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Factors controlling metal content of mining waters

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ABSTRACT: High contents of heavy metals (Pb, Zn, Cu, Cd, Mn, Fe) and aluminum in the waters connected with mining and associated deposits (dumps, tailings) reduce water quality and degrade the community structure in streams. Mobility of the metals is determined by water acidity. An investigation of mines of the southern part of Russian Far East has determined that the major factors affecting heavy metal load of waters are: the quantity of acid-forming sulphide minerals (pyrite, pyrrhotite, etc.) in exhausted ores; the composition of ore-containing rocks and their neutralizing capacity; degree oxidation of the minerals; the manner of ore excavation; the peculiarities of ore dressing; the age of anthropogenic ore-rock deposits; water quality of drainage waters; and the process of water auto-cleaning in streams.

1 INTRODUCTION

Ore bodies that are subjected to action of supergenic factors always are sources of metals for natural waters. Mining of ore leads to "geochemical explosion:" heavy metal concentrations rise drastically in drainage waters. There are three principal types of sources of heavy metals: (1) waste water from a mine, adit, quarry; (2) drainage of dumps with sulphide minerals; (3) drainage of analogous tailings. The processing of ore accelerates oxidation processes of sulphides and formation of acid waters. The acid conditions are favorable for dissolution of heavy metals from ore minerals and aluminum from ore-containing rocks. The ecological danger of modern mining is connected with high quantity of heavy metals, arsenic aluminum, etc., that come in natural streams. These factors degrade water quality and destroy water biocenosis. The aim of this work was to estimate heavy metal input to natural drainage systems from different mining deposits and factors controlling the input in the southern part of Russian Far East.

2 OBJECTS AND METHODS

The principal types of inspected ore deposits are: (1) skarn-polymetallic Pb-Zn ores; (2) polymetallic veins in silicate sedimentary rocks; (3) quartz-cassiterite veins; (4) scheelite-sulphidic ores. Waters from pit and/or adit, drainage from under dumps, water from tailing pools and drainage from under tailings, as well small watercourses accepting polluted water were sampled. In the cases of many mines in one basin integrating river was sampled. All samples were filtered through 0.45 micron filters. Dissolved and suspended substances were analysed separately. Most part of liquid samples were concentrated with complex-forming reagents. Suspended matter was decomposed by the mixture of acids. Heavy metals were determined by flame AA-spectrometry, aluminum and arsenic-colorimetrically. In all samples pH and main cations and anions were determined.

3 RESULTS AND DISCUSSION

In this report generalized results from more than 270 different water samples are communicated. In addition to absolute concentrations the relative index was used - Clarke concentration (the ratio of concentration in sample and average concentration in the background waters of region, sampled from springs and small streams). Average concentration of elements from 42 samples are presented in the first line of Table 1.

The results demonstrate that the degree of acidity does not necessarily determine the heavy metal load of waters which may be determined by other factors.

The main factor is the quantity of sulphide minerals in ore and ore-containing rocks (pyrite, pyrrhotite, arsenophytite, etc.) the oxidation of

Table 1. Chemical analyses of mining waters (mg/l).

No	pH	Cu	Pb	Cd	Zn	Fe	Mn	Al	As
1	7.35	1.7	0.7	0.05	9	10	3.5	<10*	<2*
2	7.40	26	2.8	8.2	644	12	2300	22	5
3	3.15	5210	190	502	25440	131850	13910	3170	200
4	5.16	2	1.3	0.2	68	16	152	11	5
5	3.48	140	318	56	24470	101940	20890	4300	18
6	4.78	1180	40	558	36490	73	24000	2260	<2
7	7.16	58	2	36	4460	44	4010	32	2
8	6.85	51	4	76	28740	69	12040	14	<2
9	3.30	8680	265	1470	350520	13210	40810	21470	4
10	7.24	1	50	0.6	120	53	1640	<10	2
11	7.96	19	6	1.4	26	3170	300	410	158
12	4.26	172	9	1.1	27	66300	2400	1280	10
13	6.95	66	10	12	1500	9	3570	95	8
14	6.24	257	2	12	1650	15	2150	266	<2
15	3.15	5210	190	502	25440	131850	13920	-	200
16	3.22	4680	105	362	22800	81920	13750	-	44

