

The Role of Anionogenic Elements (As, Sb, Mo, Se, S, P, N, Cl, F, C) In The Formation of Technogenic Geochemical Anomalies

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Abstract. The study was conducted on the example of sulphide-containing mine tailings with a varying amount of sulphide and arsenide minerals, from three distinct tailings dumps situated in Russia: Karabash Mine Site, South Ural; Komsomolsk tailings impoundment, Kemerovo region; Khovu-Aksy mine site, Tuva Republic. The aim of the study was to compare the mobility of anionogenic elements (As, Sb, Mo, Se, S, P, N, Cl, F, C) and their role in migration, precipitation, and concentration of metals during the water-tailings interaction depending on the physicochemical parameters (pH, Eh) of the medium and the mineral composition of the waste material. Using slightly acidic leaching experiments the quantitative estimation of mobile forms of elements is given. Based on the compositions of the obtained water leaching solutions, aqueous speciation of chemical elements and saturation index of key minerals in the experimental solutions were calculated. The results of calculating forms of chemical elements made it possible to construct series of mobility of metals and metalloids in solutions with different physicochemical parameters. In the alkaline conditions, Sb>As>Cd>Cu>Zn>Fe>Pb, when the medium is acidified, the series changes, As>Cd>Cu>Zn>Pb>Sb>Fe; in weakly alkaline conditions, Sb>Mn>As>Zn>Fe; however, when the medium is acidified, the series changes to Cd>Mn>Pb>Cu>Zn>Sb>Ni>Fe>As; under acidic conditions Cd>Cu>Zn>Pb>Mn>Fe>Se>Mo>Sb>As>Ni. The mineral composition of the tailings was investigated, which will allow to determine the sources of toxic elements and to understand the processes of secondary mineral formation in technogenic objects. Arsenopyrite and pyrite predominate in the heavy fraction of the Komsomolsk tailings impoundment, arsenopyrite grains are often corroded, Sb contained in Sb oxide and Sb sulfide. The pyrite and barite are determined in the solid matter of the Karabash Mine Site and chalcopyrite, sphalerite, tennantite Cu_3AsS_3 , and tetrahedrite $(Cu,Fe)_{12}Sb_4S_{13}$ are determined in the form of inclusions in grains of pyrite.

1. Introduction

Among the natural and man-made structures formed under the influence of the mining and metallurgical industry, a special place is occupied by tailings dumps. Wastes stored in the dumps contain toxic elements (As, Sb, Fe, Pb, Cd, Cu, Zn, Ni, Co, etc.), which are actively carried by infiltrating precipitation into surface and groundwater, creating technogenic geochemical anomalies. In the study of technogenic systems, special attention is paid to the effect of mine drainage to the environment [1,2], the establishment of regularities and forms of migration of elements in drainage [3]. To date, a large quantity of data has been accumulated on the content of heavy metals in drainage



solutions and river bottom sediments, however, in most cases, only the total concentration of metals is given. In this case, the distribution of elements between chemical forms undoubtedly carries more important information than its total content since different chemical forms of the same element may have different toxicity. During the interaction in the "solution-solid" system as a result of complexation, adsorption, coagulation, changes in oxidation-reduction (Eh) and acid-alkaline (pH) conditions, the chemical forms of elements are transformed. To investigate the forms of occurrence and behaviour of chemical elements in the "solution-solid" system, laboratory experiments are conducted on the leaching of waste material, field experiments, and thermodynamic modelling using data on the composition of real and model solutions [4]. The most commonly used method for evaluating the forms of occurrence of toxic elements in a solid is the method of sequential chemical extraction [5]. In addition to increasing the mobility of metals, anionic elements can concentrate them, forming insoluble compounds, thereby minimizing their harmful impact on the environment.

In this respect, the main aim of this report is the comparative estimation of the mobility of anionic elements (As, Sb, S, N, Cl, F) and their role in migration, precipitation and concentration of heavy metals in depending on changes in the physicochemical parameters of the medium and on the mineral composition of the substance.

2. Materials and methods

For investigation the sulphide-containing mine tailings with a varying amount of sulfide and arsenide minerals from three distinct tailings dumps situated in Russia was chosen: Karabash Mine Site (KMS), South Ural; Komsomolsk Tailings Impoundment (KTI), Kemerovo region; Khovu-Aksy Mine Site (KAMS), Tuva Republic.

