Cadmium in the anthropogenic load on the biota

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Abstract
Environmental safety of mineral resources exploitation is an essential component of sustainable development. Currently, active work is carried out on the normalization of permissible impact on the environment. However, the current ecology of mining and processing industries is more economically focused and it is reduced to minimizing costs and fines for environmental damage. Mining enterprises are the source of anthropogenic cadmium entering the hydrosphere and soil. Cadmium can be accumulated in plants and living organisms, and then spread through the food chains. Cadmium and zinc are minerals genetically related to each other, for this reason, a number of chemical properties of these elements is similar. The degree of adverse effects on biota for cadmium is significantly higher than those of zinc, which is due to its toxicity at low concentrations. pH environments and sorption processes have a significant impact on the cadmium content in water and soil. On the basis of geochemical properties of cadmium and zinc, the measures to reduce the absorbability of cadmium by plants were proposed.
The measures suggested by authors on cleaning waste water of mining enterprises from cadmium will limit penetration of toxic substance and its compounds in the surface water, which will significantly affect the ecosystem of the regions locating close to the enterprises reducing the anthropogenic load on soil, plants, and final recipient - human.
Key words: CADMIUM, ZINC, SOIL, PLANTS, HEAVY METALS, ANTHROPOGENIC IMPACT, ECOLOGY

Waste water treatment is performed in several steps and involves the removal of the main pollutants. Cadmium, as one of the most toxic heavy metals, is not in the great interest due to its small volume in the total weight of contaminants.

Activities on the extraction of cadmium from wastewater do not carried out, primarily due to low economic attractiveness of this metal on the market, as well as its small amounts in wastewater. While standards costs for the discharge of 1 ton of cadmium are twice more than the genetically related component - zinc. They are 55 096 rubles respectively [1]. This, in turn, is associated with greater toxicity of cadmium, which causes entering of cadmium in category II according to the degree of danger of polluting substances.

The main source for the extraction of cadmium is hydrothermal sulfide deposits. Cadmium is found in the form of an isomorphous impurity in many minerals and it is always in zinc minerals. They contain from a few hundredths to a tenth of a percent of cadmium. Cadmium distribution in the Earth's crust is invariably associated with the distribution of zinc. [2]. The average concentration of cadmium in sphalerite does not exceed 0.4-0.6%. In lead and copper ores cadmium concentration does not exceed a few hundredths of a percent. In pyrite ores, cadmium content ranges from 0.0031 to 0.218%.

Table 1. Comparison of the characteristics of zinc and cadmium

Physicochemical properties	zinc	cadmium
percentage abundance in the earth's crust, %	$8.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-5}$
order number	30	48

atomic weight	65.39	112.41
atomic radius, nm	0.139	0.156
ionic radius, nm	0.103	0.099
Melting t, °C	419.6	321.1
Boiling t, °C	906	766.5
pH precipitation of hydroxides	8.0-9.5	5.2-8.3
electronegativity kJ / mol	1.7	7.5
MRL, mg/l	0.05	0.005
Hazard Class	III	II

In chalcophilic elements, which include zinc and cadmium, the polarization properties rise with increasing of order number and increasing their ability to form complex compounds [3]. The increase and decrease in the valence of the ion radius also promotes complexation. Consequently, cadmium is more movable than zinc, while it is more dangerous for the environment. The metallic cadmium does not have toxic properties. Cadmium compounds, regardless of their aggregate state (dust, smoke of cadmium oxide, vapors, fog), are poisonous. In connection with toxicity of cadmium and its compounds their contact with the components of the biota is not allowed. Heavy metals are protoplasmic poisons, i.e. their toxicity is risen with increasing of atomic mass. Therefore, the degree of negative impact on biota for cadmium is significantly higher than that of zinc, and it determines its toxicity at low concentrations.

When the development of massive sulfide deposits at all stages of the process multicomponent acidic wastewaters different in their chemical composition and concentration of polluting substances are formed.

Flotation is the main method of ores dressing and, accordingly, for this processing technology the use of a large amount of water in main and auxiliary beneficiation operations and in other workshops is provided.

In addition to water occurring when the current development of deposits and directed through the treatment plants to discharge into natural water bodies, a significant amount of industrial wastewaters is accumulated in the waste pits and tailings ponds. Chemical elements in the tailings ponds are present in geochemically mobile form, therefore, wastes of processing plants, along with industrial wastewater enterprises represent the greatest environmental risk. Seeping through the dams and bed of facilities, tailings ponds filtration waters contribute entering the pollutants in surface water and groundwater [4].

