +$$

$$+ HCl \leftrightarrow Ti(OH)_4 \cdot H_2O + HCl \quad (1)$$

Pure aluminium sulphate and aluminium oxychloride (average basic) was used in samples for comparison.

Testing coagulation was conducted in laboratorial flocculator JLT 4 (VELP), with quick mixing time 2 min, slow mixing time 8 min and deposition time 30 min. Samples of purified water were analyzed for content of suspended particles.

Efficiency of obtained reagent was evaluated on the following samples of waste water:

• Waste water from gas purification process at the coal preparation shop in the coke chemical plant;

• Waste water from gas purification system at electric steelmaking furnace in the machine-building works;

• Waste water from gas purification process at the coking shop in the coke chemical plant.

Water samples were preliminarily filtered through a net sieve 200 μm and dehydrated during 10 min for separation of coarse particles from quickly depositing fraction.

Content of suspended substances was determined via gravimetric method, and also using portable turbidimeter HANNA (HI 98703-02).

Size and zeta-potential of colloid particles were determined using Zetasizer Nano (Malvern) и Analysette 22 NanoTec (Fritsch) devices.

## Experimental results and discussion

It was revealed on the base of analytical results that suspended particles in waste water forming during the processes of coal preparation and coking are presented by carbon particles, bearing positive charge on their surface, what correlates with bibliographic sources [17]. Oxides of silicon, iron and metals being part of content of alloying compositions were the main components of dispersed particles presented in waste water of the gas purification system in the electric arc furnace. Parameters of water samples are displayed in the **Table 1**.

Optimal CC dose providing maximal purification efficiency was revealed at the first experimental stage. Efficiency of purification of waste water depending on CC dose is shown on the **Fig. 1**.

The **Fig. 1** displays that CC efficient dose does not depend practically on the source of waste water forming or pH initial value and makes 20 mg/l summarized for metal oxides. High purification efficiency during CC usage is caused supposedly by flocculation appearances occurring during polymerization [18] of titanium compounds and nucleation processes [19, 20] on the surface particles of products forming during hydrolysis of titanium compounds. These particles had negative charge and lowered surfacial positive charge of coal particles, what played a definite positive role.

Evaluation of summarized purification efficiency was conducted at the next experimental stage for efficient coagulant dose. The efficient dose of CC and aluminium oxychloride made 20 mg/l (summarized for metals), while for aluminium sulphate it made 25 mg/l (for $Al_2O_3$). The comparing data for maxi-

Table 2. **Parameters of removal of suspended substances**

| Waste water | Time of complete slime deposition, s | | | Filtration rate, ml/min | | |
|---|---|---|---|---|---|---|
| | Aluminium sulphate | Complex coagulant | Aluminium oxychloride | Aluminium sulphate | Complex coagulant | Aluminium oxychloride |
| Gas purification of coal preparation | 246 | 97 | 119 | 42 | 72 | 61 |
| Gas purification of electric arc furnace | 260 | 85 | 104 | 41 | 92 | 79 |
| Gas purification of coking | 100 | 78 | 98 | 94 | 113 | 98 |

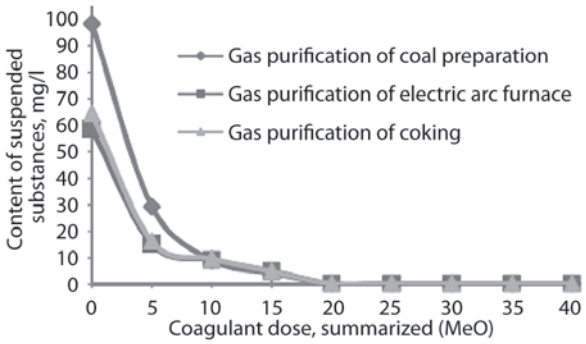


**Fig. 1. Influence of complex coagulant (CC) dose on residual content of suspended substances**

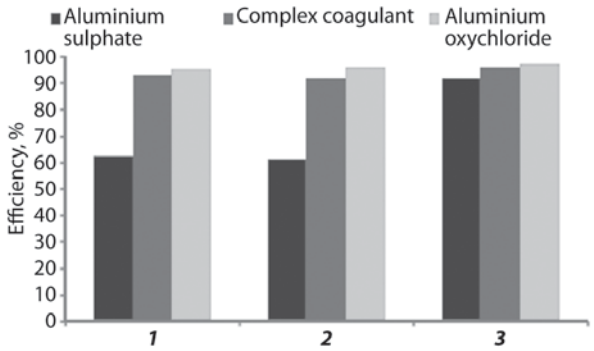


**Fig. 2. Comparison of efficiency of coagulants:**
*1* — gas purification of coal preparation;
*2* — gas purification of electric arc furnace;
*3* — gas purification of coking

mal achieved purification efficiency are presented on the **Fig. 2**.

**Fig. 2.** displays that CC is comparative in its efficiency with aluminium oxychloride — the most efficient and widely spread at present time. Lowered efficiency of aluminium sulphate is caused by low pH of processed water.

Addition of titanium compounds can rise efficiency of aluminium sulphate due to specific processes of joint hydrolysis of aluminium sulphate and titanium compounds (increase of hydrolysis rate), forming of wide spectrum of hydrolysis products [15] as well as appearances occurring on the surface of products of hydrolysis of titanium compounds [18–20].

Essential difference in deposition processes (rate of deposition, form and morphology of a sediment) in the process of slime coagulation was noted during experiments.

Filtration rate was measured by pouring of purified water through the filter of "Blue ribbon" type with size of pores 3-5 μm. Parameters of sedimentation and filtration of sediment are presented in the **Table 2**.

**Table 2** data testify that usage of CC leads to significant increase of rate of deposition and filtration of coagulation sediments. Probably this appearance is caused by increase of size of forming substances due to flocculating effect of products of hydrolysis of titanium compounds, as well as neutralization and nucleation processes on their surface. This aspect has applied character because it allows to decrease substantially time of slime deposition and filtration and, respectively, sizes of corresponding water purification equipment.

## Conclusion

It can be concluded on the base of obtained experimental results that introduction of products of hydrolysis of titanium compounds in coagulant composition leads to intensification of coagulation processes for dispersed particles of different size and sedimentation process of forming slimes.

It was proved that usage of complex reagents allows to rise substantially purification efficiency in comparison with traditional aluminium sulphate. Complex coagulant has more wide pH range and does not give up in its efficiency to aluminium oxychloride that is widely used. According to the preliminary economical evaluation, the cost of aluminium oxychloride is higher by 2.0–2.5 times in average than CC cost. Besides that, large-scale wastes of high tonnage can be initial raw material for obtaining of complex reagents. Usage of complex coagulants makes it possible to increase significantly deposition rate of suspended particles and to decrease processing time of purifying effluents in dehydrating boxes as well as to reduce their sizes.

Usage of new high-efficient complex reagents (coagulant/flocculant [13] or adsorbent/cationite [21] in purification processes of waste water in metallurgical industry allows to decrease essentially negative effect on hydrosphere. Slime obtained in coagulation process can be used for manufacture of titanium-bearing products [22] and respectively for realization of the waste-free production strategy [23] and putting into practice the best available technologies in metallurgy [24].

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