

Behaviour of As and Sb in 'technogenic lake – environment' system

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In this presentation the geochemical state of the Komsomolsk collection pond (technogenic lake) is discussed. The pond has been formed as a result of stockpiling and settling of waste waters after cyanidation of gold-arsenopyrite-quartz ores and after antimony recovery (Kemerovo region, South-West Siberia). Tailings impoundment is located in a valley at an altitude of 800 m above sea level, closed from three sides by the natural relief and from the fourth one – by the filled dump. It contains about 3.5 mln. tons of mineral processing waste. The main sulphide minerals are pyrite, pyrrhotite, and arsenopyrite. Together with galena, chalkopyrite and sphalerite sulphide minerals represent less than 5%. Gangue minerals are composed mainly by quartz, feldspar, calcite. In general neutralization of draining solutions was done by adding $\text{Fe}(\text{SO})_4 \cdot 7\text{H}_2\text{O}$ to the settler, and the effluent was subsequently discharged into river Voskresenka. The objectives of this investigation were: a) to determine tendencies of behaviour of the potentially dangerous components: heavy metals As, and Sb in 'water - solid tailings' system during storage period; b) to study geochemical conditions of the lake to reveal speciation of toxic components; c) to establish accumulation routes of dissolved forms of toxic substances in pore and underground waters.

Field and analytical methods. Field work include sampling of different components: surface lake water; sediments; dry part of the tailings impoundment; underground water. Three profiles of surface water of the lake were sampled. The water was filtered through filters with a pore size of 0.45 μm . Three 30–60 cm deep sediment cores were taken and sliced. First core (¹ 1) was taken from the lake part located near the pulp-line to study a substance with minimal action of oxidizing process during storage

period. The second core sampling (¹ 2) was done in the shallow part of the lake at the opposite bank of the lake. The third core (¹ 3) was sampled near the natural slope of the valley where there is an abundant water vegetation and the lake bottom is covered by residue of organic material. Pore water was pressed out from each subsample of the three cores. All sample types were chemically analysed by multi-element techniques (ICP-MS, AAS, X-ray fluorescent measurements; anions were analysed by ion chromatography). Arsenic speciation in surface, pore and underground water was analysed using HPLC with different types of detectors: atomic-absorption, spectrophotometry, fluorescence). Thermodynamic calculations of possible elements' speciation were done using database and computer code WATEQ4F (Ball and Nordstrom, 1991).

Results. The maximum excess above the background is observed for As and Sb (on the average 203 and 3600 $\mu\text{g}/\text{l}$ correspondingly). Their concentrations are three orders of magnitude higher than the background value. Despite of the content of Sb in solid tailings is only half that of As the content of Sb in water is 170 times higher than of As.

Although arsenic and antimony are distributed uniformly over surface of the lake water, a tendency of their increase has been found towards the pulp-line. Concentrations of dissolved heavy metals (Fe, Pb, Zn, and Cd) are significantly lower because of different behaviour of the minerals over interaction with cyanide solution. The heavy metal content is not shown here because the investigation was concentrated on As and Sb. An increase of concentration of the investigated metals was found in water at shallow parts of the lake. It is caused by more intensive oxidation of sulphides under action of atmospheric oxygen and higher temperature.

The intensity of interaction of the solid tailings with water can be estimated through contents of dissolving Sb in pore water. In particular, the Sb content in pore water from core 1 (located just near the pulp-line) is determined by composition of discharged waste processing water and reflects the result of interaction of the recovery substance and cyanide solution. The Sb content in pore water here does not exceed that of in lake surface water. Intensive dissolution of Sb compounds occurs in the shallow parts of the lake where content of Sb in pore water reaches up to 11000 $\mu\text{g/l}$ with clear trend of an increase downwards of the column. Antimony content is lower in the part of the lake, which adjoins a natural slope of the valley and is overgrown with aquatic vegetation. The balance estimation of Sb distribution between water, inorganic solid and organic solid was done.

Contents of As and Sb decrease after chemical treatment of the lake effluent, which occurs through the drainage hole. Analyses of water from river Voskresenka (see Scheme and Table, column 5) show quite satisfactory results: toxic metal content in the river is lower than the maximum permitted concentration. At the same time high concentrations of As and Sb were measured in underground water. Comparison of As speciation in different type of water showed that the most important chemical forms are arsenite and dimethylarsenite.

Discussion. In fact, oxidation of sulphide minerals occurs slowly under conditions of permanently flooded tailings, that is reason for low heavy metal concentrations (Pb, Cu, Zn, Cd) in water of the lake. Thermodynamic calculations of element speciations in water and estimation of system approximation to equilibrium using calculated Saturation Indices allow to suggest preferable precipitation of the heavy metals in sediments as (hydro)oxides. However, an arsenopyrite oxidation supplies a comparatively high amount of As into water. The peculiarity of the Komsomolsk tailings composition is the presence of Sb. Its speciation in the initial substance (Sb_2O_3 and Sb_2O_5) determines the release of Sb into solution. Cyanidation of the ores under oxidizing conditions and alkaline solution leads to formation of easily dissolving compounds such as $\text{NaSb}(\text{OH})_4$ and $\text{NaSb}(\text{OH})_6$, which makes the main contribution to Sb contents in water. As it was shown by *Bowell and Bruce (1995)*, for As sorption processes play dominant role in variation of its content in water. Nevertheless, for Sb importance of sorption under these conditions is insignificant. It is shown on the

base of pore water ionic composition and experimental data on sediment leaching that over interaction in the system 'water-sediments' the process of arsenopyrite dissolution and As re-precipitation of As together with Fe-hydroxides is not completed due to kinetic limitations. First of all, it is expressed in sharp supersaturation of solutions with respect to ferrous solid phases. At the same time, the content of dissolved Sb is stabilized nearly 3600 $\mu\text{g/l}$ and controlled by high solubility of its oxides.

Obviously, the Sb forms in the initial substance and absence of geochemical barriers are the main reasons for extremely high concentrations of Sb in different waters of the Komsomolsky lake. An increase of Sb leaching intensity into pore water of cores 1 and 2 have demonstrated that the problem of control of the lake state is rather complicated than it was considered. Despite of satisfactory operation of the treatment system through the drainage hole, soaking and filtration of pore water containing very high toxic metal concentration causes release into underground water.

It is well known, that aquatic vegetation particularly filamentous green algae effectively accumulates metallic pollutants. Transfer factors of some elements in green algae species can reach 10^3 – 10^4 values. This is the reason why plants in many cases are used as bioindicators (*Kurtács et al., 1994*). Presumably lower concentrations of toxic metals at sites with dense vegetation are due to this biogenic factor. This quality of the aquatic plants can be used for environmental restoration actions. Intensified growth of the vegetation artificially enhanced by adding nutrients (N, P) could result in removal of the majority of soluble pollutants from the water. Testing of the idea of biological cleaning needs further research efforts in this direction.

The dominant species of As as As(III) and dimethylarsenite indicate a high toxicity of these waters. Analytical determination of Sb species has not finished yet but judging by literature data (*Chwastowska, 1995*), significant part of the total Sb can be in Sb(III) form. Obviously, the medium of the tailings impoundment is not enough oxidizing to transform these elements into 5-valency (*Cherry and Bruce, 1995*). The migration of water with high contents of As(III) and Sb(III) may be responsible for disastrous contamination of the environment especially at alteration of existing conditions (physico-chemical, hydrological etc.) and breaking of equilibrium.