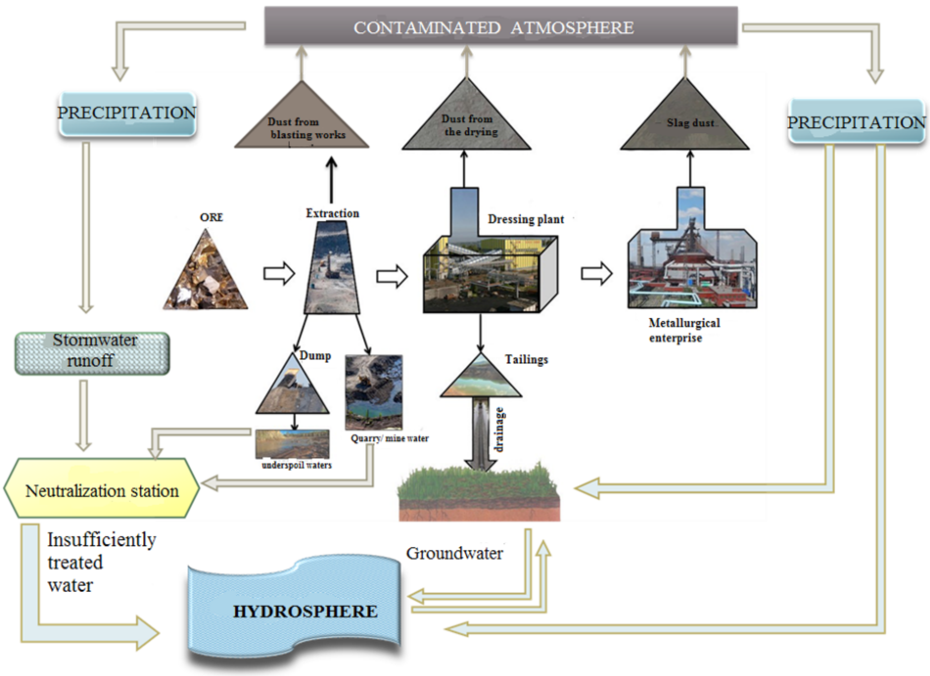

Figure 1. Sources of cadmium entering the soil and hydrosphere

On example of Karagaily and Hudolaz rivers experiencing the impact of wastewaters from Sibay branch of UGOK, let us consider anthropogenic impact of cadmium.

Table 2. Frequency rate of exceeding the MRL in the Karagaily river

Sampling point	points	Zinc, MRL	Cadmium, MRL
Background section	1	10	10
Impact section of the mine flows and underspoil waters	2	1940	94
Section in top pool of the pond	3	1120	106
Section in bottom pool of the pond	4	2000	112
Section below output of industrial enterprises of Sibay city	5	1240	52
Section in the area of SOF dam	6	1110	40
Section in the area of tailings ponds	7	650	50
Section in the Hudolaz river estuary	8	180	270

Karagaily river pollution occurs due to entering of heavy metals from wastewater of SF UGOK, Sibay underground mine, Kamaganskiy quarry. In the southeastern part of Sibay quarry, the site of Karagaily river falls to the dumps [5]. Hudolaz river is contaminated by the waters of its tributary of Karagaily river and drainage from the tailing ponds-storages and leaching of residual discard. Water quality of Hudolaz river stably meets quality class 7 - "very dirty". It should be noted that the high gradient of the seasonal variability of the pH value and the qualitative and quantitative composition of waters are due to climatic factors. [6]