The tailing dump of Karabash Mine Site was formed from 1934 to 1952 as a result of storage of waste from flotation enrichment of sulphide ores. Wastes consist of pyrite (up to 25% by weight), silicate phases (quartz, mica, fragments of rocks, 38-42% by weight), chalcopyrite, sphalerite are also presented.

Komsomolsk tailings impoundment is a natural basin, which since 1964 was filled with cyanidation wastes of gold-arsenopyrite-quartz ores and wastes from the extraction of gold from antimony cakes. The solid waste material consists mainly of the vein (quartz, feldspar, calcite) and sulfide minerals: pyrite, sphalerite, galena, pyrrhotite and arsenopyrite (the first %) [6].

Khovu-Aksy mine site contains wastes of hydrometallurgical processing of arsenide nickel-cobalt ores from the Tuvakobalt plant, which operated from 1970 to 1991. Dumps consist of a vein mass containing unoxidized arsenides and sulphides [7].

The elemental composition of the chosen for experiments materials was conducted by applying the X-ray fluorescence analysis method using synchrotron radiation (SR-XRF) at the VEPP-3 station at the Institute of Nuclear Physics SB RAS, Novosibirsk. Detailed chemical and mineral analyses of the tailings were conducted using microscopic investigations. The presence of impurities in the major minerals was analyzed by high-resolution electron microscopy (microscope SEM LEO 1430 VP) and energy dispersive analysis (EDS (Oxford) spectrometer).

Water-soluble metal species were extracted first from a 10 g sample of the tailings in distilled water (100 ml). After the separation of the water-soluble species of the elements the sample was dried and an exchange form was extracted by the ammonium acetate buffer at pH = 4.7. A sample weighing 8 g (charge after the extraction of water soluble species) was poured with 40 ml of buffer solution. The samples were shaken and mixed for one day.

Aliquots of the obtained solutions after the aqueous leaching and weak acid leaching were separated by filtering through 0.45 µm membrane filters.

Next, the solutions were divided into two parts. One portion of the solution was used to determine the trace element concentrations and the other portion was used to determine the pH, Eh, S value and major ion concentrations (water leaching solution).

The trace element concentrations in all of the obtained water samples were measured using ICP-MS. The solution pH and Eh were measured during the experiment using an EKSPERT 001. Electrical conductivity was measured with a Cond 315i/SET device (WTW, Germany). The major anion concentrations were determined using photometric (SO_4^{2-}) and titrimetric methods (HCO_3^-), and the Cl^- , F^- , NO_2^- concentrations were measured using calibrated meters.

The modelling tests have been done using standard tools as WATEQ4F [8]. Aqueous speciation of chemical elements and Saturation Index of key minerals in the experimental solutions were calculated according to the pH and Eh parameter and solution composition.

3. Results and discussions

The water leaching solutions were isolated in three regions according to pH-Eh values (Figure 1). Solutions KAMS lie in the alkaline region with a pH of 8.15 to 9.16. Solutions KTI lie in the slightly alkaline region with a pH of 7.59 to 7.98, but three samples from the upper oxidized horizon: KTI-1, KTI-2, KTI-3, fell into the acidic region, and water leaching solutions of KMS lie in the acidic region with a pH of 2.61 to 2.89.

In water leaching solutions a wide spectrum of elements was determined. In Table 1 the contents of the main elements under the study are shown. Among all the samples the following elements have the highest concentration: Fe, Mg, Ca. The content of aluminium is high in acid solutions of KMS, and varies from 37 mg/l (sample № KMS-3) to 109 mg/l (sample № KMS-4) and in three samples KTI: from 12 mg/l (sample № KTI-3) to 31 mg/l (sample № KTI-1). Mn forms the largest part (% of the total content in the rock) of water-soluble forms up to 0.0n% in KTI solutions, in the same samples the content of water-soluble forms of Fe is up to 0.00n%. The maximum percent of water-soluble forms of iron are found in the most oxidized samples: KMS-1, KTI-1, 2, 3, 4, 5 and KAMS-6, 8.

