ESTUDO DOS FLUXOS DE ÁGUA DO CICLO TECNOLÓGICO DA ÁGUA E ÁGUAS RESIDUAIS DA PRODUÇÃO METALÚRGICA NO QUE SE REFERE AO CONTEÚDO DA POLUIÇÃO

THE STUDY OF WATER FLOWS OF TECHNOLOGICAL WATER CYCLE AND WASTEWATER OF METALLURGICAL PRODUCTION CONCERNING POLLUTION CONTENT

ИЗУЧЕНИЕ ВОДНЫХ ПОТОКОВ ТЕХНОЛОГИЧЕСКОГО ВОДООБОРОТА И СТОЧНЫХ ВОД МЕТАЛЛУРГИЧЕСКОГО ПРОИЗВОДСТВА НА СОДЕРЖАНИЕ ЗАГРЯЗНЯЮЩИХ ВЕЩЕСТВ

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RESUMO

Este trabalho é sobre a definição da composição dos fluxos de água do ciclo tecnológico da água e águas residuais da saída da produção metalúrgica, foi realizado para o período pesquisado. Águas residuais de instalações de pirrena, instalações de rejeitos, instalações de concentrado e túnel de comunicação durante o período de Maio a Outubro de 2016 foram estudadas. A quantidade excessiva de poluentes foi registrada em todas as amostras de teste de todos os indicadores analisados, e é por isso que as águas residuais podem constituir um perigo no caso de sua entrada em corpos d'água naturais. A faixa de variações das concentrações de poluentes no período pesquisado foram definidas. Recomendações sobre o uso de métodos de tratamento de águas residuais são fornecidas.

Palavras-chave: *métodos de tratamento de águas residuais; materiais suspensos; DQO; DBO; extensão de concentrações.*

ABSTRACT

The work concerning the definition of the composition of water flows of the technological water cycle and wastewater of metallurgical production outlet for the researched period has been carried out. Wastewater of pyrrhotine facilities, tailings facilities, concentrate facilities and communication tunnel over the May to October 2016 period was studied. The excess of pollutant content was recorded in all samples of test subjects by all analyzed indicators, that's why wastewater can constitute a danger in case of their entry into natural bodies of water. Ranges of fluctuations of concentrations of pollutants over the researched period were defined. Recommendations on the use of wastewater treatment methods are given.

Keywords: *wastewater treatment methods; suspended materials; COD; BOD; span of concentrations.*

АННОТАЦИЯ

В работе определен состава водных потоков технологического водного цикла и сточные воды металлургического производства за исследуемый период. Авторами были изучены сточные воды пирротиновых установок, хвостохранилищ, концентрационных сооружений и коммуникационного туннеля за период с мая по октябрь 2016 года. Превышение содержания загрязняющих веществ выявлено во

всех исследуемых образцах. Поэтому сточные воды могут представлять опасность в случае их попадания в естественные водоемы. Авторами определены диапазоны колебаний концентраций загрязняющих веществ за исследуемый период. В работе представлены рекомендации по использованию методов очистки сточных вод.

Keywords: *методы очистки, взвешенные вещества, ХПК, БПК, диапазоны концентраций.*

INTRODUCTION

It's necessary to study the water flows to obtain the statistically-valid amount of data by the composition of recycling water and discharge water of iron and steel plants. Currently, the absence of the sufficient amount of information about the content of pollutants is confirmed (pH, suspended materials, dry residue, chlorides Cl^- , sulphates SO_4^{2-} , calcium Ca^{2+} , magnesium Mg^{2+} , total Iron Fe, copper Cu^{2+} , nickel Ni^{2+} , cobalt Co^{2+} , arsenic As (for reference only), Sodium Na^+ , Zink Zn^{2+} , Lead Pb^{2+} , chemical oxygen demand (further – COD), nitrates NO_3^- , nitrites NO_2^- , ammonium, nitrogen N, polyphosphates PO_4^{3-} , phosphorus P, carbonate CO_3^{2-} , oil products, BAF (aerofloat), Kx (butyl xanthate of potassium), BOD_5 , $\text{BOD}_{\text{compl}}$).

There's a periodical need for such information when preparing initial data on the condition of water flows to choose water purification methods taking into account their composition and concentration. Such researchers, therefore, are necessary and relevant for the selection of optimal flow chart of recycling water purification and the choice of effective materials and reagents, which is quite a difficult task resulting from the diversity of qualitative and quantitative composition of recycling water and a wide range of fluctuation pollutants.

