Automation of the Process of Stepwise Adjustment of pH and Eh Parameters in the Treatment of Metal-containing Wastewater

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Abstract— **The system of complex multistage control of process of sewage treatment from heavy metals by stepwise regulation of parameters Eh and pH is developed. Each of the control steps consists of a series of reagent dosing periods and a stabilization period. Reagent dosing is managed by local regulators, whose tuning parameters are determined for each step and adjustment period.**

Keywords— waste waters; heavy metal; automatic regulation pH and Eh; stepwise dosing of reagents.

I. Introduction

One important component of environmental protection is the prevention of the discharge of under-treated industrial wastewater containing heavy metal ions and other impurities into water basins. The major pollutants of this category are Classes 1 and 2 and are extremely negative for living organisms because they have cumulative and toxic properties.

The most hazardous to the environment and humans are sewage, which contains toxic impurities such as cyanides, hexavalent chromium, phenols, rodanides, organic impurities, which, when treated with reagents, can form dichloromethane and other intermediates having carcinogenic properties. Such wastewater must be pre-disposed of and subsequently disposed of as non-toxic wastewater.

For the removal of toxic impurities, metal-containing multi-component wastewater is treated with chemical reagents that change the magnitude of the active reaction (pH) and the magnitude of the redox potential (Eh) of the aqueous medium [1]. As a result, toxic impurities are destroyed by the formation of non-toxic products or transferred to another phase state (solid, gas).

In the next purification step, metal ions are precipitated as insoluble compounds, other soluble components are sorbed on special materials. Further, the insoluble products formed are separated from the wastewater using such technological processes as sedimentation, flotation, clarification in the suspended sediment layer, filtration on special structures (sedimentation tanks, flotators, clarifiers, filters, etc.) [2].

II. Results of Research

The most common method of treating such wastewater is a single dosage of oxidants / reducing agents while maintaining the active pH of the medium within certain limits until it reaches equilibrium in the reactor with subsequent laboratory analysis of the impurity content in order to decide on the need for additional reagent addition [3].

The disadvantage of this process is the considerable cost of reagents and the duration of wastewater treatment. This is due to the fact. that in the course of chemical reactions of oxidation-reduction takes place the consumption of hydroxyl (OH^-) or hydrogen (H^+) ions. This, in turn, disrupts the dynamics of the change of Eh and the pH of the aqueous medium, since the change in pH leads to the opposite change of Eh and vice versa, which inhibits the processes of oxidation-reduction. the processes of oxidation or reduction of impurities effectively proceed only within a given acceptable pH range.

Changing the pH beyond acceptable limits can lead to significant inhibition of the oxidation-reduction processes, even to the stopping of reactions, as well as to the release of toxic products. This requires, in addition to regulating Eh, the introduction of acids or alkalis to maintain the required pH values within acceptable limits.

In addition, the regulation of the values of Eh and pH is also complicated by the fact that the oxidant or reducing agent itself changes the pH of the medium. As a result, the single addition of oxidants or reducing agents to achieve the required values of Eh will be difficult or even impossible and requires dosing much greater than the stoichiometric amounts of oxidants or reducing agents required for the oxidation-reduction of impurities according to chemical reactions [4].

Chemical processes of oxidation-reduction take some time to complete the reaction, in particular, when oxidized, it can reach from several minutes to tens of minutes, especially in the presence of multicomponent wastewater. Therefore, after administering a dose of oxidant or reducing agent to the wastewater, it takes time to stabilize this parameter.

Given the significant interplay between pH and Eh during wastewater treatment, it is advisable to apply a complex control of these parameters, which is that Eh gradually increases to a value that provides complete oxidation-reduction of impurities, while maintaining the pH value in allowable limits that provide the necessary conditions for the efficient course of the redox reaction and prevent the release of toxic products [4].

The method of complex multi-stage control of the process of purification of multicomponent metal wastewater consists in a stepwise, sequential at each of the stages of dosing of reagents by measured values of redox potential Eh and active reaction of the pH medium with subsequent stabilization of redox. This method makes it possible to develop a microprocessor-based automated dual-channel control system for the purification process by step-by-step adjusting of the Eh and pH parameters. A block diagram of complex regulation of pH and Eh with the introduction of different reagents is shown in Fig. 1.

