Using Redox potential in water quality assessment of energy facilities

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Abstract. The question of natural water quality for a long time has wondered researchers and ordinary citizens. Cities expanded, population increases, it leads to a deterioration in natural waters by sanitary-chemical and microbiological indicators. In this regard, this article concerns the question of the monitoring of physicochemical indicators and introduction the new indicator – Redox potential (Eh). Dynamics of Eh changes in the rivers of the Republic of Tatarstan and surrounding areas as well as natural and artificial water reservoirs, including basin-coolers of energy facilities are researched in this article. Conducted full-size data and experiments made it possible to establish the Eh sensitivity in relation to the pH. In the article has showed the possibility of introducing Eh indicator into the assessment of water quality on the assumption of further consideration and detail.

Introduction

Currently, the expansion of urban areas a matter of quality drinking and natural water is really an issue. In this regard the relevance of monitoring water facilities no doubt.

Public monitoring of water reservoirs is a system of observation, assessment and prediction the changes of water objects within federal property, property of subjects of the Russian Federation, municipal property, property of natural and legal entities [1]. It is a part of the Public environmental monitoring.

The object of water and environmental monitoring is assessment of there quality and level of pollution as necessary condition for the adoption of science-based decisions about the effectiveness of environmental protection measures. Conducted monitoring allows to determine the practical use of the water body: drinking, recreation, fisheries, irrigation, technical. The greatest interest is the reservoirs, related to multiple uses. An example of such reservoir is the Lake Sredniy Kaban in the city of Kazan, which since 1931 year has been the basin-cooler of the Kazan CHPP-1, has experienced anthropogenic load from sewage of industrial enterprises and since 2013 has been the sport object on which international competitions for rowing are held [2].

Currently formed a lot of parameters for controlling the water quality. A complete list of monitored parameters is provided in the normative and technical documents of water-sanitary legislation. However, this list is missing such indicator as redox potential. Redox potential is a measure of the chemical activity of elements or their compounds in reversible chemical processes associated with the change in the charge of ions in solution [3].

To answer the question about the possibility of using Redox potential in water quality assessment of energy facilities is required:
• analysis of the possible range of Eh values in natural waters;
• general understanding of changing processes of water Eh values.

Redox potential of natural waters

To analyze the possible range of Eh values changes in natural waters we researched Eh values in rivers and in natural and artificial reservoirs. To determine the Eh values used ion meter I-160 MI.

Focusing on major rivers, the territory of the Tatar ASSR divided into 3 parts on the orography – Predvolzhie, Predkamie and Zakamie. Predkamie on the river Vyatka is divided into West and East. Zakamie on the rivers Verhni Chereshman and Shesma River is divided into Western Zakamie (low) and Eastern Zakamie (high). In accordance with this division all collected data of Eh-value in rivers (total amount of investigated rivers is 30) are shown in Figure 1.

The analysis of the collected data showed that the range of Eh changes from -21,1 mV to -166,1 mV [4]. Minimum and maximum values are in the small rivers of Western Predkamie. The amplitude of variational series is 145 mV. The great range of values is confirmed by the standard error of the mean (Figure 1). Minimal variations observed in the Kuibyshev reservoir and on the Kama River.

The range of Eh values changes in lakes and natural ponds more wide compared to Eh values in rivers. For example, only in the Republic of Tatarstan the range of Eh values changes in lakes from 7,5 mV to -226,4 mV [5]. The amplitude of variational series is 233,9 mV. It is in 1,6 times higher the Eh amplitude in rivers. For reservoirs, experiencing the action of energy facilities (for example, the Sredniy Kaban lake of Kazan) the average value of Eh in zone, not suffering from action of energy facility (Kazan CHPP-1), is -53±8,5 mV. In the area of direct impact of energy facility Eh value drops to -80 mV, average value is -70±8,5 mV [2]. The value of -80 mV, characterized for zone of confluence heated water of offtake into the lake Sredniy Kaban, is according to Eh values in small rivers of Predvolzhie and the Kama River.

Redox potential in artificial systems

For the general understanding of changing processes of water Eh values at the “Water bioresources and aquaculture” Department of Kazan state power engineering university was devised an experiment. Artificial ecosystem was created by using aquarium (water volume is 600 l) (Figure 2) with the continual aeration of water. At the time of the experiment in the aquarium contained 2 Acipenser gueldenstaedtii, 12 Carassius gibelio and 8 Acipenser ruthenus (Figure 3). For control was used tap water by which filled the aquarium. The experiment was conducted without using biofilter and with
water changing (1 time in 3 days) for estimation of fish metabolites. The number of series of the experiment is 3. Measurable indicators: Eh (mV), water temperature (°C), pH, concentration of ammonium nitrogen (mg/l) and concentration of ammonia (mg/l).

