Heavy metal speciation in different components of technogenious lakes

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Understanding the mechanisms of heavy metal (HM) migration and detoxication in ecologically dangerous objects – technogenious lakes – requires not only evaluation of their total content but also HM speciation in the environment. This investigation is directed, at first, on the studying HM behaviour in the 'surface lake water - bottom sediment pore water' system. Secondly, on determining possible speciation of HM in the solution and solid phases based on in-the-field sampling and laboratory analyses with thermodynamic calculation.

In-the-field experiment was pursued near the town Salair (South-West Siberia, Kemerovo region). As a result of mining activity of Salair plant the great tailing impoundments (Salagaev – now in force, Djukov – inoperative since 1967) were derived here.

Field and analytical methods

Surface and pore waters from solid substances were sampled in the Salagaev, surface and near bottom water – in the Djukov. Several 60 cm in average long sediment cores were taken in Salagaev with following split into subsamples. Pore waters were pressed from each subsample. Water was filtered through filters with a pore size of 0.45 μm. All sample types were chemically analysed by multi-element techniques (ICP-MS, AAS, and anions by ion chromatography).

Discussion

According to laboratory analyses the ionic content differs essentially in the Djukov and the Salagaev. So, concentrations of the Cl^-, NO_3^-, NO_2^-, NH_4^+, Ca^{2+} Mg^{2+}, Na^+ K^+, SO_4^{2-} in the Salagaev exceed the same in the Djukov by one or two order sometimes. HM content in the Salagaev exceeds the background ones of this region by an one order (especially Zn and Cd content). Zn and Cd concentrations in pore water are one order higher than in surface one.

Metals speciations in the surface water calculated with the help of computer code WATEQ4F (Ball, Nordstrom, 1991) differ essentially from these in pore water (see Table 1).

Solid (possible in suspended form) phases are presented (according to calculated Saturation Indices) by gypsum ($CaSO_4{\cdot}2H_2O$), ferrihydrite ($Fe(OH)_3$), tenorite (CuO). These particles have settled to the bottom, forming the sediments with the plant residual. Data analysis of the sediment and pore water components demonstrate that the Pb and Cu content in the upper part of the sediment is higher than the ones in the initial material (stored wastes). Variations of the average contents in the vertical sections are unessential (1.2–1.5 time), but for Cd is 14.5 time. The range of their fluctuation in pore water is wider. We found that content of the soluble forms decreases from the zone immediately adjacent to the pulpline to ones with relatively stable conditions.

TABLE 1.

Speciation	Surface water % of ΣMe	Pore water % ΣMe
Ca^{2+}	78–82	61–65
$CaSO^0_{4aq}$	18–22	35–39
Cd^{2+}	70–75	47–52
$CdSO^0_{4aq}$	24–28	48–53
Mg^{2+}	77–81	58–61
$MgSO^0_{4aq}$	19–23	39–42
$Cu(OH)_2$	91–99	82–86
Pb^{2+}	20–38	4–7
$PbSO_4aq$	14–31	7–10
$PbCO^0_{3aq}$	11–24	82–85
$PbOH^+$	18–37	3–4
Zn^{2+}	64–75	45–47
$ZnSO^0_{4aq}$	17–24	27–28
$ZnOH^+$	1–5	1–1.5
$Zn(OH)^0_2$	1–10	1.4–6

Suspended phase in pore water is mainly represented by $CaSO_4$, $CaCO_3$, CuO, $Cu(OH)_2$, FeOOH, MgO, ZnO, $ZnCO_3$. Moreover, analytical absence the soluble forms of nitrogen confirms the microbiological activity in pore water. So, in anaerobic conditions bacteria can produce H_2S and sulphide minerals (partially Cu and Pb) can form what is confirmed by the thermodynamic modelling.

As for Djukov, only for Zn the high concentration is exhibited (6.3 in surface and the 32.8 mg/l in bottom water). Cd concentration exceeds ones in Salagaev (0.02mg/l in Salagaev water and in Djukov water reach up to 0.11 mg/l). Contents of Cu and Pb are at the same level. The HM speciation does not differ essentially, suggesting about stability of this system. We can conclude that the bottom deposits control chemical concentrations in this technogenious lake.

Conclusions

The comparison of two different in the age tailing impoundments allows to conclude that HM mobility increases with the age. High HM concentrations in the Djukov evidence that burial in the bottom sediment is not enough safe especially if the reservoir experienced external influence.

The main forms of the metals in surface water of Salagaev are ionic form (for Ca, Cd, Mg, Zn), hydroxide form (for Cu), ionic, hydroxide, sulphate, carbonate (for Pb). In pore solution the main form for Ca, Mg is ionic, for Cu-hydroxide form, for Pb-carbonate form, for Zn and Cd the ionic and sulphate form are represented in comparable parts. As for Djukov water (surface and bottom), the main form for Ca, Mg and Cd is their ionic ones, for Cu is hydroxide form, for Zn is sulphate and for Pb is the carbonate ones.

References

Ball, J.W. and Nordstrom, D.K. (1991) Menlo Park, California: U.S. Geological Survey, 189 p.