



Removal of Fluoride Ions from the Mine Water

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Abstract

Murmansk Region is home to some major mining and mineral sites. One of the most challenging environmental problems in the mining industry is mine water treatment. For example, the rocks of the deposit operated by Lovozero Mining and Mineral Processing Company contain villiomite (NaF). It is highly soluble in water, and the mine waters at the site have a high content of fluoride ions – significantly above the maximum permissible values.

Lab-scale experiments were conducted to test various reagents and different initial concentrations of fluoride ions in the treatment of model solutions and mine water. Depending on the initial concentrations, magnesium and calcium-containing sorbents are proposed for the defluorization of water. Using scanning electron microscopy and microprobe analysis, it was found that fluorine can be bound in poorly soluble compounds, such as, for example, fluorite.

Pilot trials are planned.

Keywords: usuwanie fluoru, ścieki, sorbenty zawierające magnez i wapń

Introduction

The mining industry is highly active in Russia's Murmansk Region. Mining operations lead to the formation of wastewater with a high content of fluorine, often discharged into potable and fisheries water bodies without prior treatment or after inadequate treatment.

The urgency of developing simpler technologies for wastewater treatment using local materials or production waste is explained by large volume of wastewater requiring treatment, as well as the remoteness of the mining and mineral processing facilities from reagent and building materials manufacturers. In most cases, the implementation process of any proposed water treatment technology aimed at removing fluorine stops at the stage of a full-scale trial and requires further development of the technology.

Lovozero MMPC is located in the center of the Kola Peninsula and is the primary employer in the town of Revda. Karnasurt Concentrator has two fresh water intakes and six wastewater outlets used to discharge household, process, and drainage wastewater. At present, untreated mine water is discharged into the Sergevan River, a first order tributary of Lake Lovozero, classified in the highest category of fisheries water bodies. In addition, in 2011, due to an increase in the site's output, there was an increase in the amount of polluted wastewater discharged without treatment to 12.042 million m³.

It should be noted that the ore mined by Lovozero MMPC at the Karnasurt Mine contains villiomite (NaF), character-

ized by high water-solubility, therefore, the mine water in the mine has an elevated level of fluoride ions, significantly exceeding the existing maximum permissible values.

In this paper, we examine the possibility of using the reagents recovered from the waste and by-products of Murmansk Region's mining and minerals industry to remove fluoride ions from the wastewater.

Materials and methods

The following sorbent samples were used to defluorize the solutions: thermally activated (500°C, 2 hours) brucite, calcined (900°C, 2 hours) carbonatite, a 1:1 (by weight) mixture of thermally activated brucite and calcined carbonatite, AlCl₃·3H₂O.

The proposed reagents were tested on model solutions with a concentration of 10 and 100 mg/l, as well as on actual mine water, collected in one of the Karnasurt mine's discharge outlets and containing 51 mg/l of fluorine.

The dependence of the fluoride ion sorption on the initial concentration was studied using the following method: 200 ml of the initial solution of a known concentration (10, 100 mg/l) was placed in a 250 ml conical flask, the sample was added, the mixture was shaken periodically and the residual fluorine concentration in the filtrate was measured. The residence time ranged from 0.5 to 24 hours, reagent flow rate from 0.25 g/l to 5 g/l. The pH value of the solutions was adjusted by adding H₂SO₄ and NaOH solutions.

Tab. 1. Removal of fluoride ions from the model solution, 10 mg/l
 Tab. 1. Usuwanie jonów fluorkowych z roztworu modelowego, 10 mg/l

Time, h	Termoactivated brucite			Calcined carbonatite			Brucite:Carbonatite 1:1			AlCl ₃ ·3H ₂ O		
	0.5	1	5	0.5	1	5	0.5	1	5	0.25	0.5	0.75
Consumption, g/l	0.5	1	5	0.5	1	5	0.5	1	5	0.25	0.5	0.75
0.5	5.3	13.7	43.2	9.1	12.6	19.9	8.3	19.9	20.9	85.8	90.5	96.4
1	14.6	28.3	51.3	18	20.2	28.7	15.6	28.1	32.1	86	90.8	96.6
24	63.6	71.9	97.2	30.2	31.4	40.1	42.3	46.3	56.4	86.1	91	96.7

Tab. 2. Removal of fluoride ions from the model solution, 100 mg/l
 Tab. 2. Usuwanie jonów fluorkowych z roztworu modelowego, 100 mg/l

