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***K. V. RAEVICH***[1], *Associate Professor, Candidate of Engineering Sciences, zenkoviv@mail.ru*
***V. N. VOKIN***[1], *Professor, Candidate of Engineering Sciences*
***E. V. KIRYUSHINA***[1], *Associate Professor, Candidate of Engineering Sciences*
***Yu. A. MAGLINETS***[1], *Professor, Candidate of Engineering Sciences*

[1]*Siberian Federal University, Krasnoyarsk, Russia*

# APPLIED RESEARCH AND PROCESS SOLUTIONS IN WASTE WATER CLARIFICATION AND TREATMENT IN MINING INDUSTRY*

*The authors describe the main achievements in the sphere of recovery ecology in the mining industry, namely, in the sphere of clarification and treatment of water resources pumped out of mines or used in mineral processing. The review reveals that water treatment includes removal of both mono contaminants and a number of elements (metals and their compounds), or nonmetallic toxic compounds from water. When solving ecological problems, researchers widely use chemical, physical, electrochemical and other methods of waste water clarification and treatment. The recent ecology of water resources is collecting a new knowledge on accumulation of different metals by species of higher vascular plants, water plants, fungi and microbial communities.*

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## Introduction

Mining industry brings the largest contribution to the development of the society in the global economy. Mineral production volumes grow every year together with the environmental damage inflicted to our planet. Operating mines are known to pump out large amounts of water from underground roadways, and to use water in mineral processing circuits. Process water is then discharged to water bodies or onto the land surface. Ions of various metals and toxic compounds contained in water, such as, for instance, sulfides, exert disastrous effects on flora and fauna both in neighborhood of mines and far away from them, owing to migration of the pollutants with water flows. For the avoidance of such consequences, mines must implement water treatment before discharging it to the environment.

In the authors' opinion, at the large scale of mining operations in our day, it is objectively required to systematize the recent knowledge on ecology of water resources. The main goal of this analytical review is to reveal the chief problems connected with pollution caused by waste water of operating mines, and to identify ways of such water clarification and treatment. In view of many studies published in special literature, the choice is made in favor of the latest achievements in the sphere of water ecology, applied in mineral mining and processing [1–53].

## Basic trends in solving applied problems of water clarification and treatment in economic activities in the mining industry

Mineral mining unavoidably leads to the change in the quality of water in terms of its saturation with various metals, toxic compounds, etc. Practice shows that mine waste water can contain either one contaminant or a group of chemical elements or toxic compounds, which violently deteriorate water. This problem of the mining industry permanently draws close attention of researchers–ecologists in the sphere of global subsoil use. It is important in this case that geography of mines is of no high relevance as the chemistry of rocks on all continents includes the same chemical elements similarly defined in science and practice all over the world.

For the treatment of mine waste water containing arsenic, it is proposed to use iron oxide hydroxide enriched with aluminum (Fe/AlO(OH)). Adsorption of arsenic was greatly influenced by temperature and pH of the water medium [1]. Copper can be extracted from water through membrane distillation in combination with ions of iron, aluminum and magnesium, as well as using an ion-exchange membrane with photoanode made of $TiO_2$/carbon dots/$WO_3$. Both methods proved their high efficiency in copper extraction from water [7, 8]. Vanadium removal from mine waste water used various iron sorbents: goethite, weakly crystalline akageneite or dry remains of iron after groundwater treatment in a peat mixture [18].

For the removal of arsenite and arsenate from waste water, a porous metal-organic skeletal material was proposed in combination with iron nano particles. Efficiency of arsenite and arsenate removal reached 99.9 and 71.2%, respectively [19]. The membrane filtration with the pore size of 0.14 $\mu$m was used on a plant for the removal of copper sulfide from mine waste water [22].

With a view to remove ions of lead, arsenic and zinc from mine waste water, a high-efficiency reactor was designed, which used mass exchange of polymers, tannic acid, cerium oxide ($CeO_2$) and zero-valence iron [21]. Ions of arsenic and iron were removed from waste water from an abandoned mine using double hydroxides with the layers of Mg–Al, with the further flocculation and, for the comparison, with $Ca(OH)_2$. Water treatment with double hydroxides with the layers of Mg–Al was more efficient in reduction of number of arsenic and iron ions [25].

Extraction of Co, Cr, Cu, Fe, Mn, Ni, Th, U, V, Y and Zn from mine waste water with a complex qualitative composition, with low pH (2.6) and a high concentration of sulfates became possible owing to the use of processed and activated silt as a bio sorbent for the selective extraction of metals in the presence of water solution of $Na_2CO_3$ [5]. Sedimentation of Fe, Cu, Pb and Mn on limestone filters reached water treatment efficiency of 98, 99, 99 and 60%, respectively [12].

