

TITANIUM-CONTAINING COAGULANTS FOR FOUNDRY WASTEWATER TREATMENT

E. N. Kuzin¹, N. E. Kruchinina¹

¹ D. Mendeleev University of Chemical Technology of Russia (Moscow, Russia)

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

AUTHOR'S INFO ABSTRACT

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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Setting up a circulation water supply system is a prerequisite for a modern competitive steel making company. The most frequent problem faced by steel makers includes the challenge of removing suspended solids from large volumes of wastewater. Residual concentration of suspended solids (1-10 mg/l) is the main criterion of treatment efficiency. The most difficult task is to remove particles smaller than 1-2 microns, which stay suspended for a long time. One of the biggest sources of wastewater includes the process of removing residual molding sand from machine parts by water jet surface cleaning. Apart from high concentrations of suspended solids, process wastewater have high concentrations of dissolved organic compounds and require prior treatment before it can go to municipal wastewater treatment plants. Titanium-containing coagulants are being used more and more commonly in water treatment processes due to their high efficiency and the lack of most of the drawbacks inherent in conventional coagulants. This paper compares the conventional coagulants (i.e. aluminum and iron compounds) and coagulants containing titanium salts. In addition, complex titanium-containing coagulants were tested in the actual process of removing residual molding sand from machine parts by water jet surface cleaning. The findings show that titanium tetrachloride outperforms the conventionally used aluminum sulphate and iron chloride, while the effective dose of titanium tetrachloride is on average 2.5 to 3.0 times smaller. The obtained experimental data characterize the effect of added titanium compounds on the water treatment efficiency when conventional reagents are used. It was found that the addition 7.5 wt% of titanium tetrachloride to the conventional aluminum sulphate increases the treatment performance of the latter by 30%. The high efficiency of titanium-containing reagents is due to specific hydrolysis effects, as well as nucleation and flocculation at the surface of hydrolysis products. The rate of sedimentation and filtration of sludges resultant from water treatment with titanium-containing coagulants significantly exceeded that reached when using conventional reagents. The use of titanium-containing reagents will enable to transfer to smaller settlers and filters, reduce the consumption of reagents and reach an enhanced treatment performance. The treated water can be reused or discharged into municipal sewage treatment plants.

Introduction

Steel making and the related industries are essential for the economics of many countries. Ore mining and beneficiation, iron and steel making, as well as machining of steel parts – all these processes affect the environment.

Mould casting is the most popular technique for making complex parts. Two types of materials are used in part casting: molding sand made with sand, clay and additives; and core sand made with quartz sand, binders and antistick coatings [1–2]. Different polymer resins, liquid glass, phenol formaldehyde and phosphate binders can be used as additives [3–5]. Shake out tables, sand- and shotblasting chambers are used for surface cleaning of parts. A recent trend in steel and mining industries is to use water jet cleaning [6–8].

Water jet cleaning is used in steel making to remove residual sand from complex parts, as well as for surface finishing before painting or coating. Water jet cleaning is a personnel-friendly and dust-free technique.

Considerable amounts of wastewater carrying sand particles, metal oxides, ore particles and binding agents (phosphates, silicates or phenol formaldehyde resins) are generated during surface finishing. Some of that wastewater can be reused after treatment [9–11]. As this practice

is not widely adopted yet, most of the contaminated water is discharged into the sewer.

In most cases, however, before such wastewater can be reused or discharged, it is settled for 15 to 60 minutes so that coarse particles could be removed. At the same time, dust particles that are the result of abrasion (<1 µm) do not settle. Coagulants containing aluminium or iron salts help intensify separation of suspended particles [12–13]. In spite of low cost and high effectiveness, these reagents have their drawbacks. Thus, aluminium salts are poorly effective at low water temperature, and iron compounds are abrasive and can cause corrosion [14]. What is gaining popularity today is titanium-containing coagulants. Researcher teams from Russia and China have proved that titanium-containing coagulants have high efficiency in water treatment applications [15–20].

Objects and methods of research

The relevance of this research study is attributed to the need to reduce the amount of clean water consumed by steel industry and to maximize the efficiency of wastewater treatment operations (which also involves removal of organic contaminants and phosphates) aimed at reduc-

ing fines imposed by regulators and water and sewerage services providers.

This research study aims to analyze the efficiency of titanium-containing coagulants for wastewater treatment in the case of wastewater generated as a result of water jet surface cleaning of castings.