In this regard, the research of detention basins and water flows, systematization of all these data by their composition and intervals of pollutants' fluctuation were carried out.

The following purpose was set: definition of the composition of water flows of the technological water cycle and wastewater of iron and steel plant over the researched period.

MATERIALS AND METHODS

To prepare initial data on the condition of water flows of the researched objects, samples were collected. Sampling was carried out into

plastic 10-liter cans in total 4 pieces in accordance with the number of sampling selection points. Sampling selection was carried out once a week in accordance with GOST 33.861-2012 "Water. General requirements for sampling", PNDF12.15.1-08 "Instructional guidelines by sample collection for wastewater analysis" requirements. Collected samples were sent to the laboratory for analysis concerning pollutants' content (Law of the Krasnoyarsk Territory, 2013)

Then based on the analysis a summary table was made up, data by the content of plant' water flows were systematized; fluctuations ranges of pollutants were defined.

RESULTS AND DISCUSSION:

3.1. Dynamics of Change of Pollutant Content Over the Researched Period (05.2016 – 10.2016)

Over the period from May to October the samples of wastewater at four points were collected: pyrrhotine facilities, tailings facilities, concentrate facilities, communication tunnel. Specialists carried out analysis to determine 27 indicators: pH, BOD_5 , $\text{BOD}_{\text{compl}}$, COD, suspended materials, dry residue, ions PO_4^{3-} , $(\text{P})\text{CO}_3^{2-}$, Cl^- , SO_4^{2-} , Fe_{total}, Co^{2+} , Na^+ , Cu^{2+} , Ni^{2+} , Pb^{2+} , Ca^{2+} , Mg^{2+} , NH_4^+ , Kx, BAF, H/pr, As.

It should be noted that indicators BOD_5 and $\text{BOD}_{\text{compl}}$ differ insignificantly over the period of research, which leads to the fact the majority of organic pollutants are oxidized in 5 days.

The content of calcium and magnesium ions changes within a very wide range. Besides, minimal concentrations fall at the beginning of summer, which may be related to the dilution of wastewater with melt-water. Significant exceed of pollutant content as compared to maximum allowable concentrations is observed in all researched water flows (San PiN 2.1.5.980-00). Wastewater of the objects of research is characterized by high salt content. The general content of dry residue in wastewater is significant, on the average: in pyrrhotine facilities – 2299; in tailings facilities – 7878; in concentrate facilities –

4779; in communication tunnel– 2044 mg/dm³. Wastewater contains a great amount of chloride salts – from 57 to 312 mg/dm³, and sulfates– from 879 to 3789 mg/dm³. The significant content of mineral substances in dry residue caused by the presence of, firstly, chlorides and sulfates. The content of heavy-metal ions also exceeds standards many times (Kushney, 1987; Smirnov and Genkin, 1989; Turovsky, 1984).

3.2. Analysis of interdependence of indicators under study

COD and BOD. Oxygen reactions, which allow oxidizing organic impurities in water, take place at natural self-clarification of water. Thus, their partial or complete decomposition occurs. COD – is an indicator of oxygen investment at oxidation of different intermixtures as part of water, and BOD is an indicator of oxygen consumption for intermixtures oxidation when interacting with bacterial aerobiotic preparation in water and wastewater treatment facilities (Chebakova, 2001).

COD indicator is a general indicator of industrial wastewater pollution. The amount of oxygen in mg/l when carbon, hydrogen, sulfur, phosphorus, and other elements (except nitrogen), if they present in an organic matter, oxidizes to CO₂, H₂O, P₂O₅, SO₃, and nitrogen turns into ammonium salt, is called the theoretical value of COD. In the course of defining this indicator not only organic but also non-organic deoxidizers oxidize if they're in the sample (GOST31859-2012). By the analyses of oxidation characteristic value, one can judge about the ratio of oxidation-proneness (easy/hard). Thus, the difference between the results of definitions of oxidation susceptibility by COD and BOD can define a share of easily oxidized organic matters in wastewater. The ratio of BOD_{compl} and COD characterizes the degree of wastewater intermixture capacity to biological oxidation. The ratio of BOD indicators, indicators of nitrogen ammonia and phosphates allows estimating the sufficiency of biogenous elements for successful carrying out of biological wastewater treatment.