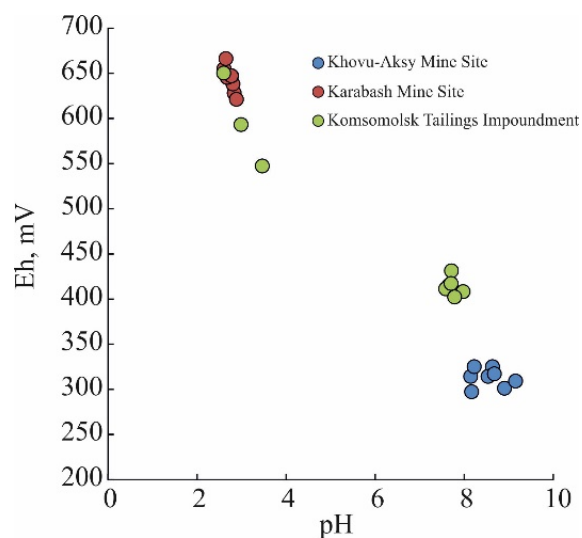


Figure 1. Physicochemical parameters of the water leaching solutions.

For the water-soluble forms of trace elements, the following patterns were revealed. The maximum amount of water-soluble form of zinc was found in the water leaching solutions of KTI and KAMS, up to 0.0n%, but not in the solutions of KMS despite the high content of Zn in the tailings of KMS. The number of mobile forms of copper is lower: the maximum percentage are 0.00n% (solutions of KAMS). Copper was determined in the water leaching solutions from KTI substance (alkaline solutions) and KMS (acidic solutions), due to high copper contents in the tailings. Cadmium, Pb, and Ni was defined in the water leaching solutions of KMS.

In the water leaching solutions of all three tailings dumps, Sb and As were detected. The largest shares of their mobile forms was determined in the solutions of KAMS and KTI. The concentrations

of metals (Pb, Ni, Cd) in solutions increase with decreasing pH. For Cu and Zn, there is no strict dependence on the acidity-alkalinity of the medium. Arsenic and antimony are more mobile in solution with a pH from 7 to 9.

Table 1. Content of main chemical elements under the study in water leaching solutions

№	Al	Ca	Mn	Fe	Cu	Zn	As	Sb
KAMS -10	0.0055	2.5	bdl	0.015	0.0037	0.0003	1.9	0.074
KAMS -1	0.032	8.4	0.0033	0.029	0.0019	0.00023	5.2	0.056
KAMS -4	0.0095	3.1	0.0016	0.02	0.0043	0.00017	3	0.065
KAMS -6	0.0077	3.5	0.0018	0.016	0.003	0.00019	2.9	0.063
KAMS -8	0.023	7.6	0.0015	0.036	0.004	0.00035	5.6	0.06
KAMS -3	0.0022	3.7	bdl	0.018	0.0056	0.0005	0.91	0.939
KAMS -2	0.081	9.8	0.0062	0.075	0.012	0.0012	3.5	0.057
KAMS -5	0.001	2.6	bdl	0.01	0.0091	0.00028	0.34	0.33
KMS -1	68	66	1.5	340	63	47	0.098	0.0015
KMS -2	110	84	2.43	230	87	22	0.019	0.00004
KMS -3	37	38	1.	210	33	8.8	0.25	0.00024
KMS -4	110	140	1.6	1200	11	8.1	1.8	0.00013
KMS -5	38	130	0.67	490	2.1	4.03	1.1	0.0047
KMS -6	72	203	1.2	690	2.3	4.04	0.49	0.00003
KMS -7	65	120	1.1	520	2	2.2	0.34	5.8×10^{-5}
KMS -8	71	150	0.92	660	3	4	0.32	bdl
KTI-1	31	130	3.1	170	1.4	15	9.1	bdl
KTI-2	17	190	1.4	230	0.67	6.2	13	bdl
KTI -3	12	92	7.3	39	1.2	31	0.82	bdl
KTI -4	bdl	84	0.11	0.021	bdl	0.0078	0.075	bdl
KTI -5	bdl	19	0.071	0.074	bdl	0.0061	bdl	bdl
KTI -6	bdl	16	0.018	0.0062	bdl	0.005	bdl	0.57
KTI -7	bdl	42	0.22	0.0041	bdl	0.00986	bdl	0.51
KTI -8	bdl	41	0.087	0.003	bdl	0.0065	bdl	0.21
KTI -9	0.056	21	0.076	0.03	bdl	0.0079	bdl	3.3

bdl – below detection limit.