Forward osmosis is recommended for removing aluminum and iron ions from waste water in the presence of water solutions of inorganic salts NaCl, KCl, $CaCl_2$ and $MgCl_2$ [14]. For the uranium removal from waste water, a membrane adsorbent with amidoxime group was created. The beneficial effect was that the membranes were manufactured using recycled plastic waste [15]. Clarification of process water during processing of kimberlite-bearing ore used electrolytic coagulation [16]. For the treatment of dirty mine water on a large industrial scale, it is recommended to use polymer fiber filtering plants [17].

Nearly all countries possess zeolite reserves. Currently, a vast experience is accumulated in using natural and modified zeolite in removal of mercury, cadmium, lead, chromium, nickel, copper, arsenic and other metals and toxic compounds from waste water [24]. Chelating ion-exchange resin chemically modified using molybdenum sulfide is recommending for adsorbing ions of Hg, Cd, Cu, Zn, Fe, Mg, Ca and Al from mine waste water [27]. A sorbent derived from sludge after water conditioning at a thermal power plant with a view to removal of iron, copper and nickel ions from mine waste

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water passed industrial testing and was recommended for water treatment in open pit and underground mining [29].

For the mine water containing negative ions of sulfuric acid and fluorine, it is proposed to use filtration with membrane separation and forward osmosis. It was studied how the modified compound of $TiO_2$, polyvinyl alcohol and polydopamine affected a thin-film composite membrane. As a result, the membrane efficiency in reduction of concentration of toxic compounds in mine water totaled 90% on the average [9]. Mine water contaminated by ammonia was proposed to treat in a plant with two composite metal–oxide electrodes–anodes made of titanium and covered with iridium and ruthenium oxides. The optimal number of the electrodes in the plant was substantiated [20].

Cycling and waste water in gold ore mining and processing contains, as a rule, much cyanide. Thiocyanates prevent water purification, as well. For water contaminated with such toxic compounds, a method of photochemical oxidation of contaminants with addition of three-valence iron ions was developed. Such approach allowed increasing velocity of oxidation reaction of thiocyanates by a factor of 20. As a sun light source, it was suggested to use KrCl excimer lamp without mercuric components. Addition of three-valence iron in the solution led to an essential reduction in energy cost of waste water treatment [33, 34].

A key problem in the mining ecology is removal of sulfide from mine or process water. Calcium oxide in combination with electrocoagulation was used in sedimentation of sulfate during mine water treatment. The use of the method enabled reduction of concentration of sulfates from 13000 mg/l to 1600 mg/l. In that research, first, the current intensity was measured. Second, different iron and aluminum anodes were tested in different monopolar and bipolar combinations. The best result was obtained with two aluminum and two stainless steel anode–cathode configurations, with preliminary treatment of water by calcium oxide to pH value of 12 [43].

The trend of using microbiocommunities in mine waste water treatment is being recently developed. Removal of arsenite from water was carried out in bioreactor, with microbiological oxidation and subsequent adsorption of arsenite. Biofilms and a consortium of acidophilic bacteria–oxidizers were effectively used in the reactor [2]. For the removal of iron, arsenic and manganese from water, the biofilter were created, with the microbiocommunties which exhibited strong resemblance with the communities in the bottom silt depositions. The species detected in the depositions promoted oxidation of arsenic and manganese, which led to settling of the metals [11].

The operation of a pilot plant for the removal of rare earth elements from water includes nitrification–denitrification using immobilized biological fillers. Denitrification bacteria *Thauera* and *Ottowia* dominated denitrification fillers in the plant [13]. Contaminated water in process water bodies arranged around a tailings pond at a magnesite mine was effectively treated using higher aerobic mold fungi *A. flavus*. The fungi resisted dissolved metals and effectively decreased contents of most contaminants [36]. Highly concentrated sulfates and calcium in water were settled in the bioreactor, on the biofilms with sulfate-reducing, autotrophic and heterotrophic, including sulfur-oxidizing, bacteria [38].

Removal of nickel from mine water used sulfate-reducing bacteria on a substrate made of lactate, formate, glycerin and glucose. The substrates provided efficiency of nickel removal not less than 95% [39]. Removal of cadmium from water was carried out using 64 species of bacteria. Finally, two species were recommended, namely, *Microbacterium oxydans* and *Rhodococcus sp*., which displayed high ability in removal of cadmium from water, and fixed 58 and 38% of lead in water, respectively [40].

A promising material for the mine water treatment is fairly waste of agriculture and food industry. Finely ground sea shells, coconut shells and wood chips bio coal were efficiently used to treat water with a view to removing metals and compounds: Al, Ca, Mg, CN, Cr, Fe, Zn, Ni, Pb, Mn and Cu [6, 10]. Remnants after sugarcane processing (bagasse) as well as solid waste of olive oil production were used in mine water treatment to remove Pb, Mn, Cu, Al, As, Cd, Fe, B and Ti [23, 26].

