

Storage and processing of acid waste waters of mining enterprises

Alexei Plyusnin^{1,*}, Olga Smirnova¹, and Paul Robinson²

¹Geological Institute Siberian Branch Russian Academy of Sciences, Russia

²Southwest Research and Information Center, USA

Abstract. In the present work, the formation of the chemical composition of acid mine waters in the area of waste disposal of mining and processing of tungsten ores of Transbaikalia (Russia) is considered. It is shown that during long-term storage of processing waste in the pore space, acidic waters with a high content of rare-earth elements accumulate. During the recycling of waste in the washings, a change occurs in the ratio of light and heavy rare earth elements. When water is neutralized with limestone, solid phases of these elements are formed, which can be extracted.

1 Introduction

In the mining industry, after extracting valuable components almost all mass of rocks is concentrated for a long-term storage. Residual ore mineralization becomes accessible to the exposure of water, oxygen and other weathering agents. Oxidation of sulfides in the waste disposed areas of tungsten mines causes the formation of aggressive with respect to wastes acid underground and surface waters with high content of REE, which can extract under recycling.

We have studied waste of tungsten ores extracted from the Dzhida tungsten-molybdenum mine as well as that of extracted from the Bom-Gorkhon tungsten mine. A group of Dzhida deposits includes such ones as the Inkursk- and the Kholtoson- tungsten deposits and the Pervomaisk molybdenum one. Ore mineralization is associated with the Jurassic polyphase Gudzhir intrusion presented on the surface by numerous dikes of acidic composition as well as the Pervomaisk stock of granite-porphyrines. Kholtoson mining occurred by adits whereas that of Inkur- and Pervomaisk deposits by quarries. Ore processing in the Dzhida tungsten-molybdenum industrial complex took place using a flotation-gravity method. While the complex was working from 1938 to 1997, more than 40 million tons of mill waste was stored in the tailing pond.

Tungsten mineralization of the Bom-Gorkhon deposit is associated with quartz veins accompanied by the zone of greisenization [1]. Mining has been taking place since 1980 by a quarry and adits. Ore processing uses flotation-gravity technology producing wolframite and sulphide concentrates. There were several tailing ponds, built to store processed waste located in the valleys of the Zun-Tignya and Bom-Gorkhon rivulets. They store more than a million tons of waste processed and recycling is still going on. During the recycling of waste, a system of settling tanks is used, which differ in the duration of storage of wash water. Wastes in the valley of the Zun-Tignya rivulet are stored for more than 30 years. In the valley of the Bom-Gorkhon rivulet, mill tailings have been stored up to the present time.

2 Methods

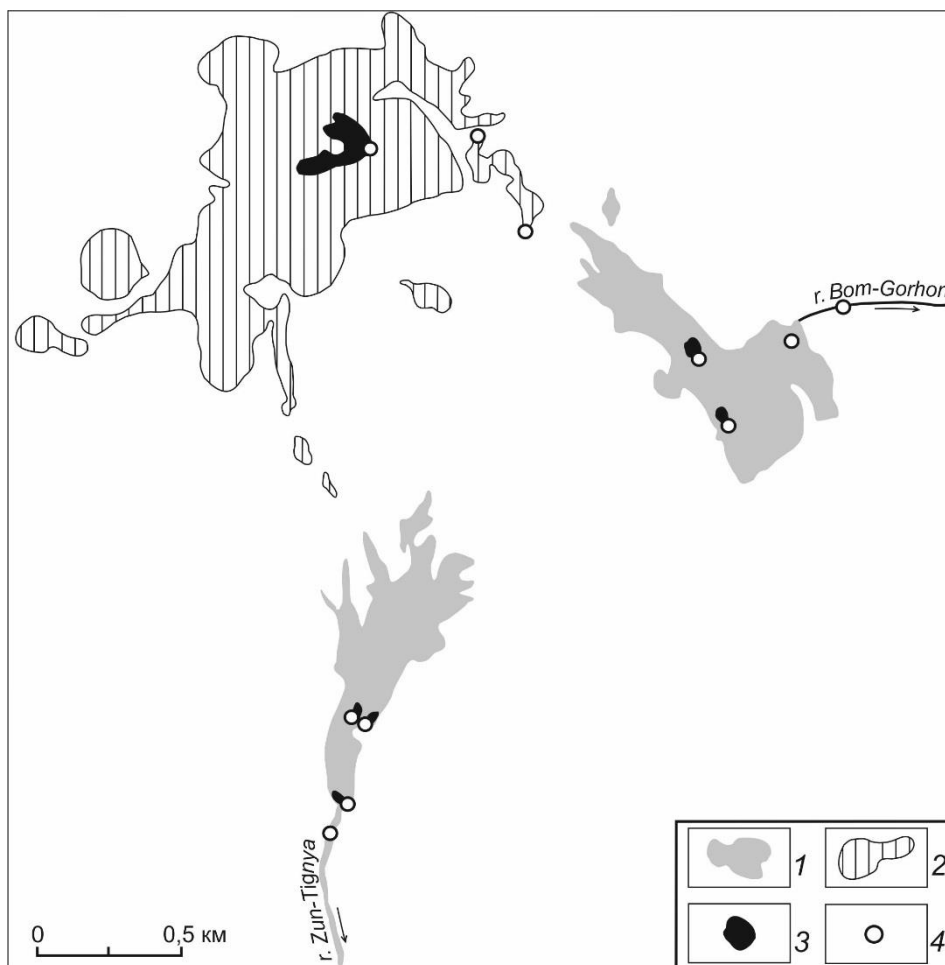
The research methods included field and laboratory experimental work. During field works, we investigated mill tailing dumps, ponds - storehouses of washed waters, mine waters poured out of adits and accumulated in quarries. Neutralization of mine waters occurred when reacted with limestone in the laboratory experiments. Composition of mineral neoplasms in samples of limestone after treatment with acidic solutions was determined with using x-ray phase analysis and the electronic scanning microscope LEO-1430VP having an energy dispersive spectrometer INCAEnergy 350. Trace element composition of waters was determined using a mass spectrometry method with inductively coupled plasma in ICP MS-XR and ELEMENT 2 devices (Finnigan MAT).

