

OLIVINE-BASED SORBENTS FOR REMOVAL OF HEAVY METALS

M. S. HAYRAPETYAN *, S. S. HAYRAPETYAN **, H. G. KHACHATRYAN ***

Chair of Inorganic and Analytical Chemistry, YSU, Armenia

Inductively coupled plasma mass spectrometry (ISP-MS) and scanning electron microscope-X-ray fluorescence (SEM-XRF) methods were used for the investigation of olivine sorption properties. It has been shown, that olivine may be applied as a cheap and available material for the sorption of metals, including heavy metals, from wastewater. The comparatively low sorption capacity of olivine may pay off by its accessibility and cheapness. The mechanism of adsorption on the olivine surface may be described as the substitution of magnesium ions by cations of various metals. One trend can be fixed – when ionic radius of the metal cations increases, their sorption increases as well. However, it is hardly possible to tie everything with the ionic radius of metal ion. The specificity of each element is also important.

<https://doi.org/10.46991/PYSU:B/2023.57.2.090>

Keywords: olivine, heavy metals sorption, sorption mechanism.

Introduction. The evaluation of different impacts on environment is necessary during and after mineral extraction. If such procedure was done non-efficient high-pyrite (FeS_2) containing deposits may become the sources of contamination by heavy metals and radionuclides, which can isolate from dumps under different weather conditions [1]. It should be noted that micro-elements may present in various forms from a molecularly-solved state to colloidal and micron-size particles. And low-molecular forms are very mobile [2, 3].

Currently, various methods are applied to remove heavy metals from wastewater (mechanical, chemical, and biological). The adsorption method is the most efficient among the physicochemical methods [4–6]. The advantage of this method is that it allows to clean wastewater containing a large amount of various contaminants (organic and inorganic as well). The efficacy of wastewater purification may reach 80–95%, depending on the chemical nature of the sorbents, their structure, and the values of the absorbing surface.

In recent years, natural sorbents and sorbents based on natural materials are applied more often for purification of wastewater [5]. The use of such sorbents is actual and of great interest, because resource-saving and environment protection are

* E-mail: mrdhayrapetyan@gmail.com

** E-mail: haysers@ysu.am

*** E-mail: gold@ysu.am

the priorities of comprehensive science and industry, and the use of wastes in industrial scales is economically efficient [6–8]. Their cost is approximately ten times less than that for artificial sorbents.

Clay materials are the most prevailed inorganic sorbents used for wastewater cleaning. Numerous non-metallic natural minerals (zeolites, clays, peat, etc.) possess series of advantages listed above [9–12]. Tree bark, chitin, chitosan, commercial ion-exchangers, composted cow dung, brown coal, peat, rice husk, vegetable compost and yeast are the samples of organic materials, when bio-carbons, limestone shales, dolomite, fly ash, limestone, olivine, slags and zeolites are examples of inorganic materials used for these purposes [13].

Metamorphosis product includes serpentine and clay minerals (chlorite, amphiboles, talc), carbonates and pseudomorphic compounds of goethite [14].

Materials and Methods. Inductively coupled plasma mass spectrometry (ISP-MS) and Scanning electron microscope-X-ray fluorescence (SEM-XRF) methods were used for the investigation of olivine sorption properties.

Olivine-Rich Materials (Blueguard®). These materials have trade mark Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C. After contact with Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C pH values for double-distilled water increase up to 10–11, suggesting that these materials give out hydroxide ions to the liquid phase.

Various methods were used to understand the structure and properties of Blueguard® materials, as well as to justify the mechanism by which these materials remove micro-elements from wastewater [14].

The goal of the article is to investigate the sorption properties of the olivine-rich materials.

Olivine Blueguard 63 (Blueguard®) material is dunite-rock source (peridotite ultra-basic rock with olivine content >90%) acquired from Sibelco Nordic Deposits, Åheim, Norway.

Experimental Part.

Preparation of the Column for Realization of the Sorption in Dynamic Regime.