It was defined that difference between COD and BOD makes up: in pyrrhotine facilities – 65.67; in tailings facilities – 173.58; in concentrate facilities – 1176.3; in communication tunnel– 228.14 mg/l. This indicates that these facilities contain a great amount of hardly oxidized compounds, probably, flotation agents (Dytnersky, 1995).

The COD indicator depends on the sampling place: this indicator is higher in the samples of wastewater from concentrate facilities, then at other points of sampling. This can be related to the presence of a large amount of flotation agents at the solid particles of concentrate facilities. The high value of COD is also registered in the wastewater of communication tunnel; it depends on the data of sampling and can be related to technological process (Baskov, 1999; Bepamyatnov and Krotov, 1987; Sokolov, 1992).

Hydrogen ion concentration – pH of water – one of the most important indicators of water quality. The value of hydrogen ion concentration does matter for chemical and biological processes, taking place in natural waters. Stability of different forms of elements, aggressive action of water on metals and concrete depend on the pH value. Water pH has an impact on the processes of transformation of different forms of elements, changes toxicity of pollutants, that's why it's important to determine the dependency of different indicators of wastewater quality on pH (Dytnersky, 1978)

The interval of the change of values pH of wastewater of tailings facilities make up from 3.17 to 4.56, pH of water sample of tailings facilities slightly changes within the range from 3.17 to 4.56, therefore, waters are acid.

The interval pH for wastewater of concentrate facilities makes up on the average from 9.5 to 11.5 – wastewater is alkaline; in the range – pH with 9.6 to 11.45 the value of COD is most close to stable one and makes up approximately 1500 mg/l.

A large spread of pH values is also typical for wastewater of communication tunnel: from 4 to 10. In the pH range from 4.8 to 6.39, the COD values fluctuate in a relatively narrow range 100-600 mg/l, in the pH range from 6.43 to 9.8 there are high fluctuations of COD values (Greg and Sing, 1984).

BOD. Biological oxidation of different organic substances occurs at a different rate. According to chemist-organic, professor Kaplin V. T. (Dolzhenko and Kaplin, 1969; Kaplin *et al.*, 1969), rate constants of their oxidation make up 1.4-0.3 of reverse days. Average place (K = 0.3 – 0.05 day⁻¹) is taken by cresols, naphthols, xylenols, anion-active surface active agents and others. Sulphanole NP-1, non-ionic surface active agents and other should be related to

slowly decomposing “biologically tough” substances ($K = 0.029 - 0.002 \text{ day}^{-1}$). Determination of BOD over the certain time of process passing (incubation) – BOD₅ is authentic if wastewater doesn’t contain “biologically tough” substances, if wastewater contains these substances, BOD complete should be carried out.

Regardless of sampling place, wastewater contains an insignificant amount of “biologically tough” organic substances, on the average to 30% (relative). The main mass of organic substances is oxidized in 5 days.

A pronounced dependence between BOD_{compl} and BOD₅ is visible, besides, the difference between these indicators don’t exceed 30%, which indicates that there are less than 30% of “biologically tough” substances in wastewater (GOST 27065-86).

Since chemical oxidation in water requires more oxygen than biological oxidation, the level of COD will be always higher than BOD level (Zhukov *et al.*, 1989)

The results of analyses of wastewater of all four studied flows correspond to theoretical regularities, i.e. COD > BOD.

Phosphates. The presence of phosphates indicates that wastewater contains surface-active agents, water softeners for boilers, *etc.* (wastewater of kitchens, showers, *etc.*). The presence of phosphates in water is determined by the GOST 18309-2014.

There’s no pronounced dependence of BOD_{compl} on the concentration of phosphates in the samples of pyrrhotine facilities and tailings facilities. However, a slight increase of BOD in the range of phosphate concentrations from 0.0154 to 0.0830 mg/l was observed in tailings facilities. Some tendency to an increase in BOD_{compl} while increasing phosphate concentration is observed in the samples of concentrate facilities and communication tunnel water; although there’s no clear dependency of BOD_{compl} on the concentration of phosphates (Vinogradov, 1998; Sokolov, 1992)