Time, h	Termoactivated brucite			Calcined carbonatite			Brucite:Carbonatite 1:1			AlCl ₃ ·3H ₂ O		
	0.5	1	5	0.5	1	5	0.5	1	5	0.25	0.5	0.75
Consumption, g/l	0.5	1	5	0.5	1	5	0.5	1	5	0.25	0.5	0.75
0.5	19.3	37.8	91.42	77.9	80.31	84.40	64.2	77.2	88.4	64.6	87.35	89.05
1	34.7	52.46	92.36	81.4	86.68	91.88	72.6	79.4	92.65	64.9	87.7	89.2
24	68.4	73.65	94.68	89.62	92.5	95.95	81.1	89.3	95.82	65.1	87.8	89.2

Tab. 3. Removal of fluoride ions from the real waste water, 51 mg/l
 Tab. 3. Usuwanie jonów fluorkowych z rzeczywistych ścieków, 51 mg/l

Time, h	Termoactivated brucite, 1 g/l	Calcined carbonatite, 1 g/l	Brucite:Carbonatite 1:1, 1 g/l
0.5	22.94	24.31	20.20
add 0.5 g/l AlCl ₃ ·3H ₂ O			
0.5	98.23	97.02	97.51

Fluoride ion concentration in water was measured by the potentiometric method using an electrode system composed of a fluoride ion-selective electrode and an additional chlorine-silver electrode. The filter precipitates were examined by scanning electron microscopy and X-ray microprobe analysis using the measurement instrument SEM LEO 1450. The residual concentration of chlorine anions, where the water was treated with aluminum chloride, was measured by liquid chromatography.

Results

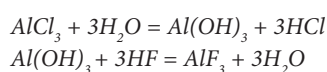
The results of the experiments on the model solutions are presented in the tables 1, 2.

The mechanism of sorption by brucite and carbonatite, as well as by a mixture of the two, is explained by isomorphous substitution of hydroxyl/carbonate ions by fluorine with the formation of poorly soluble calcium and magnesium fluorides without changes in the crystal lattice; the solubility of MgF₂ is 0.13 g/l, of CaF₂ 0.018 g/l at 25°C (Solubility Handbook, 1961). To regenerate the sorbent, a 2% caustic soda solution can be used.

In the dried precipitate of the reaction of thermally activated brucite and calcined carbonatite with the model solutions, calcium fluorides (fluorite) and magnesium fluorides were found both on the surfaces and in the newly formed phases.

In the process of water treatment using aluminum chloride, hydrolysis occurs with the formation of flocculent compounds with a general formula of the form [Al_n(H₂O)_{3n}(OH)_{3n-x}]^{x+} + xOH⁻, where x OH⁻ ions are found in

the outer layer, and 3n-x OH⁻ ions are locked in the flakes. In the hydroxyl ions of the outer layer, the charge is only partially compensated by the hydration shell and sorbed anions; in general, the particle acquires a positive charge. With a decrease in pH as a result of the partial neutralization of the charge of the OH⁻ ions by the hydrogen ions, the flake particles become more positively charged; hydroxyl ions, as a result of the weakening of the bond with the main matrix, improve their ability to exchange with anions in the external environment (Rozhdov and Silaeva, 2008).



The optimum pH value for the formation of stable Al(OH)₃ flakes and maximum absorption of F lies in the pH range of 5.5–7 (Mamyachenkov et al., 2016; Belikov and Lokshin, 2018). NaOH solution was added to the solution containing aluminum chloride until the pH was 6–7. Already during the first half hour at a minimum reagent flow rate, it was possible to reduce the concentration of fluoride ions to 1.42 mg/l and 35.4% in the model solutions containing 10 and 100 mg/l of fluorine. Secondary contamination with chloride ions does not exceed the maximum permissible.

The examined calcium and magnesium-containing reagents reduce the concentration of fluoride ions to the maximum permissible concentration at a high flow rate of 5 g/l, which is hardly viable in a production environment. These sorbents can be applied in smaller quantities for the pre-treatment of wastewater.