Firm “Bio-Rad”, USA column was loaded by olivine (fraction 0.25–0.50 mm, mass 10 g). The loading was realized using an aqueous suspension of the indicated fraction. Before passing wastewater through the column, it must be washed by distilled water (50 mL).

The analyses were carried out on Agilent Technology 8800 Triple Squad (“Agilent”, USA) instrument.

Regeneration of the Column. In this case, the leaching of Mg took place sooner than the liberation of the functional groups responsible for adsorption. And, the acidic treatment of the sorbent is realized as well. In the classical sense, the acidic treatment leads to the regeneration of the column, inasmuch as a result of such treatment the functional groups of the sorbent get out from the adsorbed metal ions and the sorbent returns to its initial state.

For the acidic treatment 50 mL of a 5% hydrochloric acid solution is passed through the column. After that, it was washed by distilled water to complete removal of the chloride-ions.

Determination of the Sorption Capacity. Langmuir and Freundlich models are used more often, where experimental data are obtained, using a great number of sorbent weighs. This circumstance complicates the carrying of experiments. We propose a model based on the following assumption – the quantity of a substance adsorbed by a sorbent is calculated according to the following formula:

$$q = \frac{V(C_0 - C)}{m}, \quad (1)$$

where C_0 is the initial concentration of the substance, g/L; C is the concentration of the substance at the given moment, g/L; V is the volume of the solution, L; m is the mass of the sorbent, g.

Transforming the formula (1), we obtain:

$$\frac{q}{C_0} = \frac{\frac{V}{m(C_0 - C)}}{C_0}, \quad \frac{q}{C_0} = \frac{V}{m(1 - C/C_0)}, \quad q = \frac{VC_0}{m(1 - C/C_0)}. \quad (2)$$

Depending on the experiment mode (static or dynamic) or on the exposure time of the sorbent in the solution, $(1 - C/C_0)$ variable becomes a function of different values. In the given example, we considered the change of $(1 - C/C_0)$ as a function of the volume of water that passed through the column (mL). The dependency curve is painted bonding the volume and the equilibrium concentration of the substance C , then the equation of the graph is determined by means of Excel Trendline. The C/C_0 values are placed in Eq. (2) and the q values are determined from the following equation:

$$q = \frac{VC_0}{m \left[1 - \frac{C}{C_0} \right]}. \quad (3)$$

Using the values of V the values of q are calculated, and then $q = f(V)$ curves are painted. Finally, the sorption capacity is determined from this curve.

The $1 - C/C_0 = f(V)$ function may be different and we choose the one that is characterized by the maximum values for R^2 . As a rule, these are logarithmic, exponential, or power functions.

The model proposed has the following advantages:

- simplicity of calculations;
- the dependence of sorption on V is used, which allows to use a single weight of the sample. That is, a negligible amount of the sorbent is necessary for determination of the sorption capacity. In its turn, this circumstance allows to shorten the experiment time and expenses;
- sorption dynamics is modeled from the point of view of the sorbent saturation depending on the wastewater volume passed through the column and the initial concentration of the sorbent.

The sorption is evaluated by means of $1 - C/C_0$ values. Issuing from $V = f(1 - C/C_0)$ curves, according to the technique described above, one can determine the olivine saturation by various metal ions.

Results and Discussion. SEM (a) and XRF (b) for olivine, are presented in Fig. 1 and Tab. 1.

