

# MONITORING OF BERILLIUM CONTENT IN WASTE WATER OF NSC KIPT BEFORE AND AFTER PURIFICATION

*Yu.A. Gordienko, A.A. Mazilov, V.Ya. Nikulina, M.V. Sosipatrov, V.N. Tkachenko*  
*National Science Center “Kharkov Institute of Physics and Technology”,  
Kharkiv, Ukraine*

In this paper, the results of applied studies on beryllium content in waste water of NSC KIPT before and after purification are presented. The most optimal conditions of physicochemical processes used in the water treatment are defined. The results obtained allow one to make a conclusion that the content of beryllium in waste water under investigation before and after purification does not exceed the threshold limit value (TLV) and is under control. All chemical analyzes were carried out by the metrologically certified laboratory of “Radiation Research and Environmental Protection” NSC KIPT.

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## INTRODUCTION

Technogenic influence on the environment over the past decades has led to irreversible damage of ecological systems [1].

NSC KIPT represents a potential source of a negative impact on the environment. Hence, ecological safety is one of the most important priorities in the Institute activity.

During the last years, the requirements towards purification of waste water being dumped in water units become stricter. Anthropogenic factors of pollution of waste water are sufficiently different and result in mechanical, chemical, and biological admixtures which are to be removed from waste water via water treatment plants.

At present, new technologies of industrial waste water treatment are being developed and the existing ones are being improved [2–4].

A wide spectrum of technological processes carried out at NSC KIPT determines the formation of waste products specific for this facility. One of the most dangerous waste products of the Institute production cycle is beryllium [5].

Beryllium has a range of the important physicochemical properties which is why it is widely used in different industrial branches including nuclear industry. According to this, attention to its possible impact, that is always negative, is quite great [6–10].

By the effects on the human body, beryllium is referred to extremely dangerous substances (first class danger). This is a highly toxic, carcinogenic and mutagenic element. It is poisonous even in the most minimal amounts. Signs of poisoning might emerge where the concentration of this element reaches 0.01 mg in 1 m<sup>3</sup> of air. For beryllium and its compounds (in terms of Be), the TLV for a work zone is 1...3 µg/m<sup>3</sup>, atmospheric air 0.001 µg/m<sup>3</sup>, water 0.2 µg/l. Inhalation of atmospheric air containing beryllium leads to a severe decease of respiratory organs called berylliosis [11].

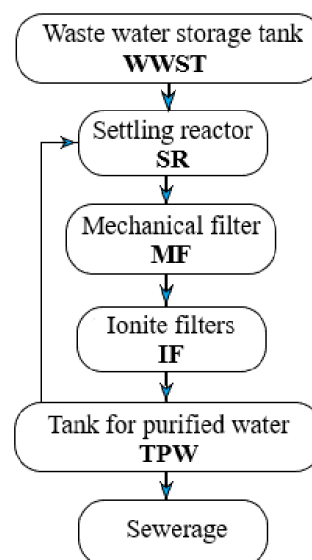
Thus, the concentration of beryllium in air and water should be constantly controlled [6, 9].

## TECHNOLOGICAL PROCESS

Beryllium waste water treatment technology was developed at NSC KIPT. The basis of the technological process of waste water treatment consists of

desalination of water using ion exchange resins under prior chemical mechanical purification [5, 11].

Waste water treatment process on site of the water treatment plant (WTP) is presented in Figure.



*Flowchart of waste water treatment process on site of the WTP*

The process of waste water treatment consists of the following main stages:

- Settling (sedimentation) of received waste water from coarse admixtures and suspended substances is carried in the waste water storage tanks (WWST);
- Waste water treatment via physicochemical methods is carried in the settling reactors (SR);
- Removal of dispersed particles and small flakes invisible to the eye using mechanical filter (MF);
- Complete water desalination via ion exchange resins (IF filters);
- Dumping in the tank for purified water (TPW).

