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Coagulant on the base of industrial ferriferous waste for the preliminary treatment of multi-component sewage

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Abstract. The paper gives the results of a study on the processing of model systems by a coagulating suspension made on the basis of dust from electric arc furnaces (EAF). Dust of electric furnace steelmaking is a large-tonnage waste containing in its composition a large number of iron compounds. When treating EAF with hydrochloric acid, formed ions FeOH^+ , FeOH^{2+} , $[\text{Fe}(\text{OH})_2]^+$ in this process provoke coagulation, which leads to the adhesion of particles in the system and their sedimentation. It is shown that the suspension is effective for clarifying aqueous media from suspended particles (kaolin clay). It has been established that precipitation occurs more effectively in a neutral and alkaline environment than in an acidic one. When processing multicomponent model systems (industrial oil stabilized with sodium lauryl sulfate and clay particles), the efficiency of clarification decreases, but remains high enough (65%). Taking into account the research results, the coagulating suspension can be used at the stage of pre-treatment of highly contaminated sewage of mixed composition to facilitate and reduce the cost of subsequent stages of water treatment.

Keywords. Water treatment, coagulation, industrial waste, wastewater, oil products, multi-component sewage, colloidal systems, clay suspension

1. Introduction

The global environmental crisis is the result of the cumulative anthropogenic impact of all states and peoples of the world on nature [1]. Water consumption has now reached huge volumes. Table 1 presents data on groundwater and surface water abstraction in some countries, 2005-2015 (million m³).

Sewage resulting from economic and industrial activities is a big problem for all countries of the world, and they require new solutions.

Most sewage is a multicomponent polydisperse system, containing chemicals of various nature and inclusions of varying sizes. This introduces difficulties in the process of water treatment, requiring the use of devices and methods in various combinations. So, one of the most toxic, and at the same time, widespread pollutants of our time are petroleum products [3-5]. Sources of their inflows into natural ecosystems are multiple and the composition of the resulting sewage is also different. In addition to the petroleum products themselves, drainages in most cases contain suspended substances, synthetic



surfactants, dyes, etc. These components lead to the stabilization of oil emulsions, and, as a result, make water treatment more difficult [6, 7]. Therefore, the pre-cleaning step is necessary in many waste treatment plants.

Table 1. Groundwater and surface water abstraction data

| Country | Groundwater abstraction | | | Surface water abstraction | | |
|-----------------|-------------------------|------|------|---------------------------|-------|---------|
| | 2005 | 2010 | 2015 | 2005 | 2010 | 2015 |
| Belgium | 636 | 612 | 632 | 5753 | 5341 | no data |
| Bulgaria | 597 | 557 | 558 | 5439 | 5403 | 5071 |
| Czech Re-public | 385 | 377 | 366 | 1564 | 1573 | 1237 |
| Estonia | 274 | 296 | 199 | 1304 | 1546 | 1525 |
| Greece | 3772 | 5615 | 5611 | 5882 | 4319 | 4297 |
| Spain | 6387 | 6601 | 6304 | 31643 | 29009 | 26613 |
| Poland | 2633 | 2722 | 2608 | 8889 | 8923 | 8486 |
| United Kingdom | 2336 | 2152 | 2053 | 7988 | 6111 | 5232 |

Coagulation is one of the most effective and easy in using methods for extracting suspended substances from aqueous systems [8-11].

Coagulation cleaning can be divided into two main stages:

- Coagulation itself, i.e. the process of destabilizing the colloid system, achieved by the use of coagulant substances having a short duration in time;
- Flocculation this is inducing the approach of destabilized particles to form agglomerates which are capable to precipitate itself under the influence of gravity, this stage can last more than half an hour [12, 13].

Depending on the size of particles dispersed in water, the time of their precipitation may vary from 0.1. s (in the case of coarse systems) to decades (fine systems), or the absence of precipitation at all. Due to the very small size, the only way to precipitate, and, subsequently, isolate such particles, is to cause their aggregation [14, 15]. However, the spontaneous occurrence of such a process is impossible due to the action of repulsive forces of like charges of particles, which determines the stability of the system to precipitation [13, 17, 18].

The coagulant substances added to the water provokes a decrease in the surface charge, after which the particles can become close and Van der Waals forces start acting (figure 1) [19].

Most of all aluminum and iron salts are used as coagulants, the hydrolysis of which is accompanied by the formation of large flakes [19–21].