3 Results

On the Bom-Gorkhon deposit liquid waste are mine waters accumulated in mines due to filtration of atmospheric precipitation through the ore lodes and washed waters from the ore processing plant that is stored in sedimentation tanks (Fig. 1). We found, that there are significant differences in the chemical composition of mine waters and those of

* Corresponding author: plyusnin@ginst.ru

sedimentation tanks. Mineral waters are of slightly acidic reaction ($\text{pH} = 5.91\text{-}6.73$), their total mineralization equals 407-913 mg/L, the fluoride contents rise up to 11.1 mg/L, higher concentrations of microelements are found in zinc and manganese, the contents of which reach 16.3 and 5.7 mg/L, respectively. In sedimentation tanks, waters are much more



acidic ($\text{pH} = 2.96\text{-}3.5$), their total mineralization amounts 3.8 g/L. Very high heavy metal contents are found such as concentrations of zinc rise up to 74.5 mg/L, contents of manganese total 53.6 mg/L and those of iron amount 23.9 mg/L.

Fig. 1. Scheme of placing the natural-technogenic system (PTS) of the Bom-Gorkhon field. Legend: 1- sites of mill waste placing of the Bom-Gorkhon mining plant; 2 - rock waste; 3 - technogenic water reservoirs; 4 - water sampling points.

Concentrations of lanthanides in the mine waters are relatively low the total contents equal only 24 $\mu\text{g/L}$. Much higher contents are in sedimentation tanks. The amount of rare earths increases with increasing the time since sedimentation tanks have existed. The total contents of lanthanides are equal to 77 $\mu\text{g/L}$ at the Bom-Gorkhon deposit in the basin of the Bom-Gorkhon rivulet and their number in the valley of the Zun-Tignya rivulet already amounts 467 $\mu\text{g/L}$ (Fig.2).

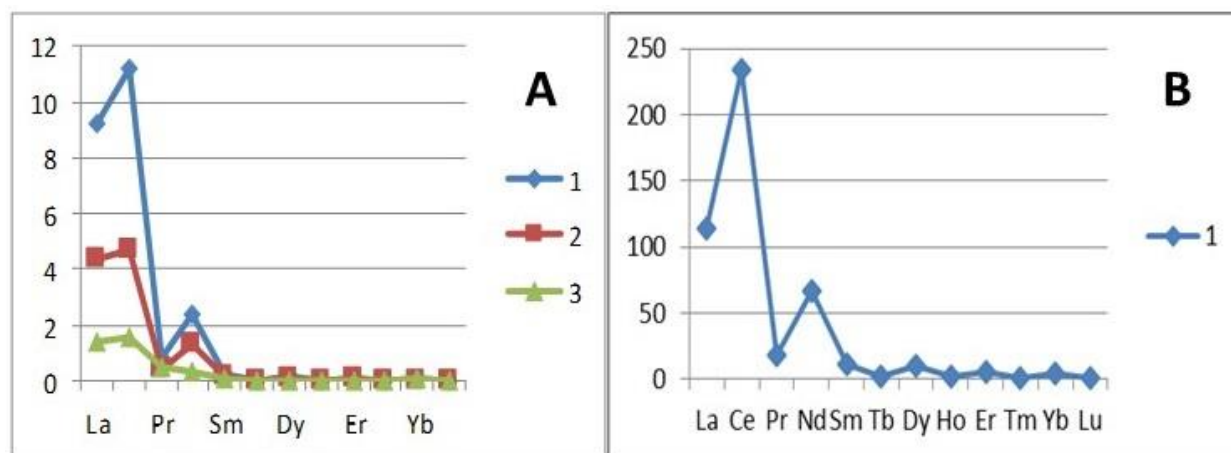


Fig. 2. Contents of lanthanides in the surface waters of the Bom-Gorkhon natural-technogenic system, ppb. A: 1- sedimentation tanks in the Bom-Gorkhon basin, 2 - mine waters, 3 - background water basin. B: 1 - sedimentation tanks in the basin of the Zun-Tignya rivulet.