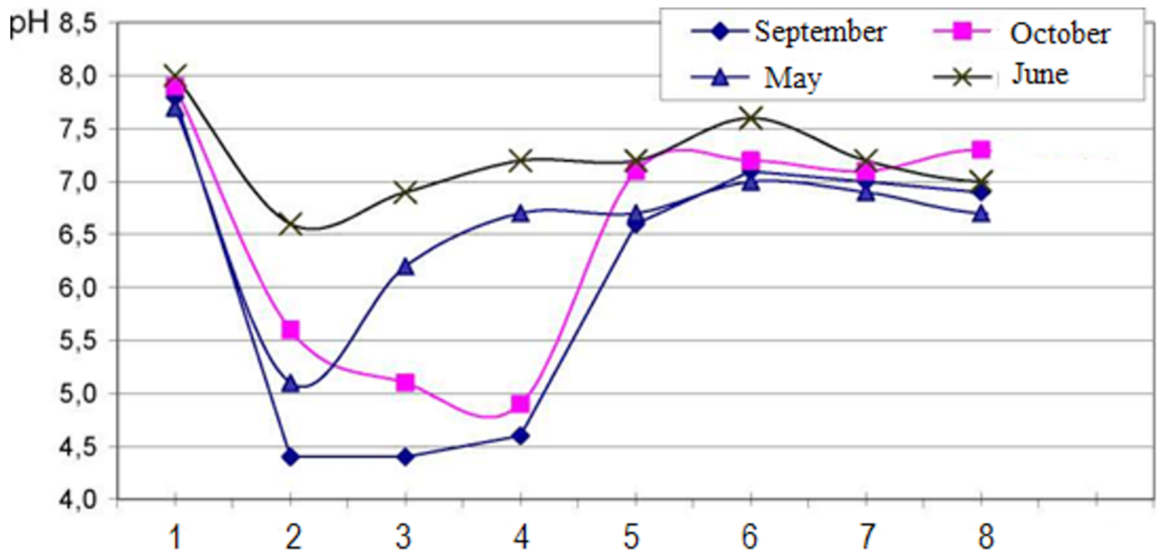

Figure 2. Changing the pH in the Karagaily river

Significant impact on the cadmium content in water have a pH of the medium and sorption processes [7]. In aqueous solutions cadmium is in the divalent state.

The high content of zinc and cadmium in the water of the Karagaily river determines its hazard for hidrobionts. Cadmium is a highly toxic metal, it is able to bind sulfhydryl (-SH) groups and change activity of many hormones and enzymes. This causes pathological changes in the internal organs characterized by vascular disorders, toxic edema of the epithelium of the gills, kidneys, brain of hydrobionts.

A significant danger is presented by cadmium-containing soils as a consequence of anthropogenic pollution of the hydrosphere. In the area of mining enterprises operation technogenic landscapes with a high content of heavy metals are produced. Mining enterprises have a strong impact on the area of acidic podzolic and sod-podzolic soils. These soils are low buffer unsaturated with bases and have low humus content with a predominance of aggressive organic compounds [8]. The accumulation of pollutants in such soils is much higher. In soils, heavy metals are present in the water-soluble, ion exchange and unstable adsorbed forms. At high pH, the heavy metals are more movable and they penetrate into the underlying layers, ground water and go beyond the techogenic landscape. At the same time, acidic soils absorb heavy metals from solutions less than neutral or carbonate containing.

Cadmium is absorbed by plants extremely easy, zinc has average degree of bioaccumulation by plants relative to the soil. The plants absorb from the soil up to 70% of cadmium and up to 30% from the air [9]. In this respect, mushrooms are the greatest danger, since they have a completely different mechanism of nutrition and can often accumulate cadmium and zinc in high concentrations. Zinc and cadmium are concentrated predominantly in plant roots while cadmium also accumulates in leaves of the plants. Organic substances are able to bind zinc in stable forms, so that its accumulation is observed. Most plant species are sufficiently stable to excessive amounts of zinc. Zinc is characterized by weak phytotoxicity: growth retardation and oppression at more than 300 mg/kg (grasses are susceptible, cruciferous and clove are tolerant). Phytotoxicity occurs in the following ways: interveinal chlorosis of young leaves, chlorosis and necrosis of leaves ends, damaged roots similar to barbed wire, growth inhibition of the plant in general. Phytotoxicity of cadmium is higher and shown as follows: changes in the permeability of cell membranes, leaf chlorosis, reddish petioles and fibers, half-grown brown roots and leaf edges, twisted leaves [10]. Cadmium substitutes zinc in plants leading to zinc deficiency. Due to the fact that zinc is responsible for the metabolism of carbohydrates and proteins this leads to oppression and death of plants.

Cd and Zn are microelements of IIb group, and therefore the number of elements and chemical properties is similar: they have a high electronegativity, easily form covalent bonds with non-metals, they are insoluble in water, in chemical compounds they exhibit valency 2. The compounds of cadmium and zinc are quickly hydrolized. Zinc is readily adsorbed in minerals and organic compounds, mostly zinc accumulates in the surface soil horizons. The most movable form is Zn^{2+}. Under acidic conditions adsorption is associated with cation exchange, in an alkaline - with chemisorption and strongly depends on the presence of organic ligands. Adsorption of Zn^{2+} is weakened at pH less than 7. With the change in pH, the role of soil components in the sorption of heavy metals alters significantly. The peculiarity of cadmium is that it practically does not bind to soil humic substances. In any soil, cadmium activity is strongly dependent on pH, it is the most easily movable at pH of 4.5-5.5. To reduce the concentration of mobile forms of heavy metals liming of acid soils is the most effective in order to increase pH. In the binding of cadmium, the leading process is competing adsorption on clays [11], it is adsorption rather than precipitation that controls the concentration of cadmium in the soil solution higher than pH values of 7.5.