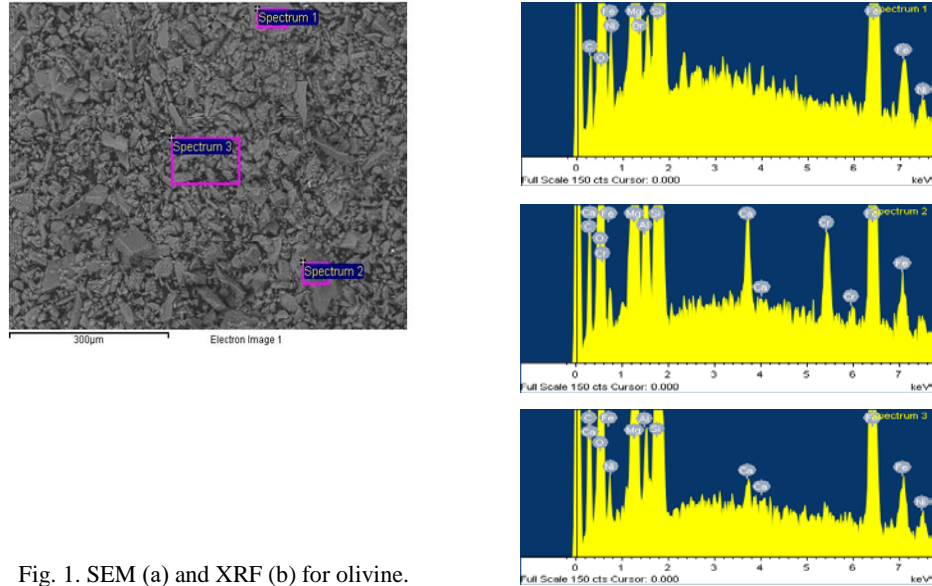


Fig. 1. SEM (a) and XRF (b) for olivine.

Table 1

XRF data for olivine

Element	Spectrum 1		Spectrum 2		Spectrum 3	
	weight, %	atomic, %	weight, %	atomic, %	weight, %	atomic, %
C	5.10	8.00	8.79	13.37	17.73	24.97
O	53.40	62.95	53.73	61.36	51.59	55.57
Mg	23.10	17.92	18.68	14.04	17.22	12.12
Al	-0.25	-0.17	2.76	1.87	0.29	0.19
Si	14.99	10.06	12.52	8.15	10.37	6.32
Ca	0.07	0.08	0.35	0.16	0.10	0.04
Cr	0.0	0.00	0.58	0.2	0.09	0.03
Fe	3.38	1.14	2.51	0.82	2.36	0.72
Ni	0.18	0.06	0.14	0.04	0.23	0.07
Br	0.08	0.01	-0.05	-0.01	-0.14	-0.03
Total	100		100		100	

The composition of the wastewater studied is presented in Tab. 2. It follows from Tab. 2, that all metals undergo sorption. After regeneration, the sorption capacity by metals mainly decreased. However, some metals retain adsorption capacity. In the case of strontium, it remains at the same level, while in the case of molybdenum, the sorption capacity decreases. Issuing from the data in Tab. 2, it is difficult to estimate the sorption capacity. So, one may to build the curves of sorption capacity for individual metals.

At the sample of potassium, it has been demonstrated the calculation of the sorption capacity (Tab. 3, Fig. 2, and Fig. 3). The same procedure was done for strontium (Fig. 4) and molybdenum (Fig. 5).

Table 2

Various metal sorption data (which do not precipitate at higher pH values)
on olivine (non-treated and after acid treatment)

