



Non-Ferrous Metal Sorbents Based on Waste and Side Products of Mineral Benefication Plants

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Abstract

The saponite-containing product from the stage of process water clearing at beneficiation plant of the PAO Severalmaz was thickened using the electrochemical separation for use as sorbent of nickel and copper ions. The product features a high sorption capacity relatively the nickel and copper ions. It has been established that the sorption capacity can be enhanced by roasting the product at 750°C to 194 and 212 mg/g for the nickel and copper ions respectively.

An organomineral sorbent for nickel ions based on copper-nickel ore tailings of the JSC „The Kolskaya Mining and Metallurgical Company”, thermally activated at 700°C, has been synthesized. The surface modification was performed by using the non-covalent immobilization of dimethylglyoxime.

Keywords: electrochemically modified saponite, sorption, thermal activation, metal ions, mine water, waste water

Introduction

For tailings ponds or waste rock piles exposed to atmospheric conditions, heavy metals (Ni, Cu) are often produced by oxidation of sulfide minerals (mainly pyrite and pyrrhotite), which also generates acid in the process (Plante, et al., 2010). Acid mine drainage (AMD) is an environmental problem that has drawn the attention of researchers in several countries around the world. This is mainly due to the presence of heavy metals in AMD, which could lead to degradation of both surface and ground water easily reach lakes, dams and rivers that are sources of water supply, making it unfit for human and animal consumption or crop irrigation (Masukume et al., 2014).

Treatment processes for metal contaminated industrial waters include chemical precipitation, extraction, ion exchange, adsorption and ultra-filtration. Clays, saponite, serpentine, overburden and tailings, containing chemically active minerals, are perspective materials for the development of highly effective sorbents for metal ions.

The present study was performed with saponite-containing product obtained using the electrochemical separation. When in aqueous medium, saponite forms a fine, gel-like suspension creating problems in operation of tailings facilities and hindering the close-loop circulation of process water. Experiments on saponite recovery from the process water of diamond mining plants are reported in works (Minenko, 2014; Chanturiya, et al. 2017) presenting a reagent-free electrochemical method for the pulp processing and equipment for the method's implementation (electrochemical separator). The apparatus incorporates realization of the processes of electrophoretic deposition of the saponite product at the anode and osmotic deposition of water at the cathode. The resulting concentrate (electrochemically modified saponite) is characterized by high concentrations of the solid phase (up

to 620 g/dm³ of suspension), high contents of saponite and montmorillonite (up to 74.5 %) and lower concentrations of quartz and dolomite compared to the initial saponite-containing product (12% and 5%, respectively).

The most promising is the production of a modified sorbent based on waste from the mining industries. The increase in the absorptive capacity was achieved by fixing the reagent (dimethylglyoxime) on the of copper-nickel ore tailings (thermally activated at 700°C), namely, by impregnation.

Sorbents obtained by using method for the non-covalent immobilization have the advantages of covalently modified matrices (chemical, mechanical resistance, etc.), and do not have such disadvantages, as high labor intensity for the processes of modification and regeneration.

Materials and methods

Electrochemically modified saponite – concentrate of electrochemical separation from process water of the Arkhangel'skaya kimberlite pipe (Minenko, 2014; Chanturiya, et al. 2017). The Lomonosov deposit of the Archangelsk diamondiferous province accommodates 10 kimberlite pipes. The anticipated volume of diamond-bearing ore and dump rock to be removed before reaching the open-pit mining limit is 300 mln t (Karpenko, 2009; Bezborodov, et al. 2003). Rock in the deposit is almost completely displaced by clay minerals, predominantly saponite, amounting to 90% in the vent facies (Karpenko, 2009).