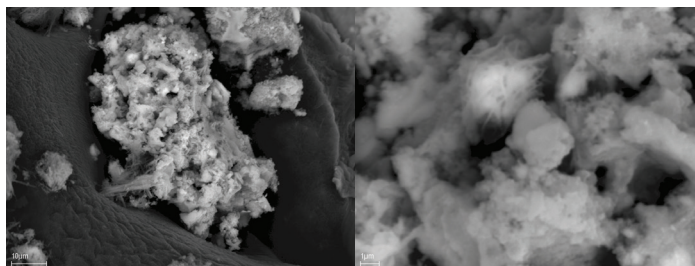


Fig. 1. Micrographs of precipitated fluorides on a thermally activated brucite surface
Rys. 1. Mikrografy strąconych fluorków na termicznie aktywowanej powierzchni brucytowej

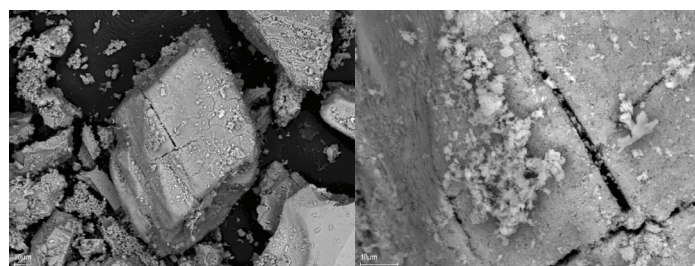


Fig. 2. Micrographs of precipitated fluorides on a calcined carbonatite surface
Rys. 2. Mikrografy wytrąconych fluorków na kalcynowanej powierzchni węglanu

In further treatment, reagents, e.g. aluminum chloride, can be used.

Using the actual mine water with an initial fluoride concentration of 51 mg/l, a two-stage treatment process.

Magnesium and calcium-containing reagents raised the pH to almost 10 and the addition of aluminum salt reduced it to 6.1–6.3; no additional adjustment of the pH was necessary.

Conclusion

Lab-scale experiments were carried out under static conditions on model solutions and the actual mine water from the Karnasurt Mine. The following reagents were tested: thermally activated (500°C, 2 hours) brucite, calcined (900°C, 2 hours) carbonatite, a 1:1 (by weight) mixture of thermally activated brucite and calcined carbonatite, $\text{AlCl}_3 \cdot 3\text{H}_2\text{O}$. The experiments showed that a high degree of fluorine removal is achieved when using a reagent based on brucite and carbonatite.

It was found that the most promising processes for the removal of fluorine from the wastewater of the mining industry

are processes combining chemical precipitation, coagulation, and sorption, making it possible to irreversibly and efficiently remove fluorine in a wide range of concentrations.

For initial fluorine concentrations of the order of 100 mg/l, chemical precipitation processes capable of removing up to 95% of fluorine are considered efficient. Either lime or magnesite, or both, will be effective in the pre-treatment stage. To further reduce the concentration of fluoride ions, it is possible to use aluminum chloride; at a low flow rate, secondary contamination with chlorine ions is unlikely.

A process is described for the separation of the mine wastewater from the Karnasurt Mine to reduce the volume of the polluted mine water and increase the concentration of the pollutant, which will improve the efficiency of fluoride ion removal using both conventional and novel methods.

Acknowledgments

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Usuwanie jonów fluorkowych z wody kopalnianej

Region Murmański jest regionem silnie uprzemysłowionym, jest lokalizacją wielu kopalń. Jednym z najtrudniejszych problemów środowiskowych w górnictwie jest uzdatnianie wód kopalnianych. Przedstawiono przykład kopalni Lovozero Mining and Mineral Processing. Złoże zawiera villiaumit (NaF). Jest to minerał dobrze rozpuszczalny w wodzie. Wody kopalniane w tym miejscu mają wysoką zawartość jonów fluorkowych - znacznie powyżej maksymalnych dopuszczalnych wartości. Przeprowadzono eksperymenty na skalę laboratoryjną w celu przetestowania różnych odczynników i różnych początkowych stężeń jonów fluorkowych w obróbce roztworów modelowych i wody kopalnianej. W zależności od początkowych stężeń do odfluoryzacji wody proponuje się sorbenty zawierające magnez i wapń. Za pomocą skaningowej mikroskopii elektronowej i analizy mikropróbek stwierdzono, że fluor może wiązać się w słabo rozpuszczalnych związkach, takich jak na przykład fluoryt. Planowane są próby pilotażowe.

Słowa kluczowe: usuwanie fluoru, ścieki, sorbenty zawierające magnez i wapń