The most effective physicochemical purification techniques are the techniques implying coagulants and flocculants and are based on the processes of sedimentation and filtration. Coagulation is the process of clarification and discoloration of water using chemical agents (coagulants) which produce sediment under the interaction with hydrosols and soluble admixtures. During the coagulation, destabilization of colloidal particles present in water occurs. These

particles are exceptionally stable due to the small size (less than 1  $\mu\text{m}$ ). Reaction between the particles and a coagulant leads to production of the so called “aggregates” and their following sedimentation. Cationic coagulants neutralize the negative charge of colloids and make micro flakes. There are a large number of factors influencing the effectiveness of coagulants action, such as: composition and properties of admixtures in waste water, dose and composition of a coagulant, temperature and pH of water, conditions of addition and mixing of reagents. Addition of coagulants into waste water causes a complicated chain of chemical and physicochemical interactions of the reagent with micelles of a substance present in water and leads to their dissociation. The polyvalent cations of coagulant  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  produced during this process enter into ion exchange with the cations of the adsorption layer consisting of the negatively charged colloidal particles of waste reducing their stability. When the state of equilibrium between the cations present in the adsorption layer of colloidal particles and in the solution is established, hydrolysis of coagulant excess happens. As a result of the hydrolysis depending on Ph of a medium, hydrophobic colloids of sparingly soluble aluminum or iron hydroxides or their basic salts are produced. These colloids have a huge active surface and play main role in the process of water treatment via coagulation [12–14].

Flocculants being charged and having a high molecular weight (long monomer chains) fix destabilized particles and bring them together along a polymer chain. As a result, at the stage of flocculation the size of particles which are in the water phase increases which is expressed in the production of flakes.

The mechanism of flocculants action is based on the following phenomena:

- adsorption of molecules of flocculant on the surface of colloidal particles;
- reticulation (production of meshy structure) of flocculant molecules;
- sticking of colloidal particles together due to van der Waals forces.

Under the action of flocculants, three-dimensional structures are being produced which are able to separate from the liquid phase more rapidly and fully. The reason these structures appear is the adsorption of macromolecules of flocculant over several particles together with the production of polymer bridges between them.

Thus, coagulation and flocculation are the processes of joining of tiny particles into larger ones via the forces of cohesion. Under the action of flocculants and coagulants, pollutants gain weight, stick together and sediment which make them accessible for capture [12–14].

The most common flocculants are polyacrylamide (PAA); copolymers of acrylamide, acrylonitrile and acrylates; sodium salts of polyacrylic and polymethacrylic acids; polydimethylaminoethylacrylates (PDMAEA), etc. [12–14].

After the process of coagulation, water is supplied to the MF filled with quartz sand. At this stage, water is cleaned from fine particles left after the coagulation. Sticking of suspended particles to the sand grains occurs during water filtration. At the same time, gradual compaction of the filtration layer occurs and, as a consequence, the filter resistance increases and the filtration speed decreases. The filter should be disconnected and flushed to remove contaminants.

The next stage of water treatment is its complete desalination on ion exchange resins. Natural zeolite (clinoptilolite) is possible to use at the first stage of the ion exchange. It is a cationic type ion exchanger and is highly selective with respect to beryllium ions. Ion exchange properties of zeolites are defined by the properties of chemical affinity of ions with zeolite crystal lattice. The disadvantage of clinoptilolite use lies in the inability of its regeneration. However, clinoptilolite use is appropriate because it adsorbs a large part of beryllium ions.

Then, in our case, water passes through filters filled with ion-exchange load – ampholyte AMY-22. It is used for sorption of metals out of solutions. At this stage, there is additional cleaning of water to meet the threshold limit value (TLV) requirements.

After the chemical quality control, purified waste water is partially supplied to the setup for reuse and the imbalance is dumped to special sewerage. Slimes produced at the stage of sedimentation undergo disposal.

## RESULTS AND DISCUSSION

At the stage of preparation of water for the process of purification (waste water sedimentation in the WWST), sedimentation of coarse particles and coarse admixtures takes place. As can be seen from Table 1, concentration of beryllium in water reduces from 20 to 2 mg/ml.

Table 1

Waste water physical balance (project calculated values)

Name of operation	Received		Sent out	
	Volume, $\text{m}^3$	Content of Be, mg/l	Volume, $\text{m}^3$	Content of Be, mg/l
Sedimentation	15	20.0	14.95	2.0
Coagulation	14.95	2.0	14.65	0.008
Filtration via the MF	14.65	0.008	14.65	0.002
Ion exchange	14.65	0.002	14.65	0.0002

After the process of sedimentation, waste water is supplied via a pump for physicochemical purification.

In this paper we used aluminum sulfate  $\text{Al}_2(\text{SO}_4)_3$ , ferric sulfate  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  or ferrous sulfate

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  as the coagulants. A decrease of the beryllium concentration from 2 to 0.008 mg/l was observed at the stage of waste water clarification (see Table 1).