Initial concentration in wastewater*	Li, $\mu\text{g/L}$	Na, mg/L	Mg, mg/L	K, $\mu\text{g/L}$	V, $\mu\text{g/L}$	As, $\mu\text{g/L}$	Sr, $\mu\text{g/L}$	Mo, $\mu\text{g/L}$	Ba, $\mu\text{g/L}$
	1.5	6.4	0.86	730	0.44	0.3	120	56	11
20	0.52	1.9	4.5	50	0.043	0.08	3.8	55	1.4
50	1.0	4.3	5.4	175	0.032	0.11	11	66	2.8
100	1.3	5.5	5.0	340	0.039	0.13	21	66	3.9
455	1.6	6.4	3.0	710	0.058	0.15	67	59	6.6
1125	1.6	6.5	1.8	800	0.085	0.16	98	59	7.6
1637	1.6	6.4	1.3	730	0.05	0.17	110	57	21
2425	1.6	6.4	0.97	750	0.11	0.20	120	57	9.8
3100	1.6	6.3	0.95	740	0.097	0.19	120	57	9.8
4490	1.6	6.2	0.95	720	0.13	0.18	120	57	9.8
	olivine (acid treated)								
	1.7	7.3	0.96	840	0.60	0.45	130	56	11
30	0.072	4.3	6.4	540	0.016	0.008	16	0.26	17
60	0.080	7.4	7.2	720	0.019	0.011	20	0.26	20
110	0.070	7.9	6.7	760	0.026	0.011	23	0.34	17
174	0.057	7.7	6.0	750	0.022	0.010	27	0.75	14
314	0.37	7.6	3.4	850	0.027	0.022	63	13	13
1119	1.3	7.6	1.3	870	0.087	0.15	120	52	11
1819	0.94	7.4	1.3	840	0.045	0.084	120	47	10

* The volume of the water passed through the column, mL .

Table 3

Determination of the sorption capacity of olivine towards metals (potassium in this case)
issuing from $1 - C/C_0 = f(V)$ equation

V, mL	C/C_0	$C_0, \mu\text{g/L}$	V, L	$1 - C/C_0$	V, L	$q, \mu\text{g/g}$	$y = 0.5531 \exp(-1.315x)$
20	0.068493	50	0.02	0.931507	0.02	0.053872	0.974
100	0.465753	340	0.10	0.534247	0.10	2.155912	0.8768
455	0.821918	600	0.455	0.178082	0.455	10.45618	0.5497
1125	0.931507	680	1.125	0.068493	1.125	20.09489	0.2278
1637	0.958904	700	1.637	0.041096	1.637	27.45961	0.1162
2425	0.972603	710	2.425	0.027397	2.425	31.38309	0.0412
3100	0.986301	720	3.10	0.013699	3.10	33.48177	0.017

Fig. 3 demonstrates the sorption capacity of olivine non-treated and acid-treated towards potassium. The sorption capacity of non-treated olivine is $30 \mu\text{g/g}$, while the sorption capacity after acid treatment is only $8 \mu\text{g/g}$, that is, the sorption capacity of olivine decreases by almost 4 times after acid treatment.

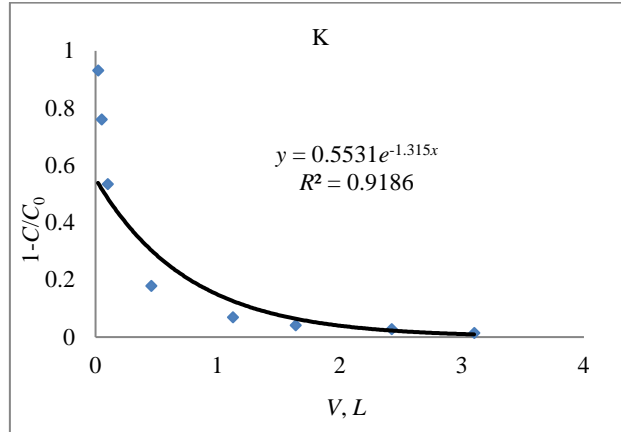


Fig. 2. The sorption of potassium on olivine.

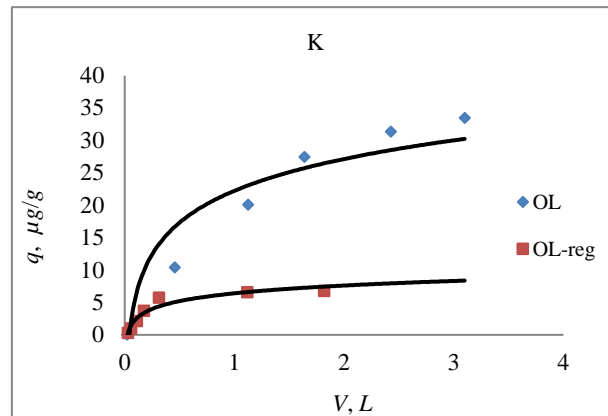


Fig. 3. The sorption capacity of olivine and acid-treated olivine by potassium.