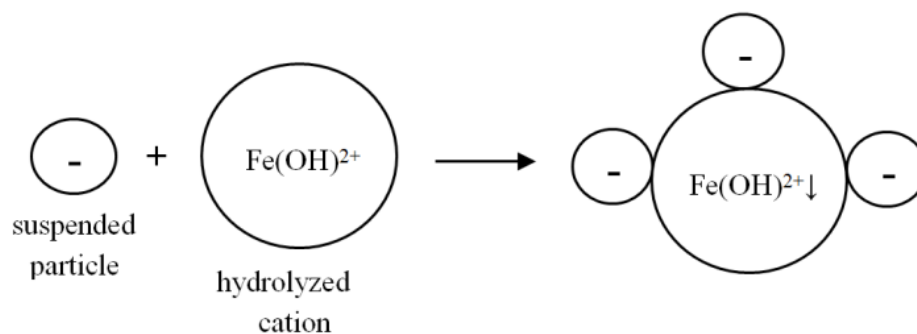


Figure 1. Mechanism of adsorption coagulation

Various parts of plants can be used as coagulants. There are known works on the application of Okra (*Abelmoschus esculentus*) [22], *Moringa oleifera*, *Dolichos lab lab* and *Cicer arietinum* [23].

In work [12], KlarAid CDP1326 coagulants (contains ferric sulfate), KlarAid PC1195 (1, 2 – ethanediamine) and KlarAid IC1176 (contains aluminum chloride) were used to purify sewage contaminated with oil products and suspended substances.

Thus, coagulation cleaning is an important stage of water conditioning and purification in the treatment of multi-component sewage, which permit to isolate a significant part of the dispersed pollutants.

Dust of electric furnace steelmaking is a large-tonnage waste containing in its composition a large number of iron compounds (figure 2) [24, 25].

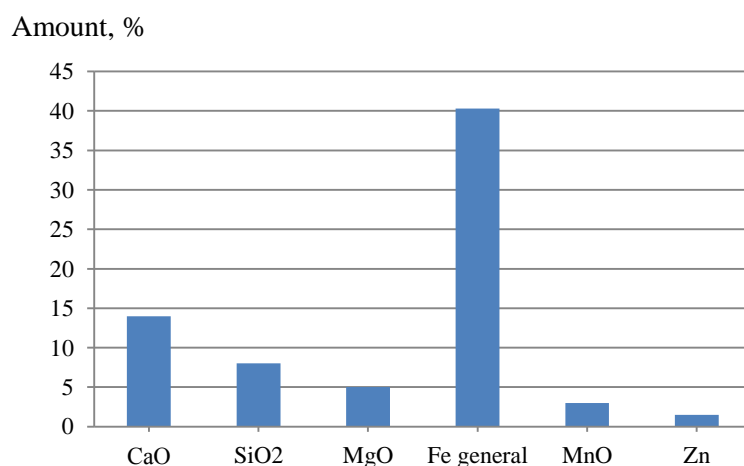
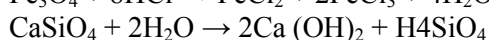
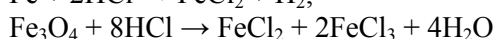
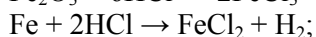
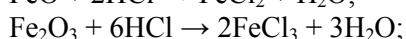
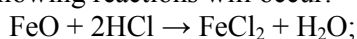


Figure 2. Element-oxide composition of EAF dust

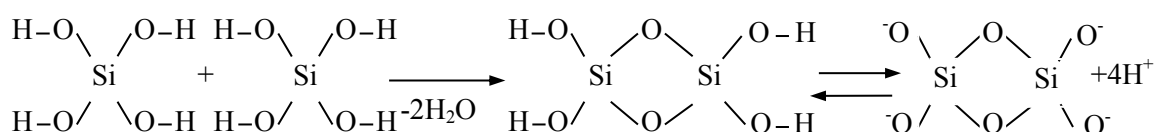
According to the well-known scientific data [26], when treating EAF with hydrochloric acid, the following reactions will occur:



The formed ions FeOH^+ , FeOH^{2+} , $[\text{Fe}(\text{OH})_2]^+$ in this process provoke coagulation, which leads to the adhesion of particles in the system and their sedimentation [27].

Since a significant amount of calcium oxide is present in the form of compounds in the dust composition of EAF, then when the pH of the medium is increased due to their dissolution, the following ions can be formed: $[\text{Fe}(\text{OH})_4]^-$, $[\text{Fe}(\text{OH})_5]^{2-}$, $[\text{Fe}(\text{OH})_6]^{3-}$ and others [21, 28].