Neutral or carbonates containing soils absorb heavy metals from solutions to a greater extent than acidic soils. Carbonate, calcium-rich soils adsorb heavy metals better, in this case cadmium ion forms unstable complexes. At pH = 6 and the absence of such binding anions as phosphate or sulfide, Cd^{2+} is completely dissolved in the aqueous medium. Formation of $Cd(OH)_2$ starts at pH = 9 reaching a maximum at 11. Zinc is predominantly adsorbed in an acid medium and cadmium – in alkaline. Soil holds the more heavy metals, the higher cation exchange capacity and correspondingly plants and organisms receive less pollutants. Excess of moisture promotes the transition to the lower degree of oxidation in more soluble forms. It increases the accessibility of heavy metals to plants.

Geochemistry of cadmium and zinc is generally similar, but cadmium has a greater mobility in acidic media. The interaction of zinc and cadmium is moot point, since there are data of the synergies [12] and antagonism of these cations and it is controlled by the ratio of cadmium to zinc in the living environment of the plant. But overall, there is a general trend – zinc reduces the absorption of cadmium by roots and leaves, at a ratio $Cd/Zn < 0.01$ cadmium content is reduced.

Conclusions

To reduce the absorbability of cadmium by plants, the following measures can be applied:

- the use of alkaline carbonate geochemical barrier;

- the use of chelating reagents. The metals go into the labile form and fall to the soil level, which is below the root system. But the use of complexing agents leads to the contamination of groundwater.

- removal of the contaminated layer;

- to reduce the bioavailability of cadmium, the coating over the contaminated soil of uncontaminated soils is possible with thickness of 30 cm.

Measures for wastewater treatment of mining enterprises from cadmium will limit penetration of this toxic substance and its compounds in the surface water, which significantly affects the ecosystems of the region locating in close proximity to enterprises reducing the anthropogenic load on soil, plants, and the final recipient - human.

References

1. Russian Federation Government Resolution dated June 12, 2003 n 344 "On norms of payments for emissions of air pollutants from stationary and mobile sources, discharges of pollutants into surface and underground water bodies, including through the centralized sewerage systems, waste disposal and consumption "
2. *Gornaya enciklopedia* [Mining Encyclopedia] (Electronic resource). Available at: http://www.mining-enc.ru.
3. Shcherbov D. P., Matveets M. A (1973) *Analiticheskaya himiya kadmiya* [Analytical chemistry of cadmium]. Monograph. Moscow: Nauka.
4. Orekhova N. N. (2004) *Ratsionalnoe ispolzovanie vodnyih resursov* [Rational use of water resources]. Magnitogorsk: MSTU. 105 p.
5. The Ministry of Natural Resources and Ecology of the Republic of Bashkortostan "National Report on the State of Natural Resources and Environment of the Republic of Bashkortostan", 2013.
6. Smirnova T. P. (2009) *Rol himiko-biologicheskih faktorov v formirovanii ekologicheskogo sostoyaniya malyih rek v zone vliyaniya gorno-obogatitelnyih kombinatov* [The role of the chemical and biological factors in the for mation of the ecological state of small rivers in the zone of influence of mining and processing plants]. Abstract of dissertation for the degree of Candidate of Chemical Sciences. Kazan.
7. Shadrunova I. V., Orekhova N. N. (2009) *Izvlechenie tsvetnyih metallov iz gidromineralnyih resursov: teoriya i praktika* [Extraction of the non-ferrous metals from hydromineral resources: theory and practice. Monograph]. Magnitogorsk. 180 p.
8. Sviridov E. A. (2001) *Biodinamika kadmiya v organizme zhivotnyih i ee farmokokorektsiya* [Biodynamics of cadmium in the bodies of animals and its pharmacocorrection]. Dissertation of the candidate of biological sciences, Voronezh.
9. Orlov D. S., Sadovnikova L.K., Lozanovskiy I. N. (2002) *Ekologiya i ohrana biosferyi pri himicheskom zagryaznenii: Uchebnoe posobie dlya him.,him-tehnol. i biol. Spets. vuzov* [Ecology and protection of the biosphere at chemical contamination: Textbook for chemical, chemical-tehnol. and biol. universities]. Moscow: Vyisshaya shkola. 334 p.
10. Maystrenko V. N., Khamitov R. Z., Budnikov G. K. (1996) *Ekologo-analiticheskiy monitoring supertoksikantov* [Ecological and analytical monitoring of supertoxicants]. Moscow: Khimia. 319 p.
11. Kabata-Pendias A., Pendias Kh. *Mikroelementyi v pochvah i rasteniyah* [Trace elements in soils and plants].
12. Eichler V. (1986) *Yadyi v nashey pische* [The poisons in our food, Translation from German]. Moscow: Mir. 202 p.