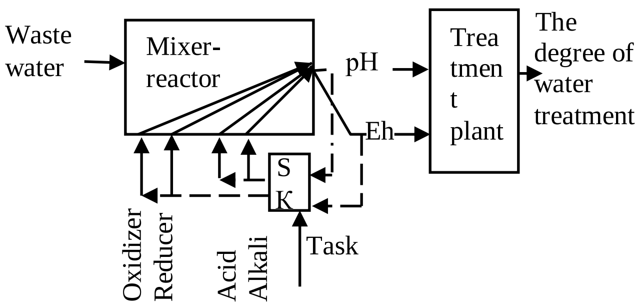

Figure 1. — Structural scheme of wastewater treatment with regulation of pH and Eh with the introduction of various reagents (SK - control system)

Wastewater is supplied to the mixer reactor, where the reagents are dosed for the oxidation-reduction of impurities and to maintain the value of active reaction of the medium required for these processes. Separation of the formed low-toxic contaminants from wastewater occurs during the passage of water through subsequent treatment facilities, which provide the necessary degree of wastewater treatment.

To ensure the quality of pH and Eh regulation, reducing the amount of reagents introduced, it is necessary to take into account the effect of these parameters on each other in the process of dosing of chemical reagents. This can be ensured not only by adjusting each parameter individually, but also by creating a control action to change one parameter (Eh) when changing another parameter (pH) or vice versa, ie to provide corrective relationships between these parameters that take into account the interaction of pH and Eh parameters .

Such conditions can be ensured by the multi-step administration of two-channel adjusting reagents (Eh and pH) with a process delay without dispensing the reagents after each introduction of an oxidant or reducing agent. In this case, the value of Eh gradually increases (decreases) to the set final value, which corresponds to the complete oxidation / recovery of contaminants, for example, with the excess of this oxidant (reducing agent).

Since the optimum rate and completeness of the oxidation (reduction) reaction is achieved with a stable pH value, it requires continuous maintenance over a certain range during the redox process.

In automatic mode, two-stage multi-stage pH and Eh adjustment are as follows. Initially, acid (alkali) is dosed into the waste water to bring the pH of the wastewater to the set values. In the following, a certain amount of oxidant (reducing agent) is introduced up to the first intermediate value Eh for partial oxidation (reduction) of impurities. Thereafter, the process of oxidation (reduction) of the impurities without the introduction of reagents takes place over a certain period of time, resulting in the stabilization of the value of Eh and the accompanying change of pH.

After stabilization of Eh, the dosage of acids or alkalis is again carried out to adjust the pH to maintain the limits of its values. Then again the oxidizer or reducing agent is dosed to another, greater (or less) intermediate value of Eh and the chemical process is stabilized. This stepwise dosing of reagents for pH and Eh adjustment is carried out until the final value of Eh is reached, which ensures complete oxidation-reduction of toxic impurities at the set pH of the aqueous medium.

The task of the controller Eh is set depending on the intermediate and final values of Eh. The possibility of using intermediate values of Eh during redox processes is explained by the fact that multicomponent wastewater refers to buffered systems in terms of Eh change. In such systems, an intermediate potential Eh can be established, which becomes conditionally equilibrium, although redox processes occur in water, albeit slowly.

Such potential does not correspond to the equilibrium of any of the redox systems and is determined by kinetic factors. However, since it is relatively stable, it can be used as a process parameter. The final value of Eh can be set according to its value at the complete completion of the process of oxidation-reduction of impurities and a given pH value. Ensuring pH is stabilized in a given range by a separate control loop.

The block diagram of the proposed two-channel control of pH and Eh parameters is shown in Fig. 2.

Since overdose of the reagent can lead to undesirable effects (change of pH beyond the specified limits), as the approximation to the intermediate and final values of Eh is required, the amount of reagent that can be achieved by the use of feedback systems and proportional-integral regulators should be reduced. the law of regulation.

A mathematical model of the control system was constructed and simulation of the purification process was performed using the example of hexavalent chromium and cyanide extraction. The simulation results show that the developed control system, including the method of selecting its parameters and the algorithm of operation, can be used to automate the processes of purification of multicomponent metal-containing wastewater from redox impurities with different properties at the treatment plants of industrial enterprises.