Silicates present in the dust are able to dissolve in an acid medium with the formation of silicic acids, and then polysilicon, both linear and volumetric types [25]:



These compounds have the properties of flocculants, which intensifies water treatment.

It was previously established that the coagulant suspension (CS) is effective for the precipitation of suspensions due to the presence of natural clay particles, as well as organic emulsions formed from components of cow and soy milk [29, 30]. It was of scientific interest to find out the effectiveness of the release of suspended substances from model systems of mixed composition: oil product emulsions and inorganic suspended substances.

2. Materials and methods

The test involved a coagulating suspension produced on the basis of EAF dust treated with HCl (1N solution), and model wastewater. For making efficient coagulating suspension, according to the preliminary studies, the proportion of 6.5 ml HCl / 1 g of dust is necessary.

For making suspended particles in a modeled wastewaters kaolin clay was used.

To prepare the model emulsion, an industrial oil of general purpose I-20A (GOST 20799-88) [31] in the amount of 1 g / dm³ and sodium lauryl sulfate (0.005 g / dm³) was added to the tank with tap water to stabilize the water-oil system. The emulsion obtained after stirring on an automatic mixer for 24 hours was characterized by high stability and did not break down for several days.

The clarification of the emulsions was determined by the turbidity (NTU) using the HI 98703 Portable Turbidimeter (Hanna Instruments, USA)

3. Results and discussion

Some studies have been carried out to determine the applicability of the obtained CS for the purification of various aqueous media containing inorganic and organic pollutants.

Figure 3 shows the graphs of clay precipitation in model sewage without the addition and with the addition of CS (1 cm³ / dm³).

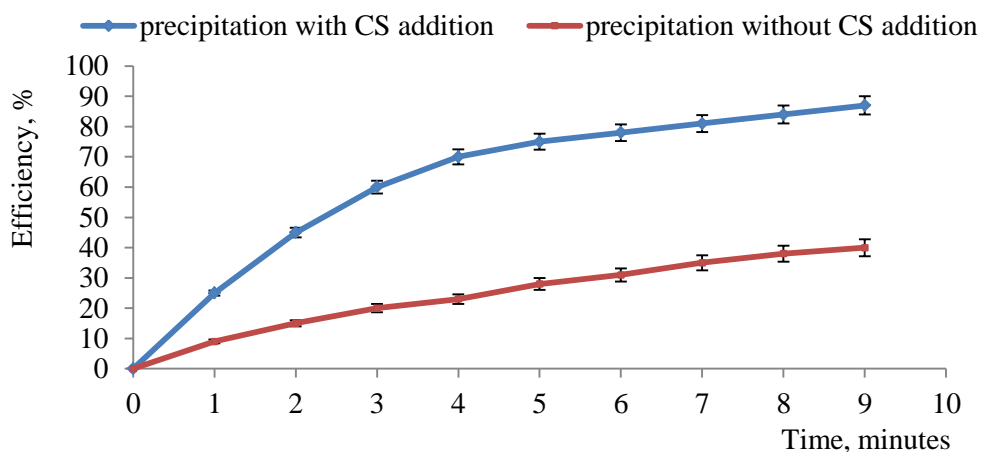


Figure 3. Sedimentation curves of precipitation of suspended substances in clay suspension

It is obvious that the addition of a CS to the water system intensifies the precipitation of suspended particles, which confirms the previously expressed assumptions.

Some researches were carried out to study the effect of the amount of CS added to the model systems on the efficiency of particle deposition (figure 4).

From the data presented in the last figures, it is seen that the addition of a suspension in amounts of 1 and 2 ml / dm³ allows achieving high cleaning efficiency in the first 30 minutes of interaction; the greatest effect is achieved during 2 hours. Adding more amount of CS does not lead to an increase of results, on the contrary, efficiency decreases, especially it is seen at prolonged defecate. This is probably due to the fact that the coagulation limit for this system is in the range of 1.5-2 ml / dm³. When the

concentration of CS is increased in the system, the particles are recharged in the suspension, as a result of which the cleaning efficiency decreases.

