Mine Waters of the Mining Enterprises of the Murmansk Region: Main Pollutants, Perspective Treatment Technologies

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Abstract

One of the most important environmental tasks in the activities of the mining industry is wastewater cleaning. The main difficulty lies in large volumes of water. This leads to high economic and material costs in the implementation of various cleaning schemes. The priority contaminants of mine waters of two mining enterprises of the Murmansk region were analyzed: JSC Kola MMC and LLC Lovozersky GOK. Thus, for the water of Severnyi Mine, JSC Kola MMC, the main pollutants are sulfate (720 mg/L), nitrogen compounds (70 mg/L), nickel (0,35 mg/L), copper ions (0,007 mg/L), and suspended solids (25 mg/L). The priority pollutant in the mine water at Karnasurt Mine, LLC Lovozersky GOK is fluoride (15 mg/L). For each enterprise, strategies and perspective technologies for mine waters treatment were considered.

Keywords: mine waters pollution, priority contaminants of mine waters, technologies for mine waters treatment

Introduction

Murmansk Region is home to of the largest mining and minerals projects in the Russian Arctic and in the Russian Federation as a whole. The region supports a major share of the national economy demand for phosphate ore, zirconium, vermiculite, niobium, tantalum, rare earth metals. Nickel, copper, cobalt, iron ore, and nepheline minerals are extracted in Murmansk Region (Masloboev et al., 2016).

One of the greatest environmental challenges in the mining industry is mine water treatment. The main challenge is the large mine water volume resulting in the high costs involved in the implementation of treatment processes. Besides, mine water is a complex multicomponent system containing – in addition to solutes – colloids, suspended inorganic and organic solids.

For instance, JSC Apatit, a major apatite-nepheline ore mining and concentration project, operates two open-pit and two underground mines and two processing plants. Wastewater (mine and pit water, storm runoff, and industrial wastewater) is discharged from seven outlets into five fishery water bodies. Common pollutants include suspended solids, petroleum products, nitrogen compounds, aluminum, molybdenum, fluorine.

JSC Kovdorsky GOK extracts and concentrates complex ores into three salable concentrates – iron, apatite, and baddeleyite. Key pollutants in the site's wastewater are manganese, molybdenum, strontium, sulfate, phosphates.

The wastewater produced by JSC Olkon, the operator of six open-pit and one underground ferruginous quartzite mines and a concentrator plant, exceeds the maximum permissible concentrations of nitrogen compounds – nitrates, nitrites, and ammonium ions.

In this paper, we use two major mining operations in Murmansk Region – JSC Kola MMC and LLC Lovozersky GOK – as case studies to study mine water removal and treatment solutions and key pollutants. For each operation, we examine their respective wastewater strategies and prospective treatment processes.

Description of mining operations and wastewater

Severnyi Mine, JSC Kola MMC

Severnyi Mine extracts sulfide copper-nickel ore, which is supplied to Kola MMC's smelter and concentrator. Its central industrial processes are drilling and blasting, ore extraction and overburden removal, ore handling and transportation.

Mine water is handled at Severnyi Mine by two pumping stations at the horizons -33 m and -440 m. The pumping station at the horizon -33 m is fed from the pumps evacuating mine water from the ventilation rockshaft's and cage shaft's different horizons. The pumping station at -440 m is fed from the pumps evacuating mine water from the central ventilation shaft's and western ventilation shaft's horizons. The daily mine water flow is nearly 28,000 m^3. Water discharge flows vary considerably over the years. Fluctuations are up to 12% of the average and are related to the inflows for process needs.

Mine water treatment plant with a capacity of 500 m^3/h is composed of a mine water receiver tank, a mixer, primary treatment facilities – two interconnected settling ponds, high-rate filters, a chemicals feed plant, a pumping station for feeding wash water to the tower, a chlorinator plant, and a wash water tank. Wash water from the filters and sediment from the clarifiers is discharged into the concentrator's tailings sump.