The acid treatment practically does not influence the strontium sorption. The sorption capacity of olivine towards strontium is 7–8 $\mu\text{g/g}$. The same is the sorption capacity after acid treatment (Fig. 4).

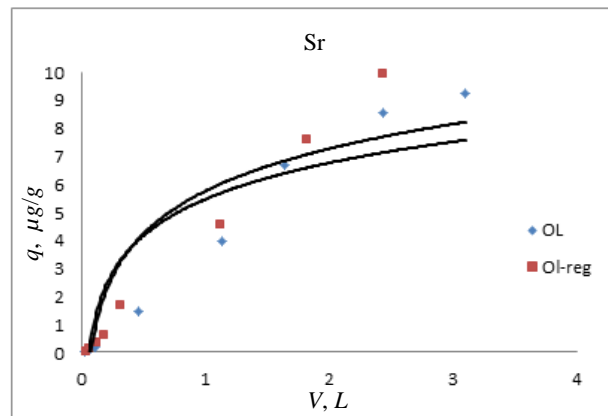


Fig. 4. The sorption capacity of olivine and acid-treated olivine by strontium.

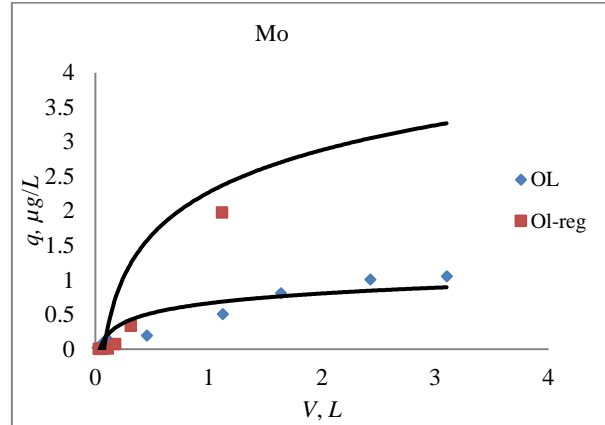


Fig. 5. The sorption capacity of olivine and acid-treated olivine by molybdenum.

In the case of molybdenum, the reverse picture was observed. The sorption capacity of the initial olivine towards molybdenum is $0.9 \mu\text{g/g}$, after acid treatment it increases to $3.2 \mu\text{g/g}$, i.e. after acid treatment the sorption capacity of olivine increases 3.6 times (Fig. 5).

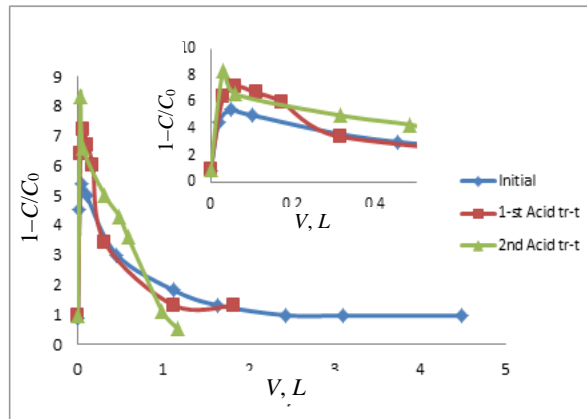
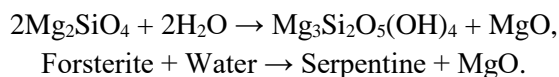


Fig. 6. Leaching of magnesium during the contact of olivine with water.