* - low analytical limit

Sample objects: 1 - background waters of low-order stream; 2 - mine waste of a quartz-cassiterite deposit; 3 - mine waste water of cassiterite-sulphidic deposit; 4 - drainage from under a tailing of scarn-polymetallic ores; 5 - drainage from under a tailing of Pb-Zn ores in silicate rocks; 6 - drainage from an adit of cassiterite-sulphidic deposit on the altitude of 1060m; 7 - drainage of an adit of the same deposits on the altitude 714m; 8 - water from a quarry of polymetallic deposits; 9 - drainiage from under dumps of a same polymetallic deposits; 10 - drainage of a tailing having been filled only eight years; 11 - waste pulp after dressing scheelite-sulphidic ore; 12 - drainage of a tailing of the same deposit; 13 - mine waste waters at a quartz-cassitetite deposits; 14 - the same waters after a settling pool; 15 - red stream - waste waters from an adit of a cassiterite-sulphidic deposit; 16 - mouth part of the same red stream.

which leads to forming of sulphuric acid. The abundance of sulphide minerals determines the possibility and dimension of forming acidic sulphate waters. Quartz-cassiterite deposits without sulphides have associated different chemistry of water than polymetallic and cassiterite-sulphide deposits. Comparison of analysis line 2 and 3 of Table 1 demonstrates that in both cases all metals are in anomalous amounts, but in the second example the development of sulphur-acid processes gives rise of high metallic load of waters and particularly large output of FE(II), Zn, Mn, Al. At a neutral condition mine waters are slightly enriched with only Mn, Cd, Zn.

The second important factor is the composition of ore-bearing rocks. Sulphur-acid production actively develops in silicate rocks that are poor in basic elements, but the rocks enriched in carbonates inhibit the process. A dramatic contrast can be seen from comparison of chemistry of drainage waters of different tailings (line 4 and 5 of Table 1). In the first case tailings were waste of scarn-polymetallic ores enriched by calcite, wollastonite, hedenbergite. Basic cations of these minerals neutralise acidity and pH is not below values where heavy metals become highly mobile. In the second case the tailing was full of silicate material without neutralizing minerals and as a consequence drainage waters are metals-rich.

The extent of the oxidized ore zone has great importance for determining metallic loads of water. Prepared by preliminary oxidation of sulphides metals more actively go out in drainage waters. For example, samples from adit at the altitude 1060m above sea level, near the top of a mountain range have concentrations of metals 8-20 times larger than samples from adit at 715m (line 6 and 7). Fresh sulphides do not readily produce acid drainage waters and the latter have a moderately low metallic load. The threefold elements group (Mn, Cd, Zn) has the most mobility in both circumstances if it is considered in Clarke concentrations.

The next important factor is the method of ore extraction (by quarry or adit, pit). When ores are extracted by open-cut quarry many more sulphidized rocks are translocated to react with oxidation agents. The formed dumps are powerful contributors of sulphuric acid metals, particularly if ore minerals have been touched by weathering processes. Drainage waters from under dumps of polymetallic deposits in silicate rocks have Mg-Al-Zn or Mg-Zn-Ca composition of cations. Some heavy metals are the main cations of chemical composition (line 9 of Table 1). Water from quarry of the same deposits has much less metals (line 8).

The age of dumps and/or tailings has an important effect on the heavy metal load of drainage waters. The increase of residence time of dispersed mineralised rocks in supergenic conditions can increase the release of heavy metals. Comparison can be made of drainages from under tailings which started to be filled 45 years ago, but presently are not used, (line 5) to tailings of accumulated wastes of the same deposit during only the last 8 years (line 10 of Table) 1) demonstrates the possible importance of time-factor for forming acidic metal-rich flow. In the relatively fresh tails sulphate waters have been formed, but they have low concentrations of heavy metals. Fresh sulphide minerals should have lag-phase time for development of oxidation processes. Acidification of waters and dissolution of metals are indubitably in the future. Out put of metals may increase with time.