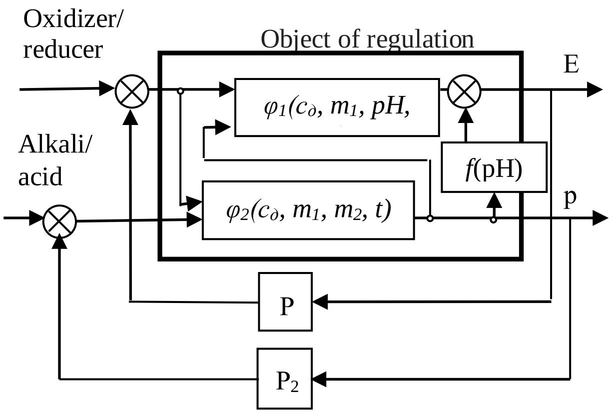

Figure. 2. Structural scheme of two-channel system of regulating the dosage of reagents: P_1 - regulator Eh; P_2 - regulator pH; φ_1 - function of transforming redox process; φ_2 - function of transformation of process of acidification; *f*(pH) - dependence Eh on pH; $c_д$ - concentration of admixtures; m_1 - mass of added reducer; m_2 - mass of added acid; *t* – time

The method of parameter selection and algorithm of operation of the control system are developed. The control of the operation of local regulators, the transition between stages and periods under the fulfillment of the necessary conditions, the change of the task and the parameters of adjustment at each of the stages, protection against the output of the pH parameter beyond the allowed limits, control over the execution termination conditions.

In the case of fluctuations in the initial concentration of contaminants, the need to fix intermediate values of Eh, the considerable duration of the course of redox reactions, the qualitative regulation of the pH and Eh values is achieved only when using batch reactors, which ensure the stability of the composition and the concentration of impurities.

Their work includes the operation of salvoid wastewater filling, dosing of reagents with the necessary adjustment of pH and Eh and subsequent discharge of treated water. At the same time, various reagents can be added to the batch reactors, stabilize the chemical reactions of change of pH and Eh after dosing of individual portions of the reagents, maintain the necessary parameter values, since the concentration and composition of the contaminating components in the volume of waste water is constant.

The advantage of such reactor mixers is that when they are filled with sewage, the concentration of impurities is averaged over them, which ensures the efficiency of chemical processes throughout the volume of the apparatus. Such mixers-reactors allow for ongoing and final monitoring of Eh and pH, which ensures complete neutralization of contaminants, and, if necessary, laboratory monitoring of the quality of treatment before discharging the disposed wastewater for further treatment facilities.

In addition, in such reactor mixers, it is possible to settle the treated wastewater from the formed low-soluble metal compounds, which improves the quality of water purification and reduces the cost of treatment facilities.

Schematic diagram of the production mixer reactor of periodic action is shown in Fig. 3.

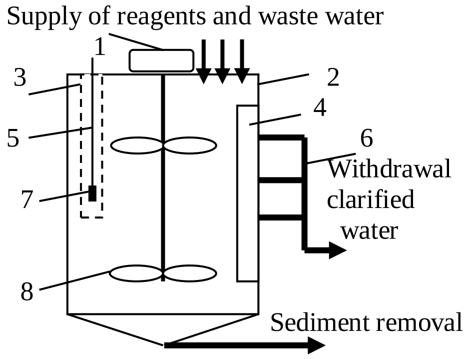

Figure 3. The scheme of the mixer-reactor of periodic action with mechanical stirring and with the function of settling: 1 - electric motor with gearbox; 2 - the housing of the mixer reactor; 3 - perforated protective tube; 4 - vertical plates; 5 - rods for fastening pH and Eh converters; 6 - pipelines for drainage of clarified water; 7 - pH and Eh converters; 8 - the blades of the mixer

III. Conclusion

On the basis of the conducted researches the mathematical model of the mixer-reactor of periodic action as an object of control with variable structure and the method of synthesis of local control systems of parameters Eh and pH at their stepwise periodic regulation was developed.

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