Mechanism of Adsorption. It was mentioned above that the sorption of metal ions on olivine may be a result of the substitution of magnesium ions in the olivine structure. It follows from Fig. 6, that when the volume of water passed through the column increases, magnesium content in water initially increases and then decreases gradually. After the acid treatment, the maximum magnesium content is $4.3 \mu\text{g/g}$. It means that in places, accessible for leaching, the deficiency of magnesium ions is observed, and it reflects on the magnesium leaching. It is important to note that during the acid treatment, the magnesium leaching will be much more than during the passing of wastewater through the column. Thus, one can state that the sorption of other ions takes place due to the substitution process. The scheme of serpentinization of Forsterite, which is also an olivine-type material, is described in [14]:



Forsterite is a magnesium-rich end-member of olivine materials and serpentine is a hydrous magnesium-iron phyllosilicate. Magnesium oxide MgO is released during this process, and it leads to the appearance of hydroxide ions and, as a result, to the increase in pH values. For some metals it is not at all sorption, but precipitation, because the majority of metals form hydroxide at higher pH values.

It is known, that Blueguard® 63 type olivine, upon contact with distilled water, increases pH values up to 10 [14]. Therefore, it is necessary to consider the mechanism of metal ions sorption on olivine just from this point of view.

The dissolution of magnesium during the contact of olivine with water passing through the column may become a key to explaining the mechanism of sorption on olivine. It would be also important to note that adsorption processes on olivine take place under adverse conditions (at pH 10 and higher). After all, for the sorption of the majority of metal ions weak-acid media (pH 4–6) are more optimal. In fact, olivine itself creates adverse conditions for sorption, however, at the same time it manages to sorb metal ions.

The investigation of the sorption process on olivine at lower pH values is meaningless, because more intensive leaching of magnesium will take place at lower pH, and it will interfere with sorption processes. One can suppose that during the acid treatment and due to the substitution of magnesium ions by other metal ions, their sorption will take place. A somewhat different picture was observed, when olivine undergoes acid treatment. The leaching of magnesium continues (not to speak of the leaching during the acid treatment). After such acid treatment, the sorption capacity mainly decreases, however, the sorption of some metals, such as strontium and molybdenum, remains at the same level or increases.

It follows from Fig. 6, that the sorption of some metals was accompanied by the substitution of magnesium cations. The latter transfers to the solution and magnesium content in it decreases 7.5 times (from 0.9 mg/L up to 7.2 mg/L). After regeneration, the magnesium content in the solution increases 5.8 times (from 0.86 mg/L up to 5.0 mg/L). It is necessary to account for desorption processes during the water passing through the column, because there are no specific functional groups on the olivine surface, which could irreversibly adsorb metal ions.

Conclusion. The Blueguard® 63 type olivine, as the sorption material, can extract metals from wastewater. The sorption takes place together with magnesium leaching from the olivine structure, which is the opposite event happening at the same time, indicating that the sorption mechanism is the magnesium ions' substitution by metal ions.

The regeneration process (acid treatment) for the majority of metal ions leads to the sorption capacity decrease. In the case of strontium, such treatment does not influence the sorption capacity, and in the case of molybdenum, the reverse picture is observed – after the acid treatment the increase of the capacity is observed.