Figure 2. Aquarium (water volume is 600 l).

Summary data (average of three series) of dynamics of pH and Eh values are shown in Figure 4.

Figure 3. Hydrobionts of aquarium: 1 – Acipenser gueldenstaedtii; 2 – Carassius gibelio; 3 – Acipenser ruthenus.

Figure 4. Dynamics of pH and Eh (mV) values in the water with hydrobionts (a) and in water without hydrobionts (b).

From data provided in Figure 4 you can see that on the first day of the experiment, both in control and in an aquarium with fish, the Eh values in water have been dropping, and pH values have been increasing. On the second and third day there has been a gradual increasing of Eh values in aquarium water (oxidation processes) associated with the accumulation of metabolites and lowering of Eh values in the control sample (reduction processes). Thus, redox potential allows you to keep track of time when it’s need to improve the quality of water.

Considering that the initial water for the aquarium and control are identical, it can be assumed that the difference of Eh values in aquarium water and control sample is the value characterized the highlight activity of hydrobionts and mostly concerned with nitrogen substances. Monitoring and analysis of the allocation of nitrogenous substances (Figure 5) by fishes in the context of the experimental aquarium is make possible to find relation between the concentration of ammonia
nitrogen and redox potential which corresponds to the vital functions of hydrobionts. The coefficient of determination is 92.73%. The regression equation is presented in Figure 5.

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y = -24,715x^3 + 209,11x^2 - 570,83x + 434,05
\]
\[R^2 = 0,9273\]

**Figure 5.** Relation between the concentration of ammonia nitrogen (mg/l) and redox potential (mV).

A similar experiment was done in closed-containment aquaculture system (CCS) with using the biofilter. In the CCS contained *Cyprinus carpio var. koi* (Figure 6). The experiment lasted from the moment when the process was characterized by dynamic and swinging until the sustainable up trend of Eh. This time amounted to 17 days. The experiment allowed to take into account not only the influence of fish metabolites on changing of the hydrochemical indicators, but also see the influence of biofilter organisms to changes of characteristics of water ecosystem.

**Figure 6.** Dynamics of Eh and pH values in CCS (orange marked morning measurements, before fish feeding).
Analysis of the obtained data allowed to find a prosperous phase of water ecosystem, which is characterized by fluctuations of pH and Eh values ranging from 6.4 to 7.3 and from -40 mV to -77 mV respectively (the first 11 days) (Figure 7). The next stage is deterioration of water ecosystem. In this phase increasing Eh values from -40 mV to -7.5 mV and lowering pH values from 6.4 to 5.1 (Figure 7). The analysis shows that redox potential, as the monitoring indicator, determine the process of declining the water quality before pH (in the CCS). In highly industrialized forms of fish farming, especially on the heated waters of energy facilities, diagnosis the water quality is becoming a critical factor for the success of the breeding process. By pH value the water acidification and out of equilibrium systems (since the moment when morning values are not higher or equal then the evening values) is going through the 300 hours (the concentration of ammonium nitrogen is 1 mg/l) or 12 days. By Eh value it happens through the 264 hours, or 11 days (the concentration of ammonium nitrogen is 0.9 mg/l).

Figure 7 illustrated the difference between morning and evening values of pH and Eh in CCS. In the control sample of water this difference is absent (Figure 8).

![Figure 7](image7.png)

**Figure 7.** Morning and evening pH and Eh values in CCS: 1 – prosperous phase of water ecosystem; 2 – deterioration phase of water ecosystem.

![Figure 8](image8.png)

**Figure 8.** Dynamics of Eh and pH values in control sample (orange marked morning measurements, before fish feeding).
The amplitude range of pH is from 5.1 to 7.3; Eh from -7.5 mV to -76.9 mV. The amplitude of variation series of pH is 2.2 units; of Eh 69.4 units. The amplitude of variation series of Eh in 31 times higher compared to pH.

Thus, redox potential is more sensitive indicator compared to pH. According to our researches we revealed that 1 unit of pH corresponds to 58,873 mV of Eh. Experiments have confirmed the sensitivity of Eh indicator to lower water quality (for example, in CCS). Redox potential can be used in water quality evaluation of water ecosystems and basin-coolers of energy facilities after detailed elaboration.

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