Environmental monitoring data collected by Kola MMC since 2010 indicate that the mine water from Severnyi Mine discharged into the rivers Bystraya and Hauki-Lampijoki falls short in terms of its chemistry of the applicable environmental and health standards for suspended solids, sulfate, nickel, nitrogen compounds, and petroleum products.

Chemical analysis of the mine water and water samples collected from the mine's different horizons revealed some patterns of the distribution of pollutants and identified local pollution maxima. By its composition and the total content of pollutants, the most polluted water samples come from the pump sump at the horizon -200 m (the pump's share in the combined flow is approx. 10%). By nickel sulfate content, the most polluted water samples come from the pump sump at the horizon -80 m (share approx. 20%).

Karnasurt Mine, LLC Lovozersky GOK

LLC Lovozersky GOK's Karnasurt Mine extracts and concentrates ore into a loparite concentrate. Loparite is a source mineral in the production of rare earth metals, tantalum, and niobium. LLC Lovozersky GOK is a major Russian supplier of these mineral commodities. The company operates Karnasurt Mine, including a concentrator and auxiliary plants and facilities.

The mine's tunnels accumulate seepage water from the penetrated aquifers and due to precipitation and surface runoff seepage through cracks in the rock. To avoid flooding of the underground workings, the accumulated water is pumped to the surface.

The deposit's rocks contain a highly water-soluble mineral – villiomite (NaF). Therefore, the mine water pumped to the surface has an elevated content of fluoride ions, which is substantially above the applicable MPCs. In addition, the mine discharge has elevated concentrations of manganese, iron, and petroleum products. The suspended minerals in the discharge originate from the ground ore surfaces, petroleum products (kerosene, gasoline, fuel oil) leak from the mining machinery and mechanisms used to extract the ore and are in a dissolved and emulsified form.

Mine water is collected by catchwater drains, sent to the receiver and pumped from there to the surface. Untreated mine water is then discharged into the Sergevan river. The mine water flow rate varies considerably throughout the year. As a result, there are substantial fluctuations in the concentrations of pollutants, with an sharp increase during the spring flood. The daily mine water flow is nearly 27,000 m^3.

Selection of a mine water treatment strategy and process

Severnyi Mine, JSC Kola MMC

The main pollutants of the initial mine water composition have been identified on the basis of physical and chemical analysis

Table. *Main mine water pollutants*

Sample name	Color, grade	pH	Biochemical oxygen demand, mg/L	Suspended solids, mg/L	Ions, mg/L					
					NO_2^-	NO_3^-	NH_4^+	Fe	Ni^{2+}	Cu^{2+}
Initial	19	8	1,07	24,2	2,74	58,9	6,8	0,101	0,354	0,007
After purification	<1	9,3	<0,5	2,9	0,187	0,163	1,26	<0,05	0,02	0,007
MAC	-	-	3	3	3,3	45	1,5	0,3	0,02	0,001

(Table). Taking into account pollution type, operating and capital expenditures, as well as large volumes of waste mine waters for their purification, the following methods were tested: chemical coagulation, electric coagulation, mechanical filtration, sorption filtration and their combining, which were chosen from the most widely used methods (reverse osmosis, ion-exchange, chemical coagulation, electric coagulation, filtration, cementation, sorption and others).

Due to chemical coagulation inefficiency, caused by low water temperature (below 4 °C) and high supply rate of reagents, the process including the following main stages (fig.) has been suggested for industrial implementation of waste mine waters purification.

- mechanical treatment of the input mine water to remove coarse particles by settling in ponds,
- electrochemical treatment (electro-coagulation using soluble electrodes of grade St.3 steel) of the clarified water,
- flocculation (formation of Fe^{2+} compounds) and additional oxidation of electrochemical coagulant (Fe^{2+} to Fe^{3+}) by air oxygen,
- coagulant settling in thin-layer sedimentation tanks (batch thickeners) with a selective feed of a flocculant in a wide range of pH values (5-10),
- mechanical filtration of the clarified water,
- sorption post-treatment in carbon filters,
- sediment collection and dewatering.