The process of coagulation is more effective if flocculants are added. Flocculants are widely used for the purification of natural and waste water from dispersed admixtures, for the concentration and dehydration of suspensions, and for the improvement of filtration characteristics of sediments. Also, flocculants are utilized to intensify the formation process of flakes of aluminum hydroxide and iron hydroxide to increase the speed of their sedimentation, to decrease a dose of the coagulants, to reduce the duration of the coagulation process.

In this paper, studies of effects of different combinations of coagulants and flocculants on the efficiency of the water clarification process were carried out. The following flocculants were used: PAA – polyacrylamide, PPS – polymer of pyridine salt (poly-1-2-dymethyl-5-vinylpyridindimmethylsulfate) and PDMAEA – acetic salt polydimethylaminoethylmethacrylate. The studies were carried out using “Cascade” set-up which is a sequence of steps with tanks imitating filters.

It was obtained that the process of coagulation does not go efficiently when FeSO<sub>4</sub> is used as a coagulant and PPS, PAA and PDMAEA are used as flocculants. If the coagulant Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and the flocculant PPS are added, the flakes are not produced, however, if other flocculants are added, the reaction of coagulation goes more efficiently. Using PDMAEA is less efficient than using PAA.

When using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as a coagulant, it is possible to use PAA, PPS, and PDMAEA flocculants. The most optimal option for the process under consideration is the addition of PAA.

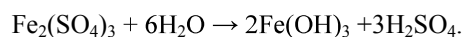
The process of coagulation goes efficiently in case of use of FeCl<sub>3</sub> as a coagulant and PPS, PAA, and PDMAEA use as flocculants. It should be noted, however, that the use of FeCl<sub>3</sub> as a coagulant has a significant disadvantage since it leads to strong pipeline corrosion. For this reason, its use seems inappropriate.

Efficiency of impact of joint and sequential addition of reagents was also studied in this paper.

The results of the most optimal cases of different combinations of coagulants and the flocculant PAA (as the most effective), influencing the quality of the sedimentation processes (at pH = 8) are presented in Table 2.

It was shown that the sedimentation process goes most efficiently under the joint addition of ferric sulfate and PAA.

The studies have found that the joint addition of ferric sulfate and PAA is the most effective option at this stage of water treatment. The coagulation reaction has the following form:



Hydrolysis of coagulants is one of the most important processes of coagulation. The completeness of its flow affects both the quality of separation of suspensions and the coagulant consumption.

In this case, iron hydroxide sediments in form of small flakes which gradually stick together to form larger flakes. Due to the force of gravity, these flakes sediment to the lower conical part of the sump forming slime. It was experimentally established the optimal value of pH = 8 which can be corrected by sodium hydroxide (NaOH), if necessary.

Table 2  
Influence of different combinations of coagulants and the flocculant PAA on the quality of the sedimentation processes

Coagulant, flocculant	Sediment, mg/l
Source water (w/o reagents)	10.5
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	26.5
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + PAA (joint)	40.0
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	41.5
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + PAA (sequential)	56.0
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + PAA (sequential)	69.5
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + PAA (joint)	77.5

At the level of pH higher or lower of this value, the coagulation reaction goes worse.

The content of beryllium in waste water was determined by the photocolorimetric technique with beryllon II use [15].

The results of this analysis obtained for the period from 2008 to 2019 are presented in Table 3.

First of all, it should be noted that during the periods 2008–2010, 2012–2013, and 2019 years no excess of beryllium content in waste water samples before and after treatment was observed.

The excess of beryllium content was detected in 2011, 2014 years and also during the years of 2015–2018. In 2015, beryllium content that was detected in water samples taken from the WWTR, substantially exceeded the TLV requirements (0.2 µg/l). The samples had beryllium content of 54.0 µg/l before water treatment. Moreover, even after the treatment beryllium was still detected in the samples (0.57 µg/l, sample No10). In this case, the water was sent for re-treatment and re-analysis.

The main characteristics of water (transparency, pH, oxidability, hardness) which were used to make a conclusion about the quality of purification are presented in Table 4. The data are given for water to be purified (sample No5, 05.04.2018) and water after the process of coagulation. The TLVs and the measured values of the mentioned characteristics for tap water are given for comparison. Additional parameters such as acidity and alkalinity remain constant and their numerical values are within the acceptable limits (acidity – 0.7, alkalinity – 6.2). All analyses were performed under the temperature of 19 °C.