The sand mass in tailings exists in a wet condition, since sands are not isolated from atmospheric precipitation. Moisture coming into the thickness of sand moves along a complex trajectory, since the thickness of sand consists of layers that are different in granulometric composition. As sands were long-term stored, there was an acidic medium found in pore waters of tailing ponds. The solution accumulated products of sulfides and rock decomposition. Total mineralization of solutions reaches 3.5 g/L in the water sand extraction from the Dzhida tailing pond, the sulfate-ion contents amount 2.1 g/L, iron contents equal 160 mg/L, those of zinc count 11 mg/L, respectively. The sum of rare earth elements in the waters investigated totals milligram values. There are differences in the ratio of light and heavy rare earth elements. There is an increase in the proportion of yttrium and heavy rare earth elements, especially in dysprosium, erbium and ytterbium for pore waters of processed tailings in the Dzhida Mining and Processing Plant. There is an increased proportion of light rare earth elements such as those of cerium, praseodymium, neodymium and samarium in pore waters of the tailing pond in the Bom-Gorkhon mining plant. The contents of europium appear to be lower in the pore waters of both tailing dumps.

In laboratory experiments found that the interaction of acidic solutions with the limestone, a solid phase appears consisting of amorphous and crystalline neoplasms located on the surface of limestone grains and in the intergranular space. Sulfates are dominant among them. The process forms a large amount of gypsum. This mineral precipitates on the limestone surface and covers it with a continuous layer. Similarly, fluorite crystallizes and forms flakes, located on the calcite surface. The formation of these compounds starts in the acidic medium and continues throughout the entire time of interaction of water with limestone. As pH increases, iron precipitates from the solution in the form of sulfates and carbonates, aluminum precipitates in the form of aluminous fluorides and silicates. These neoplasms contain ore elements and rare earths in their compositions. X-ray diffraction analysis used determined that those neoplasms included such minerals as ferrohalloysite, aravaipate, chukanovite, fougurite, lanthanite (Nd). Using an electron microscope, we detected iron hydroxides containing chromium, aluminum, dysprosium and praseodymium in their compositions.

4 Discussion

The tungsten mineralization of Transbaikalia is associated with a widespread of granitoid magmatism in this area [2]. Deposits belong to the structural type of mineralized domes [3]. Mineralization occurs in the dome-shaped protrusions on the apical surface of granite massifs located under poorly permeable horn fels of the intrusive frame. The formation of mineralization is associated with the accumulation of volatile components in the favorable parts of intrusive massifs. There is mineralization of greisen and vein types in the apical part of intrusions. Greisen mineralization occurs in the acidic environment. It is associated with carbon dioxide fluxes. Quartz vein mineralization appears from alkaline solutions [4]. It is stated, that hydrothermal solutions that caused the formation of tungsten mineralization feature high concentrations of rare earth elements. The correlation between light and heavy lanthanides changed during the hydrothermal process. By greisenization of granites, heavy lanthanides dominated in fluids and by the formation of veins light ones were dominant [5].

When storing waste from extracted and processed tungsten ore depositions, chemical elements originally been in ores and in ore-bearing rocks appear to be involved in the water migration. Rare earth elements accumulate in the acidic solutions. The degree of concentration of rare earths in solution depends mainly on their initial content in rocks. The initial amount of rare earth elements in rocks plays a fundamental role in their accumulation in the solution. When mining Dzhida deposits, they extracted ores not only from quartz veins, but also from greisenized rocks. Bom-Gorkhon deposit mines mainly quartz veins. Therefore, we observe a different spectrum of distributing rare earths - in the pore waters of mill tailing dumps from the Dzhida- and Bom-Gorkhon ore-dressing plants. Heavy rare earth elements enrich

pore waters in the Dzhida tailing pond and light rare earths enrich them in the Bom-Gorkhon ore-dressing plant. Heavy rare earth elements mostly accumulate in the solution by a long-term storage. The Dzhida tailing dump has a longer history of existence than that of the Bom-Gorkhon tailing pond. Therefore, under the influence of acidic solutions, heavier rare earth elements leached from the host rock and accumulated in the solution.