The general formula saponite can be expressed as $\text{NaMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Moreover, owing to the low charge of the layers the mineral can expand in water and has unique adsorption and ion-exchange properties caused by the presence of exchange cations. In addition, it is known that saponite, which in this product is electrochemically modified, has higher sorption characteristics in comparison with the

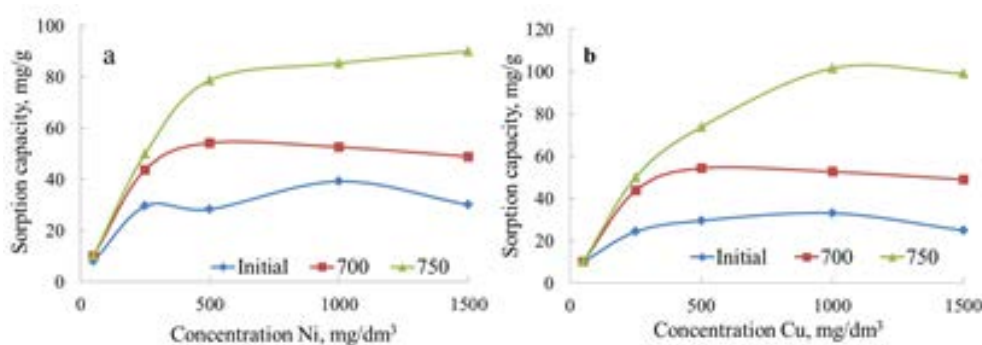


Fig. 1. Sorption isotherms of Ni(a), Cu(b) by saponite-containing products
Rys. 1. Izotermy sorpcji Ni (a), Cu (b) przez produkty zawierające saponit

Tab. 1. Kinetics of metals adsorption by electrochemically modified saponite and sintered saponite products

Tab. 1. Kinetyka adsorpcji metali przez elektrochemicznie modyfikowane saponity i spiekane produkty saponitowe

t, h	Initial			700°C			750°C		
	1:200	1:100	1:25		1:200	1:100	1:25		1:200
Sorption capacity relatively Cu, mg/g									
0.5	21.1	18.5	13.6	26.9	13.3	31.1	73.8	46.9	10.0
1	30.0	19.6	15.2	67.4	28.3	34.5	78.7	50.0	35.4
5	24.9	28.8	14.7	96.3	30.5	35.5	102.1	64.9	35.2
24	33.1	72.9	19.1	73.0	53.2	33.9	145.7	85.0	37.5
120	99.8	89.1	28.5	89.2	66.9	37.5	185.0	96.4	37.5
240	71.4	75.4	36.2	116.9	126.0	37.5	212.8	139.5	37.3
Sorption capacity relatively Ni, mg/g									
0.5	24.1	17.6	5.9	27.1	19.7	25.6	21.3	34.5	28.6
1	33.9	22.6	12.0	42.3	34.7	35.6	33.7	41.9	37.5
5	36.7	24.0	15.2	46.4	34.1	32.6	79.4	52.7	37.4
24	38.6	40.3	22.6	46.0	30.6	32.2	144.9	56.9	37.5
120	40.7	39.1	18.1	69.1	48.9	35.5	194.2	103.8	37.4
240	40.2	36.0	16.0	77.8	51.2	36.4	129.4	76.7	37.5

natural mineral. The sorption properties of the electrochemically modified saponite and its products sintered during 2 hours in the SNOL 6/11-B furnace at 700 and 750°C were investigated in batch conditions at the temperature of 20°C. This temperature range was selected after analysis of the results reported in work (Chanturiya, et al. 2014; Makarov, et al. 2005) dealing with structural modifications of dissimilar layered hydrosilicates and their sorption properties in the process of sintering.

The adsorbing solutions (further referred to as solutions) were the sulfate solutions of nickel and copper which are the main heavy-metal pollutants of natural waters in the Urals Mountains and North-West Russia. The metal concentrations in the solutions investigated were 50 to 1500 mg/dm³, which are the real concentrations in waste water affording to reveal and classify the new formations on the sorbents.