The water leaching solutions are composed of the following dissolved species of the chemical elements (Figure 2).

In slightly alkaline solutions of KTI and alkaline solutions of KAMS, for Al and Fe hydroxo complexes are the predominant species with the general formula $\text{Me}(\text{OH})_3$, $\text{Me}(\text{OH})_4^-$. For Fe, the species $\text{Me}(\text{OH})_3$ predominates, for Al - $\text{Me}(\text{OH})_4^-$ (in KAMS solutions) and $\text{Me}(\text{OH})_3$ (in KTI solutions). The species of manganese are different, so in the solutions of KTI, the following sequence of distribution of species: $\text{MnCO}_{3\text{aq}} > \text{Mn}^{2+} > \text{MnSO}_{4\text{aq}}$, and for KAMS solutions: $\text{Mn}^{2+} > \text{MnCO}_{3\text{aq}} > \text{MnSO}_{4\text{aq}}$.

In acidic solutions of KTI for Mn and Fe, the main species are hydrated cations up to 65%, followed by sulphate complexes accounting for 36%. For Al, sulphate complexes predominate, and the share of hydrated ions is up to 20%.

Sulphate complexes (up to 80%) are the predominant in solutions of KMS for Al and Fe, followed by hydrated ions (up to 12%); for Al, fluoride complexes of AlF^{2+} (up to 4%) is determined. Hydrated ions prevail for Mn, the share of sulphate complexes is up to 43% of the total.

In the solutions with an acidic pH, the main species of metals Pb, Cu, Cd, Zn, Ni are hydrated ions and sulphate complexes. For solutions of KMS, sulphate complexes predominate, with the exception of Ni, for which hydrated ions predominate. Hydrated ions are the predominant complexes for solutions of KTI.

For solutions with an alkaline pH, $\text{Me}(\text{CO}_3)_2^{2-}$ bicarbonate complexes are the main ones for Zn and Ni. For Cu, the hydroxo complexes $\text{Cu}(\text{OH})_2$ are the predominate species over the hydrocarbonate $\text{CuCO}_{3\text{aq}}$. For cadmium, a large variety of species has been determined, chloride complexes CdCl^+ up to 3% have been determined, but hydrated ions are the predominant species.

In the solutions of KTI with a slightly alkaline pH, the predominant species of Zn is hydrated ions up to 66%, hydrocarbonate complexes up to 20%, sulphate and hydroxo complexes consist of 10% and 4%, respectively.

The weak acid extracts showed much higher element concentration than the water extracts (Figure 3). The fractions of exchange forms transported into solutions under weakly acid conditions were highest for Mn - up to 29% (sample № KTI-9), Cu - up to 19% (sample № KTI-7), Zn - up to 17% (sample № KAMS-5), Pb - up to 22% (sample № KTI-10), and Cd - up to 43% (sample № KTI-4).