5 Areas of Application and Consequences

Waste from mining will be stored for all the future time. It is impossible to isolate it completely from the environment and hold geochemical processes launched by us when extracting rocks from the interior of the Earth. However, we can and must start a sewage treatment mechanism, which is going on without our participation.

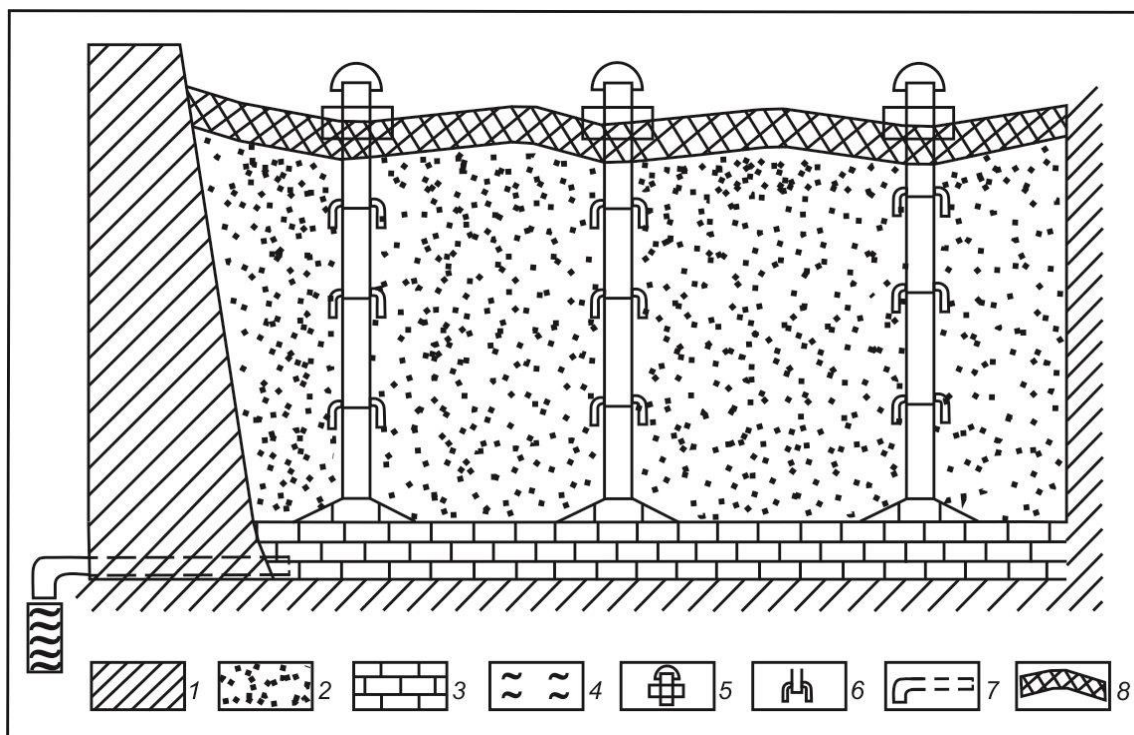


Fig. 3. Tailing pond cut. Legend: 1 - dam; 2 - technogenic sands; 3- crumb limestone; 4 - sedimentation pond; 5 - head of a drainage well with protective rings; 6 - link of the drainage well; 7- pipeline connecting the lime layer of the tailing dump with the settler; 8 - wall dividing a tailing pond into sections [6].

A key object in the system of safe storing mine waste can become a tailing pond where not only processed tailings but also mines and sewage from mining enterprises are collected (Fig. 3). The tailing pond is equipped with physical and chemical protection systems. The stored waste is not completely isolated from the environment, in certain places. There is a controlled discharge of treated waters into the receiving watercourses and reservoirs carried out by a proposed scheme. The amount of neutralizing reagents calculate basing on concentrations of under-extracted ore mineralization.

References

1. Sizykh V. *Deposits of Transbaikalia*. **1**, 1, 134138 (1995)
2. Rafe F.G. *The ore-forming potential of granites and the conditions for its realization*. M.; Nauka181 (1990)
3. Rundquist D.V., Denisenko V.K., Pavlova I.G. *Greisens and greisen deposits of the world*. - L .; Nauka, 328 (1971)
4. Matveeva SS, Spasennykh MYu, Sushevskaya TM, Bychkov AYu, Ignat'ev AV. *Geolog. of ore depos.*, **44**. 2, 111-131(2002)
5. Popova YA, Matveeva SS, Bychkov AY, Ternopolskaya ME, Bychkova YV. *Geoch. Intern.*, **55**, 2, 211-217 (2017)
6. Plyusnin A.M., Peryazeva E.G., Dabaeva V.V., Zhambalova D.I. *Tailings storage for mining enterprises waste. Patent for invention*, 2633051, Russia (2017)