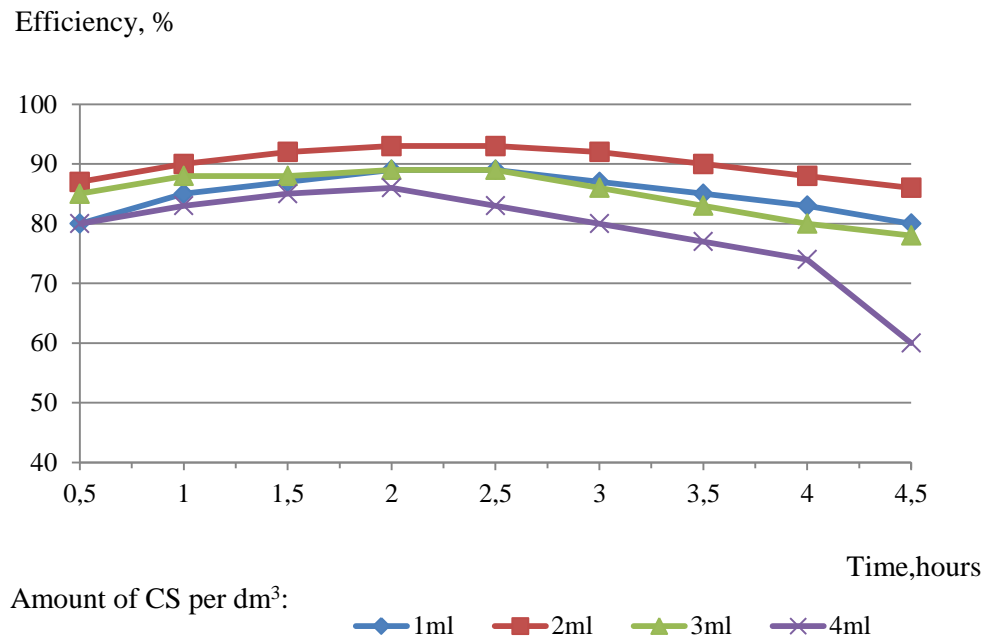


Figure 4. Influence of the amount of added CS and defecate time on the efficiency of cleaning model clay suspensions ($C_{\text{initial}} 1 \text{ g/dm}^3$)

With an increase in the concentration of clay particles in the system, the coagulation limit decreases (figure 5).

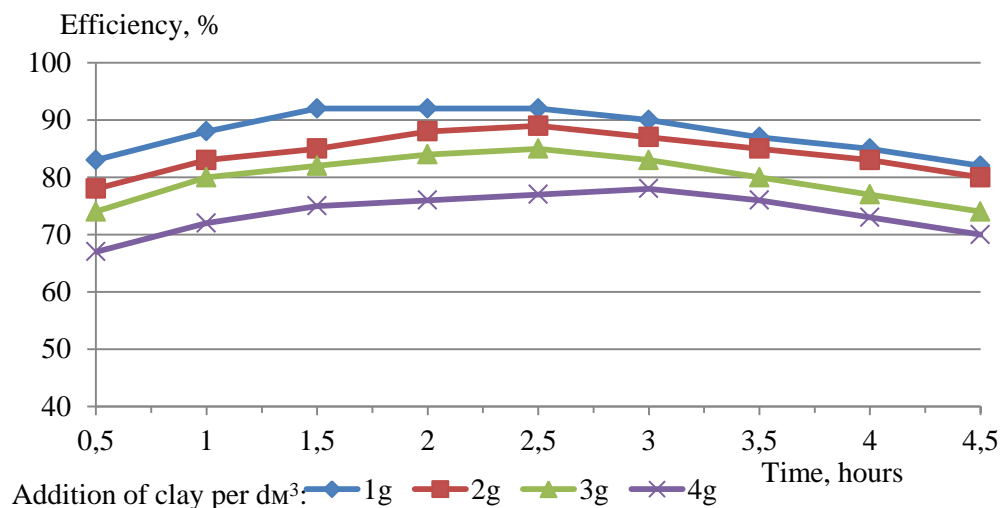


Figure 5. Influence of the efficiency of cleaning model suspensions on the initial clay concentration

Thus, it can be seen from figure 4 that the greatest efficiency of clarification of the emulsion at the initial clay concentration of 1 g/dm^3 is achieved by the addition of 1.5 ml of CS, while for the clay concentration of 3 g/dm^3 the required dose of CS is $2.5\text{-}3 \text{ ml/dm}^3$.

Thus, preliminary tests are necessary when using CS in industrial conditions to determine the optimum amount of coagulant added, based on the concentration of suspended substances in the sewage.

To clarify the effect of pH on the precipitation efficiency of suspended substances using CS, further studies were carried out.

The influence of the initial pH of the aqueous medium on the efficiency of clarification of model waters at a clay concentration of 1 g/dm^3 and the amount of the CS additive 0.5 g/dm^3 was investigated.

It has been established that precipitation occurs more effectively in neutral and alkaline environments than in acidic one (figure 6).