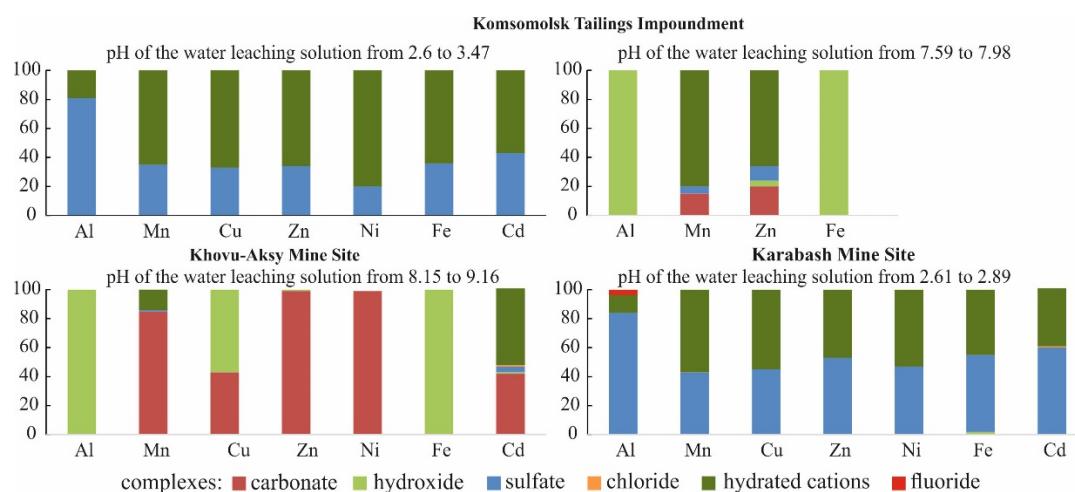


Figure 2. The distribution of main dissolved species of metals in the water leaching solutions

Attention is drawn to the very high As content in weakly acid extracts from KAMS (samples № KAMS-10 (48% -2.2 g/l) and KAMS-6 (62% to 5.6 g/l), which indicates the mobility As in both acidic and alkaline conditions.

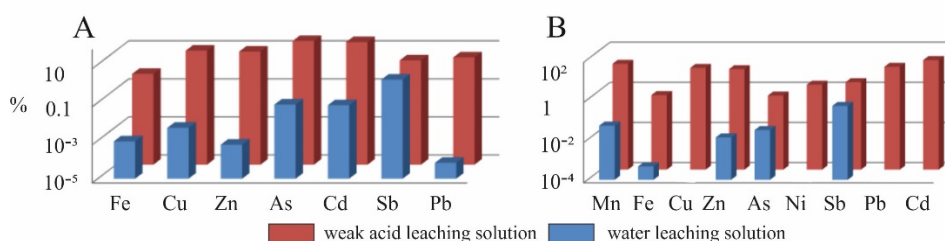


Figure 3. Fraction from the total amount of water soluble and exchangeable species: (A) Khovu-Aksy Mine Site solutions; (B) Komsomolsk Tailings Impoundment

To study the mineral composition, structure, and the presence of impurities in the composition of minerals, the grains from the heavy fraction were studied in detail using a binocular and electron scanning microscope. Arsenopyrite and pyrite predominate in the heavy fraction of the KTI, arsenopyrite grains are often corroded (Figure 4 C). Grains of Sb_2O_4 were revealed (Figure 4 B). The pyrite and barite are determined in the solid matter of the Karabash Mine Site and chalcopyrite, sphalerite, tennantite Cu_3AsS_3 , and tetrahedrite $(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$ are determined in the form of inclusions in grains of pyrite (Figure 5).

On the basis of the obtained mineral composition, it is possible to assume the following mechanisms of the appearance of metals in aqueous solutions in the interaction of tailings material with water streams:

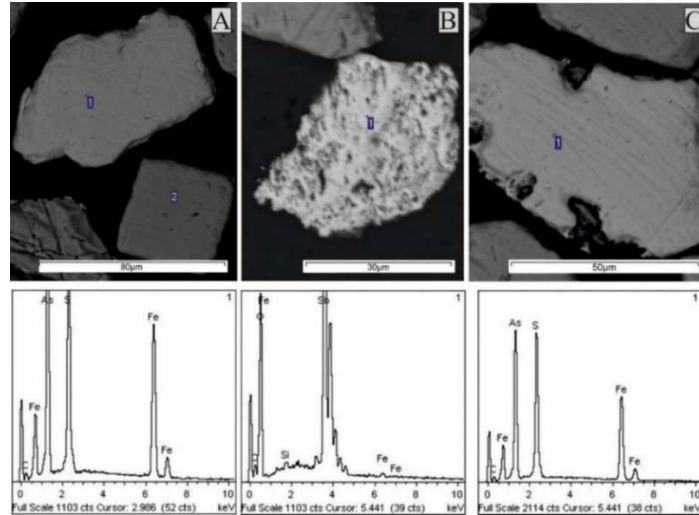


Figure 4. SEM images of minerals detected in the tailings of Komsomolsk Tailings Impoundment. (A) arsenopyrite (1) and pyrite (2); (B) Sb_2O_4 mineral phase; (C) corroded grain of arsenopyrite