Ammonia. Ammonia is an initial decomposition product of organic nitrogen-containing (including protein ones) substances. Azotic acid salts – nitrates – are final products of mineralization of organic nitrogen-containing substances. The total indicator of water saturation with the nitrogen of mineral origin reflects the joint volume of its nitrate, nitrite forms,

and ammonia. The high content of nitrates and ammonia nitrogen is a highly authentic indicator of recent pollution, and a great amount of nitrates may indicate that water was exposed to pollution quite a long time (GOST 33045-2014). Capacity for interconversion is typical for gaseous nitrogen compounds and for all its forms. The simultaneous content of all three components in water – ammonia, nitrites, and nitrates – indicates incompleteness of the process of mineralization and dangerous in epidemiologic sense pollution of water (for drinking water) (Dytnerisky and Kocharov, 1973; Gurevich *et al.*, 2009)

Heavy-metal ions are present in the water phase, notably, the presence of the forms of heavy metals salts in the studied sample depends on pH, since the formation of hydroxides of heavy metals occurs under certain conditions (GOST 31957-2012).

pH of wastewater depends on sampling point. Thus, in pyrrhotine facilities pH fluctuates from 3.82 to 7.68 – medium from slightly acidic till neutral; in tailing facilities from 3.17 to 4.56 – slightly acidic medium; in concentrate facilities from 9.51 to 11.45 – highly alkaline medium; communication tunnel from 8.24 to 9.83 – alkaline medium (Vakhler, 1997; Kocharov, 2007).

Since in pyrrhotine facilities pH varies from 3.82 to 9.04, the solution should contain iron (II), because complete precipitation of this form of iron occurs at pH = 9.7. Iron (III) should be introduced into precipitation in the form of hydroxide Fe(OH)₃ already at pH=4.1. At pH = 7.1 copper complete deposit is achieved what is confirmed by data. As well as iron (II), there’s nickel in the solution (complete precipitation pH = 9.5).

In tailing facilities medium is slightly acidic, that’s why all the forms of heavy metals are in the form of ions. The concentration of iron total significantly exceeds the concentrations of copper and nickel, since there are Fe²⁺ and Fe³⁺ in the solution (Yushmanov *et al.*, 1985; Evilovich, 1989)

In concentrate facilities medium is highly alkaline, at these values pH (9.51-11.45) all ions of heavy nonferrous metals and iron should be in the forms of hydroxides. Residue contents: copper no more than 0.05; nickel no more than 0.4, and iron no more than 0.8.

In communication tunnel medium is alkaline, ions of copper and nickel are transferred

into a solid state in the form of hydroxides (Nebel, 1993).

Oil products and flotation agents.

According to definition accepted by the Committee on the unification of method of analysis of natural and wastewater and also International symposium in the Hague when analyzing water, "oil products" are the sum of non-polar and low-polar compounds diluted in hexane, i.e. essentially, the sum of hydrocarbons (aliphatic, alicyclic, aromatic)(MUK 4.1.1013-01).

Based on this analysis, it's well demonstrated that content of flotation agents (xanthates and aerofloats) is consistent with the content of oil products' content (Baranov and Kutepov, 2005; Orlov, 1990).

Table 1. Summarizing test results

Test name	Allowed value (min-max)	Values detected
COD	15-20	15
BOD	1.4-0.3	5
Phosphates	0.05-0.15	0.0154-0.0830
Ammonia	0.05-0.1	0.3
Oil products and flotation agents	0.05-0.3	0.3
Copper	not more than 1	0.05
Nickel	not more than 0.02	0.4
Iron	not more than 0.3	0.8

CONCLUSIONS:

The authors carried out the study of wastewater of pyrrhotine facilities, tailings facilities, concentrate facilities and communication tunnel over the period from May to October 2016. The exceeding of the content of pollutants is observed in all samples of test subjects by all analyzed indicators, that's why wastewater can constitute a danger in case of its entry into natural bodies of water. The ranges of pollutants' concentrations over the researched period were determined. The purification of wastewater should be carried out in several stages:

- 1 stage – cleaning of substances, which density is lower than water density (oil products);
- 2 stage – removal of suspended materials;
- 3 stage – desalination.

For the first stage, it's necessary to use water and wastewater treatment facilities like oil remover. For the second stage, sedimentation can be used with the further evacuation of solid or filtering. For the third stage, it's expedient to use a reverse osmosis plant, electrodialysis or distillation. For wastewater test subjects, it's not expedient to use biological purification method because of the high content of nitrogen compounds and phosphates.

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