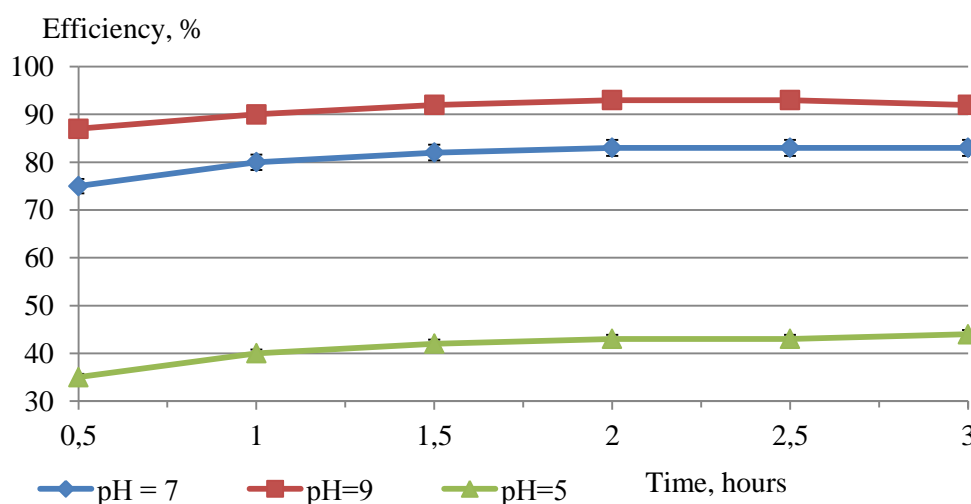


Figure 6. The effect of pH of the aquatic environment on the effectiveness of the cleaning of clay suspensions

The further researches were carried out to assess the effectiveness of clarification of multi-component sewage containing petroleum products. The emulsion with the initial content of industrial oil 1 g/dm^3 and suspended substances (clay) 1 g/dm^3 undergoes the contact with coagulating suspension in an amount of 2.5 ml/dm^3 for an hour and in this case stirring in the first 5 minutes was made for the better contact of the reagents, then the liquid was naturally defecated and the clarified layer of water was analyzed (figure 7).

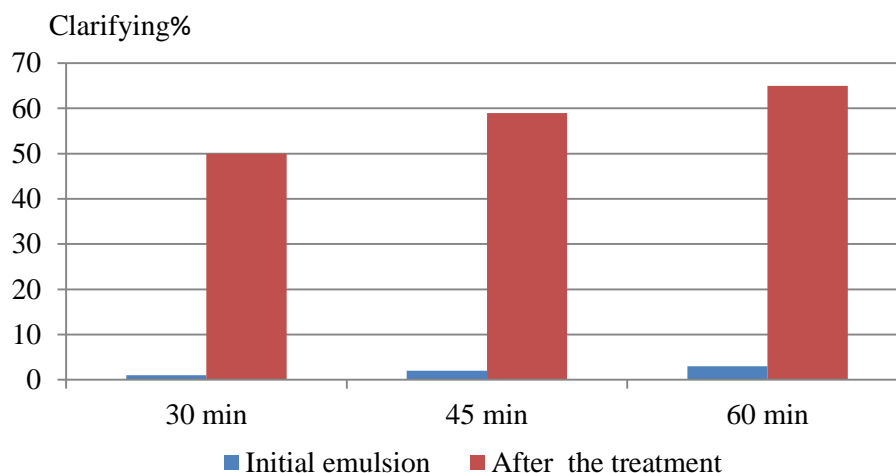


Figure 7. Efficiency of clarification of model sewage of multicomponent composition

From the results of the experiment it is evident that the coagulating suspension has an effective effect on waters of mixed composition. The stability of the system is partially violated and the effect of emulsion alteration is observed. Some of the contaminants are sedimentations on the bottom of the vessel, some part of the oil rises to the near-surface layer. Thus, the coagulating suspension can be used in the pre-treatment stage of highly contaminated sewage of mixed composition to facilitate and reduce the cost of subsequent water treatment steps.

4. Conclusion

Coagulating suspension based on dust EAF is an effective preparation for the treatment of sewage of various compositions. High efficiency is achieved during clarifying of model waters made on the basis of kaolin clay, so the efficiency in 93% is achieved by adding a suspension in the amount of 2 ml / dm³ to model waters contaminated with clay particles at a concentration of 1 g / dm³. When processing complex systems containing industrial oil stabilized with sodium lauryl sulfate and clay particles, the efficiency of clarification reaches 65%. Thus, the coagulating suspension can be used in the pre-treatment stage of highly contaminated sewage of mixed composition to facilitate and reduce the cost of subsequent water treatment steps.

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