The objectives of this research study are to understand:

If titanium-containing coagulants can be used for water treatment

If added titanium compounds could enhance the efficiency of conventional coagulants.

Coagulation efficiency was analyzed with the help of a JLT 4 flocculator (VELP). Agitation time — 2 minutes; flocculation time — 8 minutes; sedimentation time — 30 minutes.

Samples of treated water were analyzed for the concentration of suspended solids by gravimetry and using an HI 98703-02 portable turbidity meter by HANNA Instruments.

The Hach DR 2800 Portable Spectrophotometer (USA) was used to determine the concentration of iron, phenol formaldehyde, and phosphates.

The size and zeta-potential of colloid particles were analyzed with the help of the following instruments: Zetasizer Nano by Malvern and Analysette 22 NanoTec by Fritsch.

The sedimentation rate and the volume of the sediment were determined visually using measuring cups. The filtration rate was determined by putting a given amount of water through filter paper for 60 seconds.

Wastewater from the water jet cleaning facility of a machine building site in the Moscow Region was examined in the study. The as-received water had the following concentrations of contaminants: phenol formaldehyde — 12 mg/l, phosphates — 27 mg/l, suspended matter — 718 mg/l, including iron — 309 mg/l; the colloid particle charge was (– 32 mV), particle size — 1–2 μm .

The following was used as coagulants: an aqueous solution of TiCl_4 ; $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, as well as samples of complex coagulants containing a conventional reagent modified with titanium tetrachloride hydrolysis products. The concentration of the latter in the complex coagulant varied from 2.5 to 10.0 wt% (reference parameter: TiO_2).

Findings and discussion

Fig. 1 below shows comparison data on the treatment efficiency reached when using conventional aluminium, iron and titanium containing reagents.

As is shown in the graph above, the performance of the titanium tetrachloride coagulant is comparable to that of the conventional reagents. Compared with aluminium or iron salts, it takes on average 2.5 to 3.0 times less titanium tetrachloride to reach maximum efficiency. Considering the negative charge (–25 – 35 mV) at the surface of colloid particles, the coagulation mechanism can differ greatly depending on the reagent used.

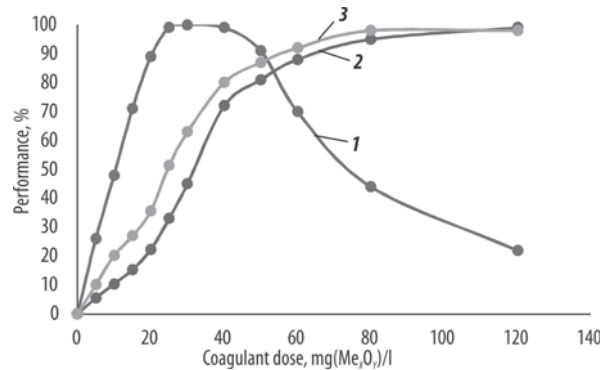


Fig. 1. Removal of suspended solids from water by coagulation: Process performance
1 — titanium chloride; 2 — aluminium sulphate; 3 — iron chloride

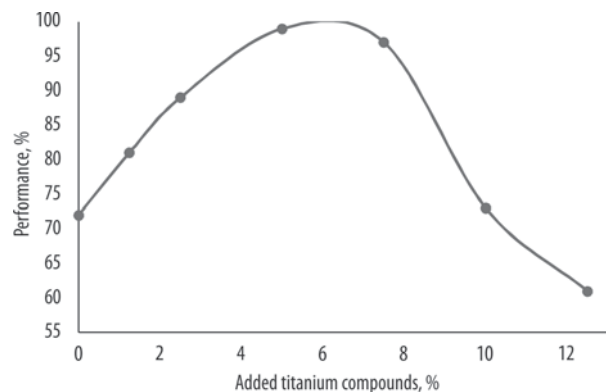


Fig. 2. Effect of added titanium compounds on the treatment performance

Thus, for aluminium and iron salts, coagulation is probably the result of neutralization occurring when negatively charged colloid particles come in contact with positively charged particles of Al and Fe hydroxides. For titanium-containing systems, it is most likely that contaminants get adsorbed by the developed surface of titanium hydrolysis products [21]. Reduced treatment efficiency occurring as a result of the dose of titanium compounds exceeding 40 mg/l is attributed to a growing negative charge at particle surface (zeta-potential is over – 45 mV) and a stabilized colloid system [22].