Thus, in this paper it was shown that the processes of coagulation (used in water treatment practice) via the layers of iron and aluminum with the following filtration through sand filters are efficient for waste water purification from beryllium.

Table 3

Beryllium content in waste water samples before and after purification for the period of 2011–2018 years

Date of taking a sample	Place of taking a sample	Content of Be, µg/l	
		Before purification	After purification
08.11.2011	Bldg. 57, WWST, sample No 23	0.15	not detected
09.12.2014	Bldg. 57, WWST, sample No 17	30.0	not detected
09.12.2014	Bldg. 57, WWST, sample No 18	36.0	not detected
15.12.2014	Bldg. 57, WWST, sample No 19	26.0	not detected
24.12.2014	Bldg. 57, WWST, sample No 20	4.0	not detected
29.12.2014	Bldg. 57, WWST, sample No 21	36.2	not detected
12.01.2015	Bldg. 57, WWST, sample No 1	27.6	not detected
18.05.2015	Bldg. 57, WWST, sample No 10	54.0	0.57*
29.03.2016	Bldg. 57, WWST, sample No 5	9.5	not detected
30.11.2016	Bldg. 57a, WWST, sample No 10	15.0	not detected
20.12.2017	Bldg. 57, WWST, sample No 2	24.0	not detected
01.02.2018	Bldg. 57, WWST, sample No 4a	31.0	not detected
05.04.2018	Bldg. 57, WWST, sample No 5	33.6	not detected
20.04.2018	Bldg. 57, WWST, sample No 7	10.0	not detected

\*Note: after repeated purification and analysis, beryllium was not detected.

Table 4

Water quality parameters

Water sample	Transparency, cm	pH	Oxidability, mg/l	Hardness, mg-eq/l
WWST before purification	10	7.27	6.015	7.8
after coagulation	36	7.45	3.11	7
tap water	38	6.5	2.29	9.48
TLV	>30	6.5-8.5	4**	1.5...7

\*\*Note: the TLV value of oxidability is given for pure ground water.

## CONCLUSION

It was shown that the value of content of beryllium in waste water after treatment does not exceed the TLV and is under control. The most efficient coagulants and flocculants are found and the optimal doses for all reagents are determined.

The analysis of experimental data lets us conclude that the treatment facilities located on the territory of NSC KIPT and also the set of developed techniques provide complete purification of waste water from beryllium.

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## **МОНИТОРИНГ СОДЕРЖАНИЯ БЕРИЛЛИЯ В СТОЧНЫХ ВОДАХ ННЦ ХФТИ ДО И ПОСЛЕ ОЧИСТКИ**

*Ю.А. Гордиенко, А.А. Мазілов, В.Я. Нікуліна, М.В. Сосипатров, В.Н. Ткаченко*

Отражены результаты прикладных исследований содержания бериллия в сточных водах ННЦ ХФТИ до и после очистки. Определены наиболее оптимальные условия проведения физико-химических процессов очистки воды. Полученные результаты позволяют сделать вывод, что содержание в исследуемых сточных водах бериллия после очистки не превышает предельно допустимых концентраций и находится под контролем. Все химические анализы проведены метрологически аттестованной лабораторией «Радиационные исследования и охрана окружающей среды» ННЦ ХФТИ.

## **МОНИТОРИНГ ВМІСТУ БЕРИЛІУ В СТІЧНИХ ВОДАХ ННЦ ХФТІ ДО І ПІСЛЯ ОЧИЩЕННЯ**

*Ю.О. Гордієнко, О.О. Мазілов, В.Я. Нікуліна, М.В. Сосипатров, В.М. Ткаченко*

Відображено результати прикладних досліджень вмісту берилію в стічних водах ННЦ ХФТІ до і після очищення. Визначено найбільш оптимальні умови проведення фізико-хімічних процесів очищення води. Отримані результати дозволяють зробити висновок, що вміст у досліджуваних стічних водах берилію після очищення не перевищує гранично допустимих концентрацій і знаходиться під контролем. Усі хімічні аналізи проведено метрологічно атестованою лабораторією «Радіаційні дослідження і охорона навколишнього середовища» ННЦ ХФТІ.