The main advantages offered by the proposed electrochemical mine water treatment process are:

1. rapid formation of floccules and sorption of the dissolved metals (iron, nickel, copper) and other impurities,
2. treated water quality unrelated to the input concentration of suspended substances and dissolved impurities,
3. high water clarification performance offered by the large specific surface area and sorption capacity of the electrochemical coagulant; possibility to remove nitrogenous and organic compounds from the water, both by sorption and through their decomposition (on the anodes) into gaseous CO_2, gaseous NO_2, and water. the high rate and efficiency of the coagulation and sediment compaction processes, since the resulting iron hydroxide floccules are denser than aluminum hydroxide floccules and act more effectively over a wide pH range,
4. lower water corrosivity (through the formation of hydrogen and Fe^{2+} compounds – both potent reducing agents – in the process of electrocoagulation) and lower corrosion rate of the piping when the treated water is recycled to the process,
5. complete exclusion of a chemical coagulant (aluminum polyoxychloride), acids, and alkalis from the process. Potential reduction in the flocculant feed rate by up to 50-100%;
6. elimination of nitrite and ammonium nitrogen oxidation (to nitrates or elemental nitrogen) with sodium hypochlorite,
7. reduced dependence of the water treatment performance on its temperature and changes in pH values,
8. reduced frequency of washing the filters and reduced pure water feed rate to the washing process,
9. reduced reagent delivery and storage costs,

10. reduced environmental impact,
11. improved safety of the water treatment process.

The proposed process is straightforward to implement and easy to operate, which allows to maintain the required water treatment performance at low specific capital and operating costs (Oncel et al., 2013).

The high rate of the coagulation processes (when using electrocoagulation) allows the use of smaller reactors.

When using electrocoagulation, the settling tanks (batch thickeners) will provide high removal performance (higher than 90-95%) of the bulk of the dispersed suspended substances, including hydrolysis products of the dissolved metals.

The proposed combined mechanical and physicochemical water treatment process allows to:

- achieve compliance of the treated water with the quality standards required for recycling the water to the process,
- in terms of some of the criteria, achieve compliance with the MPCs for fishery water bodies.

Karnasurt Mine, LLC Lovozersky GOK

The priority pollutant in the mine water at Karnasurt Mine is fluoride (15 mg/L). Currently, several processes for the removal of fluorine have been developed and are being used, including chemical precipitation and coagulation, ion exchange, sorption, electrocoagulation, and membrane processes (e.g. Jadhav et al., 2015). The effectiveness of the process used is controlled primarily by the initial concentration of fluorine and the volume of treated water.

Analysis of the mine water flow by quantity and pollution level has shown that up to 70% of the water entering the mine is relatively clean water (0.001-0.7 mg/L). It has primary pollution comparable to the MPCs in mine water released into fishery water bodies. Thus, if the secondary pollution of the water entering the mine is prevented by intercepting the seepage before it gets contaminated in the mine, the volume of treated water can be substantially reduced. It will then be possible to conduct treatment inside the mine's workings.

The strategic goal of mine water treatment at Karnasurt Mine is to bring wastewater