Creating the conditions for maximum saturation of the sorbent and complete (up to 99–100%) removal of heavy metal

cations from solutions were based on analysis of the published data on the sorption capacity of clay minerals of the montmorillonite group (Esmail, 2016). In our experiments, the sorbent to solution ratio (further referred to as S:L) was varied from 1:200 to 1:25; the exposure periods were 30 minutes to 10 days.

To obtain the organomineral sorbent, copper-nickel ore tailings of the JSC “The Kolskaya Mining and Metallurgical Company”, consisting of serpentine (60%) and magnetite (13%), were used. The copper-nickel ore tailings were represented by the following chemical composition, %: SiO₂ 37.39, MgO 28.29, Fe 18.10, Al₂O₃ 3.73, CaO 2.71, TiO₂ 0.945, Ni 0.19, Cu 0.06, Co 0.003. The tailing pond of the concentrating factory “Pechenga” (“The Kola MMC”) was founded in 1965 in the town Zapolyarny. The reserves of copper-nickel ores tailings amount to 250 million tons, the annual growth is 7 million tons.

The copper-nickel ore tailings, thermally activated at 700°C, were modified by impregnation.

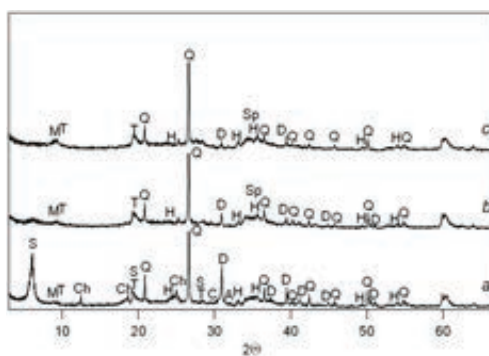


Fig. 2. XRD patterns of the sorbents after interaction with a nickel sulfate solution. Initial sorbent, exposure time of 5 days (a); sintered at 700°C, exposure time of 10 days (b); sintered at 750°C, exposure time of 5 days (c). S – saponite, Q – quartz, H – hematite, A – apatite, C – calcite, D – dolomite, M – mica, Ch – chlorite, T – talc, G – gypsum, Sp – spinel

Rys. 2. Analiza XRD sorbentów po interakcji z roztworem siarczynu niklu. Surowy sorbent, czas ekspozycji 5 dni (a); spiekany przy 700°C, czas ekspozycji 10 dni (b); spiekany przy 750°C, czas ekspozycji 5 dni (c). S – saponit, Q – kwarc, H – hematyt, A – apatyt, C – kalcyt, D – dolomit, M – masy, Ch – chloryt, T – talk, G – gips, Sp – spinel

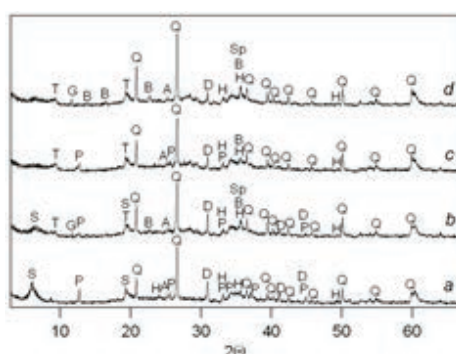


Fig. 3. XRD patterns of sorbents after reaction with a copper sulfate solution. Initial sorbent (a, 10 days); sorbent sintered at 700°C, (b, 10 days); sorbent sintered at 750°C (c, 5 days), and (d, 10 days). S – saponite, P – posnjakite, Q – quartz, H – hematite, A – apatite, D – dolomite, B – brochantite, T – talc, G – gypsum

Rys. 3. Analiza XRD sorbentów po reakcji z roztworem siarczynu miedzi. Początkowy sorbent (a, 10 dni); sorbent spiekany przy 700°C, (b, 10 dni); sorbent spiekany przy 750°C (c, 5 dni) i (d, 10 dni). S – saponit, P – posnjakit, Q – kwarc, H – hematyt, A – apatyt, D – dolomit, B – brochantyt, T – talk, G – gips

