Efficiency analysis and justification of waste water purification methods for the water protection system against pollution

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Abstract. Modern waterbodies technologies protecting from pollution are based, mostly, on methods of removing elements from contaminated water that are dangerous for people. As a result, this process accumulates wastes that must be recovered by rather expensive ways. At the same time, there are metals that have market demand. These include copper that is in good supply in Karabash industrial area`s wastewaters in South Ural in the Russian Federation. The article analyzes the efficiency of selective copper removing by two most widely used methods in the mining industry: cementation on iron and extraction. There are data that characterize the efficiency of selective copper recovery, obtained with the help of laboratory studies. The obtained results indicate that both methods for the efficiency of copper extraction from contaminated wastewater are the same. However, the extraction method gives a more pure final product - copper concentrate, besides a large amount of iron appears in water after cementation, which requires further purification of water from contamination.

1. Introduction
Analysis of methods of water purification from heavy metals has shown that practically all methods used in water body protection against pollution are quite effective. At the same time, the problem of received waste recovery, as a rule, is not solved. In the meantime, metals that can be found in extremely polluted wastewater are of market interest [1-3].

2. Methods of copper extraction from contaminated wastewater efficiency analysis
Studies conducted in the area of the Karabash copper smelter found that active metal leaching and their flow into the watercourses of the Sak-Elga River basin and further into the Argazinsky water reservoir (that is the main battery of water for the water supply of the Chelyabinsk agglomeration) goes from technogenic wastes and mines.

A large number of methods of water treatment allows choosing the most effective. The basis of the choice is primarily the effectiveness parameters of water purification from heavy metals.

When studying the hydrochemical regime of the Sak-Elga River and its tributaries, it was defined that water quality is not the same, which requires the use of various methods of purification from heavy metals [4,5].

For effective metal extraction from solutions, their concentrations in water of the Sak-Elga River and its tributaries are not enough. For this purpose, underspoil waters of the tailing dams, ground
waters of the technogenic deposits of the Ryzhy Stream, as well as underground waters of the pyritous deposits of the Sak-Elga floodplain can be used.

Potential areas of metal extraction were determined on the basis of studying the formation of the hydrochemical regime of the river along tributaries from technogenic deposits [6].

Water samples were taken from the ground waters of the technogenic deposits of the Red Creek, the tailing waters of the tailing pond and groundwater of the pyrite deposits of the Sak-Elga floodplain [7,8].

Analysis shows that many researchers consider cementation on iron to be promising selective copper extraction [9-19]. The effectiveness of this method was checked by laboratory tests. Powdered iron was used as the cementite [13,14]. The experiments were carried out in funnels with a volume of 1000 ml. The powdered iron was poured into the funnel with water taken from Sak-Elga River basin in a 1:2 ratio and mixed by hand shaking for 5 minutes, after which the solution was analyzed.

In developed countries, copper extraction method from solutions is widely spread [15-18]. The most frequently cited extractant is LIX 984, which is a mixture of LIX 860N-I 3 (aldoxime) and LIX 84-1 (ketoxime) in a ratio of 1:1 (v/v) [20-22]. The producer of this extractant is Cognis Corp., a division of the Henkel concern. Plants for the production of LIX extractants are located in the US and Ireland.

The effectiveness of this method was also tested in laboratory conditions using LIX 984N extractant (20% solution in kerosene).

Copper extraction from solutions carried out in a separatory funnel with a capacity of 1000 ml. In water phase, an organic extractant LIX984 (20%) was added into kerosene and shaken by hands for 120 seconds. After the extraction was completed, there were two phases: water-based - raffinate and organic extract, which were analyzed after separation.

Table 1 shows the results of experiments.

| Water sampling point | pH | $C_{Fe, orig}$ | $C_{Cu, orig}$ | $C_{Zn, orig}$ | $C_{Fe}$ | $C_{Cu}$ | $C_{Zn}$ |
|----------------------|----|---------------|----------------|----------------|---------|---------|---------|
|                      |    | mg/dm³        | mg/dm³         | mg/dm³         | mg/dm³  | mg/dm³  | mg/dm³  |
|                      |    | resid %pur     | resid %pur     | resid %pur     | resid %pur |

Cementation on iron

|                  |    |              |              |              |         |         |         |
|------------------|----|--------------|--------------|--------------|---------|---------|---------|
| ground waters of technogenic deposits | 2,03 | 5674 | 458 | 543 | 68908 | 73 | 84,1 | 402 | 25,9 |
| undersoil waters of tailing dams | 2,24 | 4965 | 409 | 609 | 5349 | 55 | 86,5 | 563 | 7,6 |
| groundwater of pyritous deposits | 1,98 | 7651 | 489 | 679 | 8402 | 62 | 87,3 | 607 | 10,6 |

Extraction on Extractant LIX 984N

|                  |    |              |              |              |         |         |         |
|------------------|----|--------------|--------------|--------------|---------|---------|---------|
| ground waters of technogenic deposits | 2,03 | 5674 | 458 | 543 | 5607 | 1,2 | 48 | 89,4 | 422 | 22,3 |
| undersoil waters of tailing dams | 2,24 | 4965 | 409 | 609 | 4845 | 2,5 | 59 | 85,6 | 583 | 4,3 |
| groundwater of pyritous deposits | 1,98 | 7651 | 489 | 679 | 7468 | 2,4 | 62 | 87,4 | 647 | 4,7 |

Table 1. Results of copper extraction from Sak-Elga River basin.

The analysis shows that considered methods give similar results for the extraction efficiency of zinc and copper. However, extraction presents a purer final product that is a high percentage of copper in copper concentrate. In addition, it should be noted that cementation enriches the water being purified by iron, so the problem of further purification of water from iron ions arises.
As the remaining metals, which are present in the contaminated waters of the Sak-Elga River, is not of commercial interest (at least at the present time) due to their small quantity or low cost, further purification of water from other metal contaminants can be carried out by a sorption method using a natural sorbent. The cheapest and most effective sorbent is the gaize.

To substantiate the optimal parameters for copper extracting from aqueous solutions under real dynamic conditions, a laboratory experimental setup of a full copper extraction cycle using SX EW technology was developed.

Optimal parameters of the following elements of the technology of selective copper extraction from contaminated water in the Sak-Elga basin were determined:

- contact time of the extractant with industrial water;
- rotor speed of the extractor mixer;
- ratio of industrial water and extractant;
- water temperature

![Graph 1: Contact time of the extractant with water, min](image1)

![Graph 2: The rotor speed of the extractor mixer, rev/min](image2)

![Graph 3: Temperature, degree C](image3)

![Graph 4: Ratio of water and extractant, proportion](image4)

**Figure 1.** The justification for the optimal copper extraction parameters.

The defined optimal technical and technological parameters were applied in the development of technical conditions for the industrial plant design for the copper extraction from contaminated waters in the Sak-Elga River basin of the Karabash industrial hub.

The input parameters for the justification of the technical and technological characteristics of the experimental plant being developed for extracting copper are the water inflow, the concentration of metals and the pH of the water.

According to these parameters and data on the formation of the hydrochemical composition of water in the water bodies of the Sak-Elga River basin, the most promising locations for copper recovery systems and for water purification from metals are the mouth of the Ryzhy Stream, subsoil and groundwater in the tailing dam and groundwater in the area of the pyrite fields.

Analysis of geological, technical and technological documentation showed that the potential reserves of copper in the Karabash region, which can be extracted, reaches 97260 tons.
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