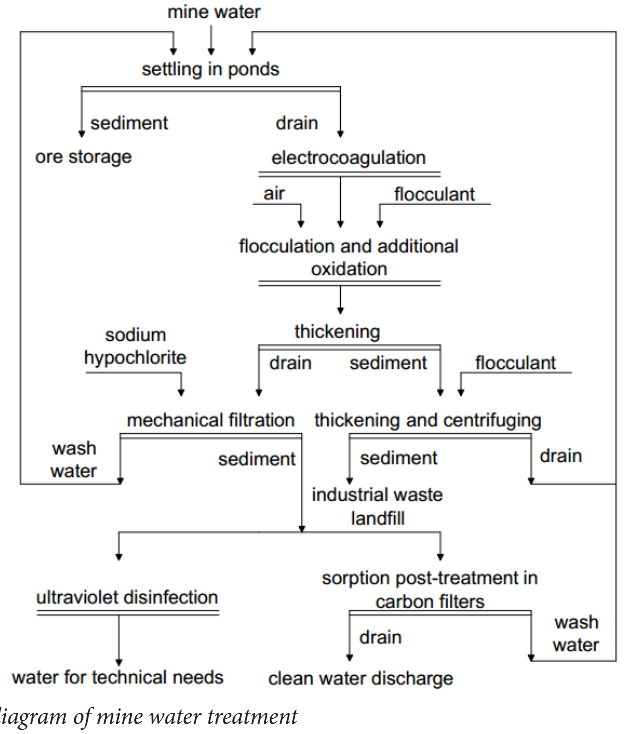

Figure *Schematic diagram of mine water treatment* released into to the Sergevan River to the requirements of the MPCs for fishery water bodies. In order to achieve this, the following is deemed necessary:

- penetrated clean water sources should not be allowed to mix with contaminated mine water by channeling via dedicated pipelines to the surface,
- in all newly developed horizons with a sufficient water inflow, local pumping stations should be deployed to be able to recycle the mine water to the process.

Retrofitting the clean water removal system for delivery into water drainage pipelines will prevent secondary pollution by suspended material in the drainage ditches of the haulage workings. To accumulate water volume and head in the haulage workings and voids, waterproof protective dams will be constructed.

One, two, and more cascade structures are planned for mine water settlement (clarification) in ponds in inclined, horizontal, and vertical mine workings with enclosing dams of various designs. To improve the performance of the process, combined reagent treatment is proposed using iron sulfate as a coagulant and flocculant Praestol 2515.

As a sorbent of fluoride ions, we investigated the use of a magnesium-containing product of acid treatment of the copper-nickel ore concentration tailings, composed of brucite $Mg(OH)_2$ with a calcite $CaCO_3$ admixture (Bajurova et al., 2015).

The use of brucite for wastewater treatment to remove potentially toxic metals and strontium was investigated by Bochkarev and Pushkareva (1998, 2009). A combined sorption process for the removal of metals from natural water and process solutions in a wide range of concentrations was proposed.

Using a mixture of brucite and calcite makes it possible to achieve a recovery of F- of up to 88-95% within an 4-5 hours, and at relatively low concentrations (1-10 mg/L), values below 0.75 mg/L, which is the MPC for fishery water bodies. Sorption by a mixture of brucite and calcite is explained by the isomorphic substitution of hydroxyl/carbonate ions with fluorine with the formation of poorly soluble calcium and magnesium fluorides without any changes in the crystal lattice. Pilot tests are being planned.

Conclusions

1. In the treatment of the mine water at Severnyi Mine operated by JSC Kola MMC, mechanical removal from the input runoff of coarse impurities by settling in settling ponds followed by electrocoagulation and filtration in mechanical and sorption filters can offer high performance. The advantages of electrochemical coagulation include wide pH ranges and the potential high degree of water purification from metal cations and organic compounds at low temperatures of the mine water.

   This will however involve changes in the storage of the resulting waste – sediment from the settling ponds is a fine-grained ore material stored in the ore stockpile, sediment from electrocoagulation can be used as an insulating layer at the tailings disposal site.
2. To implement mine water treatment at Karnasurt Mine operated by LLC Lovozersky GOK to the MPC standards for fishery water bodies, mixing of the relatively clean seepage water with the contaminated mine water should be prevented by pumping the former via dedicated pipelines to the surface. Treatment of small mine water volumes in the mine's finished voids can be organized by setting up settling ponds in inclined, horizontal, and vertical mine workings with enclosing dams of various designs.

   To improve the performance of the process, combined reagent treatment is proposed using iron sulfate as a coagulant and flocculant Praestol 2515. A magnesium-containing product composed of brucite with a calcite admixture is recommended as a fluoride ion sorbent.

Acknowledgments

This research was funded by Russian Government grants no 0138-2014-0002 and no 0226-2018-0001. The study has been performed with financial support of the Kolarctic CBC 2014-2020 Programme, Project no KO1030 "Supporting Environmental Economic and Social Impacts of Mining Activity".

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