An alcoholic solution of dimethylglyoxime was placed into the reactor, and then a sample of the tailings was added. The temperature was varied from 50 to 90°C, the modifier consumption was from 2.5 to 30%, depending on the mass of the silicate matrix. The duration of the interaction was from 30 to 300 minutes. Experiments on the interaction of modified tailings with sulfate solutions containing nickel ions were carried out. In the experiments, the concentration of the nickel sulfate solution was 0.1 N.

The sorption of nickel ions was determined at various pH values: 1.64; 3.56; 4.01; 6.86; 9.18.

The ratio of S:L was 1:50. The interaction time was varied in 5, 15, 30, 60 minutes and 3, 6, 8, 24 hours, the ratio of S:L was 1:100.

The metal concentrations in solutions were determined using the atomic-absorption spectrometry (KVANT 2A spectrometer, "Cortec" LLC).

The phase composition of the solid products and newly formed minerals was determined using the XRD at a diffractometer X'Pert PRO MPD (Shimadzu) with Cu K α radiation.

Results and discussion

Figure 1 demonstrates the relationships between the sorption capacity of saponite-containing products and the initial concen-

trations of NiSO₄ and CuSO₄ solutions at the solid to liquid ratio of 1:200 and the exposure time of 3 hours. It has been established that thermal activation of the electrochemically modified saponite enhances the sorption capacity. Interestingly, at low initial concentrations of the metals in solutions (down to 500 mg/dm³) the sorption capacity of all the samples was observed to increase abruptly. Further increasing of initial concentration does not affect the sorption capacity of saponite-containing products, which suggests transition of the sorption process from diffusion to kinetic regime. Therefore, to achieve the maximum saturation of the sorbent with copper and nickel cations, we proceeded to experiment with solutions having the metal contents of 1500 mg/dm³, and increased the exposure time to 10 days.

Table 1 presents the research results on variation of the sorption capacity of electrochemically modified saponite and products of sintered saponite with the S:L ratio and time of interaction to solution. For the initial electrochemically modified saponite, the maximum sorption capacity relatively the nickel and copper cations are 40.7 and 99.8 mg/g, respectively, and it is achieved after 5 days. On further interaction with solution the sorption capacity deteriorates probably as a result of developing/incipient destruction and resolution of the compounds newly formed on the sorbent.

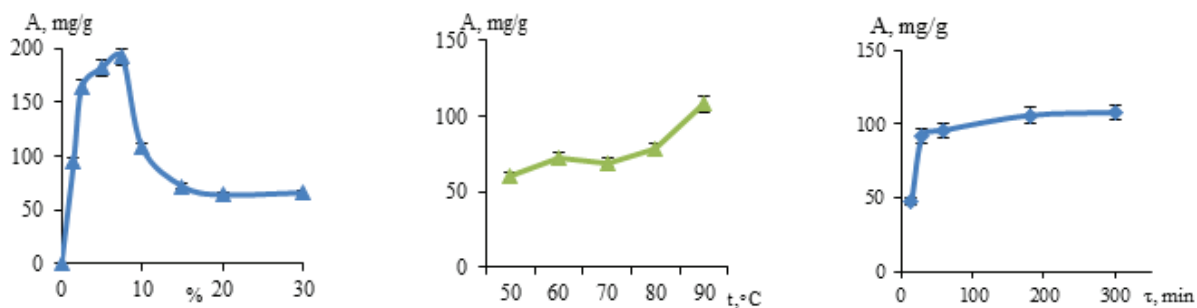


Fig. 4. Dependence of nickel ions sorption on the modifier concentration (a), on the reaction mixture temperature (b), on the interaction duration (c)
Rys. 4. Zależność sorpcji jonów niklu od stężenia modyfikatora (a), od temperatury mieszaniny reakcyjnej (b), od czasu oddziaływania (c)