The peculiarities of ore dressing are an essential factor for chemistry of mining waters. As a rule, iron sulphides and arsenopyrite are not extracted in concentrates. Very often only cassiterite is extracted from tin-sulphide ores. By this means new powerful sources of acidity and heavy metals are built up. Their life-span is not predictable because the quantity of accumulated acid-forming sulphides, and dynamic of their oxidation is unknown.

In the concentration of scheelite-sulphide ores sodium silicate is used and the waste becomes alkaline. Under this condition arsenic has a high mobility (line 11 of Table 1). Oxidation of sulphides in tailing is responsible for acidification of pore waters, which become enriched with Fe, Mn, Al. In drainage waters Fe(II) may transform to Fe (III) and form iron hydroxides which may tie up the dominant part of dissolved arsenic (line 12).

Usually mine waste waters pass through the settling pool where the bulk of coarse suspended matter is sedimented. Dissolved metals are removed from water to only a small extent in pool. Sometimes concentrations slightly increase (line 13 and 11 of Table 1). It is possible that the rise is the consequence of dissolution of metals of suspended matter. Settling pools detain suspended matter only partially, but as to dissolved metals the pools are not effective.

Processes of self-purification of drainage waters are more effective. It is connected with transformation of dissolved species to suspended forms and sedimentation of the latter ones. At the first step after the waters underwent oxidation conditions iron hydroxides are released and red streams are formed. Other metals partly co-precipitate with Fe-hydroxides. For example, the mining red stream leaking from adit at cassiterite-sulphide deposit of length about 300m has different heavy metal loads in the beginning and near the mouth (line 15 and 16 of Table 1). Removal factors of elements are in % of initial content:

As > Pb > Fe > Cd > Zn > Cu > Mn
78 45 38 27 10 10 1.2

Iron-sediments are very effective for co-precipitation of arsenic from acid solution, but other elements are removed to only a small extent. Fe-sediments and cementation crusts in many cases are enriched in metals-Zn, Cu, Pb -(0.n wt%), although they extract a minor part of dissolved metals. As the acidity conditions change after confluence with natural neutral waters aluminum hydroxides fall out, but their adsorption capacity is low. Al-sediments contain metals one order of magnitude lower than Fe-sediments.

Sometimes on the bottom of red streams very enriched by metals sediments are accumulated. Example of chemistry of such sediments has been given in Table 2.

Table 2. Metal contents in suspended matter and sediments from mine waste waters of tin-sulphidic deposits (wt% per dry matter).

No	Cu	Pb	Cd	Zn	Fe	Mn
1	0.11	0.40	0.0014	0.37	34.2	0.037
2	0.41	0.28	0.0025	0.37	18.8	0.057
3	0.90	0.28	0.35	5.50	10.7	3.84
4	0.61	0.12	0.043	8.66	3.9	5.42

1,2 - suspended matter; 3,4 - sediments

Metal-rich colloids form in mine waste waters of tin-sulphide deposits. It can be seen that they are very enriched by Zn, Cd, Mn, but are poorer in Fe than suspended matter. The bottom material is not a simple accumulation of suspended particles. Active precipitation of metals from solution to sediment is observed. There are not physical-chemical reasons for sedimentation of Zn and Mn from acidic (pH 4.9 - 5.2) waters. One of the possible reasons for the enrichment is a micro-biological activity. But this aspect is not investigated.

4 CONCLUSION

All types of mining processes pollute natural waters. Ore deposits that are riched by acid-forming sulphides produce acidic water-flows with high contents of different heavy metals. Their concentration is 3-5 orders of magnitude larger than natural levels and not always diluted to background. Sulphide poor deposits produce near-neutral waters, their concentration of metals is lower, but often they have three metals in anomalous quantity - Zn, Cd, Mn. These elements are often not readily removed from water by natural mechanisms.

To prevent the negative influence of mine waters it is necessary to determine the potential reserve of acidity in excavating rock mass and compare it with the neutralising capacity of these rocks. Transformation of dissolved species of metals to suspended forms by neutralisation at the man-made geochemical barriers will free waters from a part of metal load. An investigation of microbiological methods for this purpose may be very interesting.