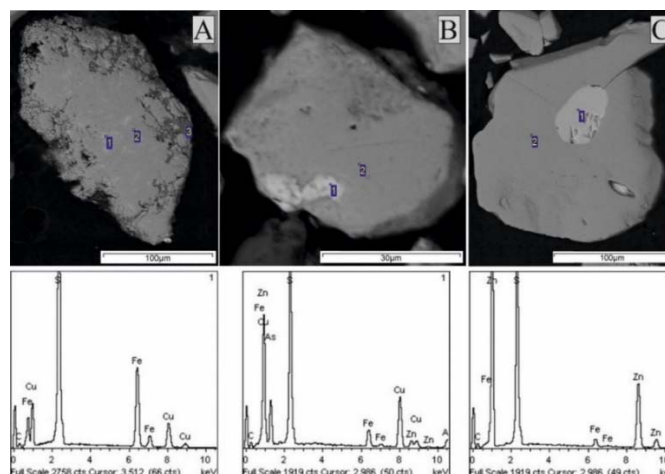
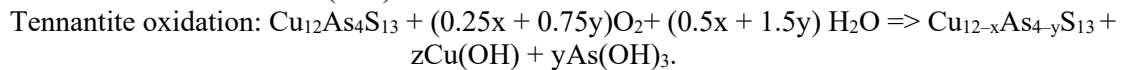
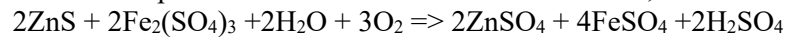
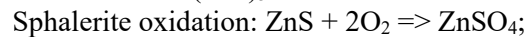
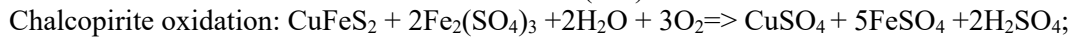
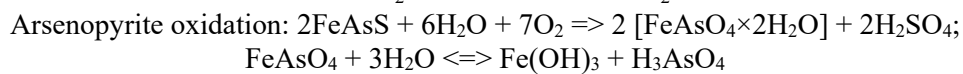
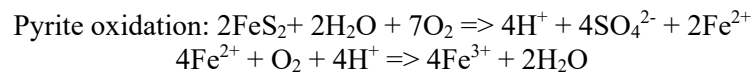


Figure 5. SEM images of minerals detected in the tailings of Karabash Mine Site. (A) grain of pyrite (2) with inclusions of chalcopyrite (1); (B) grain of pyrite (2) with inclusions of tennantite (1); (C) pyrite (2) with inclusions ZnS (1)

4. Conclusions

Differences in the mineral composition of the wastes, ore processing and the condition of waste storage for the three tailings dumps significantly influence the transformation of the substance - the oxidation of the sulfide component, the transition of metals into solutions, their migration with water streams. These were reflected in the composition and physicochemical parameters of the obtained solutions: from acidic pH = 2.3 (Karabash Mine Site) to slightly alkaline pH 7.5 (Komsomolsk tailings impoundment) and even more alkaline pH = 8.9 (Khovu-Aksy mine site). This enables to trace the change in the role of anionic elements in the mobility of metals, depending on the physicochemical parameters of the medium and the mineral composition of the waste materials. The results of calculating forms of chemical elements made it possible to construct series of mobility of metals and metalloids in solutions with different physicochemical parameters. In the alkaline conditions, Sb>As>Cd>Cu>Zn>Fe>Pb, when the medium is acidified, the series changes, As>Cd>Cu>Zn>Pb>Sb>Fe; in weakly alkaline conditions, Sb>Mn>As>Zn>Fe; however, when the medium is acidified, the series changes to Cd>Mn>Pb>Cu>Zn>Sb>Ni>Fe>As; under acidic conditions Cd>Cu>Zn>Pb>Mn>Fe>Se>Mo>Sb>As>Ni. The mineral composition of the tailings was investigated, which will allow to determine the sources of toxic elements. Arsenopyrite and pyrite predominate in the heavy fraction of the Komsomolsk tailings impoundment, arsenopyrite grains are often corroded, Sb contained in Sb oxide and Sb sulfide. The pyrite and barite are determined in the solid matter of the Karabash Mine Site and chalcopyrite, sphalerite, tennantite Cu_3AsS_3 , and tetrahedrite $(Cu,Fe)_{12}Sb_4S_{13}$ are determined in the form of inclusions in grains of pyrite.

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