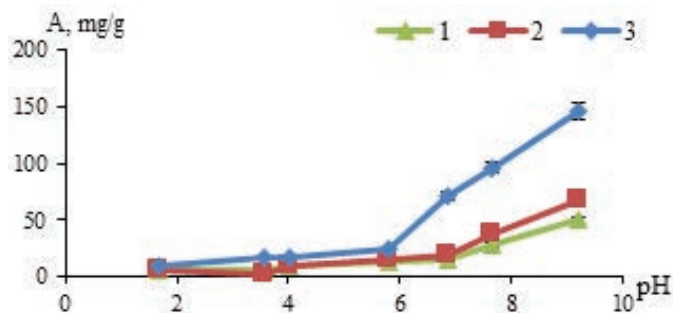


Fig. 5. Dependence of nickel ions sorption on pH medium. Initial tailings (1); tailings, thermally activated at 700°C (2); organomineral sorbent (3)
Rys. 5. Zależność sorpcji jonów niklu od odczynu pH. Odpady początkowe (1); odpady, aktywowane termicznie w 700°C (2); sorbent organomineralny (3)

The sorption capacity of electrochemically modified saponite to 77.8–126 mg/g via sintering; the level of solution purification was 94.7–100% after 5 days of exposure. The maximum sorption capacities relatively the nickel and copper cations of, respectively, 194.2 and 212.8 mg/g was observed on saponite samples sintered at 750°C at the ratios S:L= 1:200. By increasing the S:L ratio to 1:25 the solution purification from copper and nickel cations achieved 100% already after 1 day of exposure to the sorbent.

It should also be noted that at less than 250 mg/dm³ metal concentrations in solutions the extraction of nickel and copper is 100% in less than 3 hours of interaction with the sorbent sintered at 750°C.

Thus, the electrochemically modified saponite is a good sorbent of nickel and copper ions and can be further improved by sintering at 700–750°C.

XRD studies of the sorbents maximally saturated with nickel suggest that the metal sorption on initial saponite follows the mechanism of cation exchange with metals cations distributing between the mineral structure packets. Moreover, a phase with spinel structure, probably containing nickel, has been recorded. Spinel also emerges after the nickel sulfate solution reacts with a product thermally activated at 700 and 750°C (Fig. 2, b, c). In these cases, saponite transforms to a layered talc-like phase which is likely to contain nickel in the inter-packet space.

The XRD of the sorbents saturated with copper to the maximum has shown the following changes in the phase composition, which suggests entraining of calcium and sodium from the interlayer space (Fig. 3; a). At the same time, these cations may be substituted both for copper cations and protons.

As a result of heat treatment at 700°C (Fig. 3; b) the saponite reflexes decreased sharply. Afterburning at 750°C saponite disappeared almost completely (Fig. 3; c, d); weak calcium reflexes indicated the onset of dolomite decomposition.

The new copper-containing phases were identified as basic sulfates insoluble in water. Reactions of the initial product and that sintered at 700°C produced posnjakite Cu₄(SO₄)(OH)₆·H₂O (Fig. 3a, b); and brochantite Cu₄(SO₄)(OH)₆ was recorded for products sintered at 700 and 750°C (Fig. 3, c, d).

There is a slight dissimilarity between the phase composition of samples sintered at 750°C differing in reaction times with sulfate solution. Long exposure of the sintered product to the copper sulfate solution (10 days) has led to increasing of the reflex with $d = 2.52 \text{ \AA}$ ($2\theta = 35.5^\circ$), corresponding to phases with a spinel structure.