Uranium-bearing water treatment is effectively implemented through adsorption of U ions by sponge gourd (*Luffa cylindrica*) and by a natural bio-active polymer of chitosan [28, 30]. An ion-exchange polymer including methylamine phosphonic group and a resin soaked with trimethylpentyl phosphonic acid (acidic organophosphorus ligands) can remove rare earth elements from waste water [31].

From the results of experimental treatment of open pit waste water, it is proposed to use an adsorbent made of carbon-bearing remnants after pyrolysis of out-of-run large tires [32]. Agricultural waste used in water treatment became a source of production of valuable metals on a commercial scale, while wild plant bio coal was used to remove heavy metals from open pit mine water [44, 51].

The trend dynamically developing in the latest decade is the use of plant communities in waste water treatment. In manmade wetlands, in the presence of *Typha latifolia*, *Vetiveria zizanioides*, Carex lacustris, Typha latifolia and Juncus canadensis, with addition of various chelating acids, nano particles of MgO and sulfate-reducing bacteria, effective adsorption of Fe, Al, Zn, Co, Ni and Cr took place [3, 41, 42]. Accumulation of zinc, chromium and lead from mine waste water on leaves and roots of aquatic plant *Bidens pilosa* in manmade wetlands proved high efficiency of the plant in water treatment [53].

The tests of using green microalgae in purification of mine water revealed high concentrations of metals Fe, Zn and Cd in them, and the use of *Arthrospira* showed high efficiency the latter in treatment of high-sulfate mine water [4, 47]. Researchers in the sphere of mine water treatment find out that aquatic macrophyte *Potamogeton pusillus* can accumulate arsenic and mercury in its leaves and roots, which makes it a valuable phytosorbent [35]. High ability to accumulate Cr and Ni belongs to water lettuce (*Pistia stratiotes*) as well as to macrophytes *Pistia stratiotes*, *Salvinia minima*, *Ipomoea aquatica* and *Eichhornia crassipes*, which is highly promising for the phytoremediation of mine water [45, 48].

Water hyacinth was assumed to be a harmful undesirable plant for a long time. The tests of mine water treatment revealed high efficiency of the

**Main areas of activity in solving applied problems of waste water treatment in mining industry**

| Problematic field in mining industry | Reference source |
|---|---|
| **Physical and chemical water treatment methods (combination of methods)** | |
| Removal of a mono contaminant from waste water (copper, arsenic, vanadium etc.) | [1], [7, 8], [18, 19], [22] |
| Removal of a mono contaminant with a bit of associate metals (lead, zinc, iron) from waste water | [21], [25] |
| Removal of a number of metals and toxic elements from waste water | [5], [12], [14–17], [24], [27], [29] |
| Dissociation of cyanides, nitrogen compounds and metal sulfides from waste water | [9], [20], [33, 34], [43] |
| **Water treatment by microorganisms, fungi, organic materials and vegetation** | |
| Removal of toxic elements from waste water using microorganisms and fungi | [2], [11], [13], [36], [38–40], |
| Inclusion of organic substances, and waste of agriculture, feed and motor industries in water treatment plants for removal of heavy metals and toxic compounds from waste water | [6], [10], [23], [26], [28], [30], [31, 32], [37], [44], [51] |
| Absorption of heavy metals and toxic elements from water by plant communities: technologies of phytoremediation | [3, 4], [35], [41–42], [45–50], [52, 53] |

plant in accumulation of a wide spectrum of metals (Cr, Ag, Ba, Cd, Mo and Pb) and organic contaminants contained in process water in mines [46, 49, 50]. Extraction of heavy metals from the aquatic environment used a renewable biosorbent made of the biological waste of the wide-spread riverside plant *Zostera marina*. The biosorbent was tested in water treatment toward removal of manganese as a test indicator and showed a high degree of water purification [52].

Based on the review of the selected articles, the authors grouped the problems connected with the ecology of water resources used in the mining industry into seven main areas of activities (**Table**).

Each listed area of activity is promising for the further research with lab-scale and full-scale experimentation. In the authors' opinion, these research areas should be interconnected to shape an integral system defined as the interaction of all biosphere envelopes of our planet. This interaction calls for persistent development and implementation of activities aimed at improvement of ecology of water resources used in the mining industry at well-founded minimization of the environmental impact of mining.

## Conclusions

The review of the global trends in problem solving in the sphere of ecology of water resources used in the mining industry made it possible to identify basic trends of ecological research at solid mineral deposits, both mined-out and being mined, on all continents. The problematic field of the recovery ecology in the mining industry includes removal of mono contaminants, as well as the number of elements (metals and their compounds) and nonmetallic toxic compounds from water. Researchers widely use chemical, physical, electrochemical and other methods of impurity settling and water clarification. In water ecology in recent years, the new knowledge on accumulation of metals by higher vascular plants, water plants, fungi and microbial communities is being advanced.

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