One knows that titanium compounds, when added to conventional coagulants, help improve the performance of the latter while saving reagents as their effective dose would be reduced [20]. As the use of iron salts as coagulants lead to water contamination with iron, aluminium sulphates were used in further experiments.

Various doses of a 1% aqueous solution of titanium tetrachloride were added to a given amount of 2% aluminium sulphate with an equivalent concentration of Al_2O_3 — 40 mg/l. **Fig. 2** shows how the treatment efficiency would change depending on the weight of the additive.

As can be seen from **Fig. 2**, addition of 7.5 wt% of titanium compounds leads to a 1.35 times higher performance of aluminium sulphate. For comparison: it

Residual concentrations of contaminants after coagulation					
Contaminant	Unit	As-received water	Aluminium sulphate	Titanium chloride	Complex coagulant
Suspended solids	mg/l	718	35.9	10.2	11.4
Total iron		301	5.2	1.0	2.1
Phosphate ions		27	2.5	6.7	1.3
Phenol formaldehyde		12	6.4	2.3	3.1

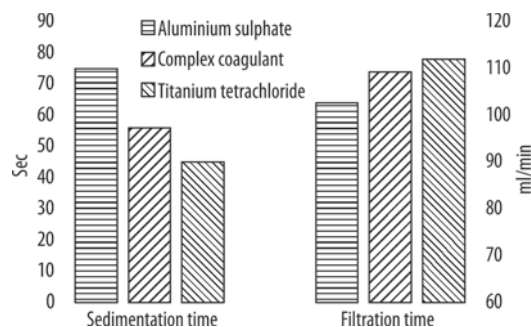


Fig. 3. Effect of added titanium compounds on the sludge filtration and sedimentation rates

took 80 mg/l of coagulant to reach the same treatment performance with aluminium sulphate. High efficiency of the complex titanium-containing coagulant is attributed to the specific hydrolysis effects that are typical of titanium (polycondensation) and a lower surface charge of the flocculates due to the presence of positively charged aluminium hydroxides and negatively charged titanium hydroxides (nucleation) [14, 23–25].

Table below shows residual concentrations of all contaminants in the water after water jetting of machine parts to remove residual molding sand when optimum doses of coagulants were used.

Table demonstrates that titanium-containing coagulants, even with smaller amounts of active components, are more efficient at removing the major contaminants from water. Considering that small amounts of titanium compounds and half as much of the key reagent are needed, the overall treatment costs are not likely to rise. A major advantage of the complex coagulant is that it is highly efficient at removing soluble organic components of molding sand. Due to this, treated wastewater can be directed to the municipal advanced water treatment facility.

The final stage of the research study included analysis of the coagulation sludge sedimentation and filtration rates. Fig. 3 shows data obtained through experiment.

Fig. 3 shows that the use of titanium tetrachloride coagulant, as well as complex titanium-containing coagulant helps intensify sludge sedimentation and filtration by 10–15% on average, which definitely speaks for the use of the above reagents. Adoption of new high-performance titanium-containing coagulants and,

consequently, transfer to smaller settlers and filters will help set up a circulation water supply system and adopt the best available technology [26] by steel and machine building companies.

Conclusion

This paper examines the process of wastewater treatment in application to wastewater generated in the course of water jetting of castings in order to remove residual molding sand.

It was established that it takes 3 times more conventional coagulants (i.e. aluminium sulphate and iron chloride) to reach the same performance compared with the used of titanium-containing reagents (25 and 80 mg(Me_xO_y)/l, respectively).

It was determined that the addition of 5.0 to 7.5 wt% of titanium compounds helps raise the performance of aluminium sulphate by 10 to 15 %.

It was found that titanium tetrachloride, as well as a complex Al-Ti-containing reagent deliver an excellent water treatment performance for all the studied components (phosphates, suspended solids, iron compounds), with the consumption of the reagents needed for maximum performance being on average 1.5 to 2.0 times lower than that of conventionally used aluminium sulphate.

It was proved that titanium compounds added to aluminium sulphate help raise the sludge sedimentation and filtration rate by more than 30% compared with pure aluminium sulphate. Due to this, the complex reagent can be used with standard process equipment (for instance, in a flotation unit [27]).

Reusing the treated water will help lower the abrasion wear of the equipment due to low concentration of suspended particles in the water. Considering the effect of dilution, such treated water can be further processed at the municipal advanced water treatment facility with no disruption to its normal operation.

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