Figure 4 shows the sorption capacity for the synthesized sorbent depending on the modifier concentration, the temperature of the reaction mixture and duration of interaction. The rational parameters of the surface modification were determined: the temperature of the reaction mixture was 90°C, the duration of the interaction was 30 minutes, and the modifier weight amounted to 2.5–7.5%. Increasing the concentration of the modifier reduced the availability of functional groups and led to decrease in the sorption capacity. As a result of modification, the sorption capacity to nickel ions was increased substantially to 180–220 mg/g.

The influence of the initial pH value varying in the range from 1 to 10 on the sorption of nickel ions was studied. It should be noted that pH increase, beginning from 6, marks the considerable growth of nickel ions sorption (Fig. 5).

An important criterion while using a sorbent for water purification is the rate of sorption. Studying kinetics of the

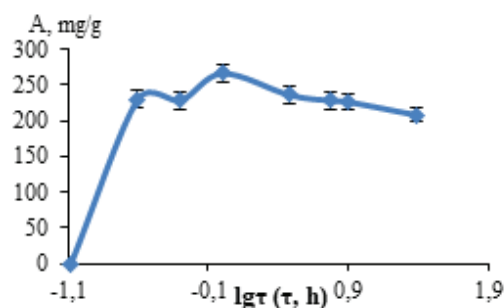


Fig. 6. Kinetics on the sorption of nickel ions by organomineral sorbent
Rys. 6. Kinetyka sorpcji jonów niklu przez sorbent organo-mineralny

nickel ions sorption by a modified sorbent showed the sharp increase within 5 minutes. The maximum value was achieved by contact for 30 minutes, then some desorption occurred (Fig. 6).

The results of the studies revealed that the surface modification significantly increased the sorption capacity for nickel ions to 220 mg/g, compared to thermally activated and initial tailings (38 and 28 mg/g, respectively, Fig. 2). The values obtained exceed the sorption capacity of sorbents, such as magnetite 1.25 mg/g (Martemyanov D. et al, 2013), glauconite 3.6 mg/g (Martemyanov D. et al, 2013), bentonite 35 mg/g (Somin, V. et al., 2014), brucite 95 mg/g.

Conclusion

This study is the first to substantiate and experimentally validate the following method for manufacturing from sa-

ponite-containing diamond-mining waste of sorbents with excellent cation exchange properties for effective treatment of process water from heavy metal cations.

Experiments have proved the feasibility of processing the electrochemically modified saponite for effective sorbents having an cation exchange capacity of over 200 mg/g, applicable in treating of process water from heavy metal ions to the MAC for fishing water reservoirs. The affinity of this sorbent towards metal ions could be arranged as follows $\text{Cu}^{2+} > \text{Ni}^{2+}$.

The modified sorbent based on copper-nickel ore tailings at the JSC "The Kolskaya Mining and Metallurgical Company" has high sorption capacity and can be proposed for purification industrial waters at the mining enterprises.

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Sorbenty metali niezłaznych na bazie odpadów i produktów ubocznych z zakładów wzbogacania surowców

Produkt zawierający saponit z etapu oczyszczania wody technologicznej w zakładzie wzbogacania PAO Severalmaz został zagęszczony przy użyciu rozdzielania elektrochemicznego w celu zastosowania jako sorbent jonów niklu i miedzi. Produkt cechuje się dużą pojemnością sorpcyjną, w stosunku do jonów niklu i miedzi. Ustalono, że pojemność sorpcyjna może być zwiększona przez prażenie produktu w temperaturze 750°C do 194 i 212 mg/g odpowiednio dla jonów niklu i miedzi. Zsyntetyzowano organo-mineralny sorbent dla jonów niklu oparty na odpadach z wzbogacania rud miedzi i niklu JSC „The Kolskaya Mining and Metallurgical Company”, aktywowany termicznie w 700°C. Modyfikację powierzchni przeprowadzono stosując niekowalencyjną immobilizację dimetyloglioksymem.

Słowa kluczowe: saponit modyfikowany elektrochemicznie, sorpcja, aktywacja termiczna, jony metali, woda kopalniana, ścieki