Received 12.05.2023

Reviewed 14.06.2023

Accepted 28.06.2023

REFERENCES

1. Kalinowski B.E., Oscarsson A., et al. Microbial Leaching of Uranium and Other Trace Elements from Shale Mine Tailings at Ranstad. *Geoderma* **122** (2004), 177–194.
<https://doi.org/10.1016/j.geoderma.2004.01.007>
2. Jeng A.S. Weathering of Some Norwegian Alum Shales, II. Laboratory Simulations to Study the Influence of Aging, Acidification, & Liming on Heavy Metal Release. *Acta Agric. Scand.* **42** (1992), 76–87.
<https://doi.org/10.1080/09064719209410203>
3. Andersson A., Siman G. Levels of Cd and Some Other Trace Elements in Soils and Crops as Influenced by Lime and Fertilizer Level. *Acta Agric. Scand.* **41** (1991), 3–11.
<https://doi.org/10.1080/00015129109438579>
4. McLaughlin R.A., Bartholomeew N. Effects of Polyacrylamide and Soil Properties on Flocculation. *Soil Science Society of America Journal* **71** (2007), 537–544.
5. Novoselova L.Yu., Sirotkina E.E. Peat-Based Sorbents for the Purification of Contaminated Environments: A Review. *Solid Fuel Chemistry* **42** (2008), 251–262.
<https://doi.org/10.3103/S0361521908040125>
6. Yeh J.T., Chen C.L., Huang K.S. Synthesis and Properties of Chitosan/SiO₂ Hybrid Materials. *Mater. Lett.* **61** (2007), 1292–1295.
<https://doi.org/10.1016/j.matlet.2006.07.016>
7. Morais L.C., Freitas O.M., et al. Reactive Dyes Removal from Wastewaters by Sorption on Eucalyptus Bark: Variables That Define the Process. *Water Res.* **33** (1999), 979–988.
[https://doi.org/10.1016/S0043-1354\(98\)00294-2](https://doi.org/10.1016/S0043-1354(98)00294-2)
8. Zamora R.M., Schouwenaars R., et al. Production of Activated Carbon from Petroleum-Coke and Its Application in Water Treatment for the Removal of Metals and Phenol. *G. Water Sci. Technol.* **42** (2000), 119–126.
<https://doi.org/10.2166/wst.2000.0505>
9. Bilgin B., Atun G., Keçeli G. Adsorption of Strontium on Illite. *J. Radioanal. Nucl. Chem.* **250** (2001), 323–328.
<https://doi.org/10.1023/A:1017960015760>
10. Tsai S.C., Ouyang S., Hsu C.N. Sorption and Diffusion Behavior of Cs and Sr on Bentonite. *Appl. Radiat. Isot.* **54** (2001), 209–215.
[https://doi.org/10.1016/S0969-8043\(00\)00292-x](https://doi.org/10.1016/S0969-8043(00)00292-x)
11. Atun G., Kilislioglu A. Adsorption Behavior of Cs on Montmorillonite-type Clay in the Presence of Potassium Ions. *J. Radioanal. Nucl. Chem.* **258** (2003), 605–611.
<https://doi.org/10.1023/b:jrmc.0000011757.59069.ba>
12. Stout S.A., Cho Y., Komarneni S. Uptake of Cesium and Strontium Cations by Potassium Depleted Phlogopite. *Appl. Clay Sci.* **31** (2004), 306–313.
<https://doi.org/10.1016/j.clay.2005.10.008>
13. Westholm L.J., Repo E., Sillanpää M. Filter Materials for Metal Removal from Mine Drainage. A Review. *Environ Sci. Pollut. Res Int.* **21** (2014), 9109–9128.
<https://doi.org/10.1007/s11356-014-2903-y>
14. Hamilton F. Wastewater Treatment Using Mineral-Based Materials. Ph.D. Thesis. University of Surrey. © F. Hamilton (2016), 159.

Մ. Ս. ՀԱՅՐԱՊԵՏՅԱՆ, Ս. Ս. ՀԱՅՐԱՊԵՏՅԱՆ, Հ. Գ. ԽԱՉԱՏՐՅԱՆ

ՕԼԻՎԻՆ ԳԱՐՈՒՆԱԿՈՂ ԿԼԱՆԻԶՆԵՐ ԾԱՆՐ ՄԵՏԱՂՆԵՐԻ
ՀԵՌԱՑՄԱՆ ՀԱՄԱՐ

Ինդիցտիվորեն կապված պլազմա-մասս-սպեկտրաչափական (ISP-MS) և սկանավորող էլեկտրոնա ֆլուրեսցենցենտ (SEM-XRF) մեթոդներն օգտագործվել են օլիվինի կլանիչ հատկություններն ուսումնասիրելու համար:

Ցույց է տրվել, որ օլիվինը կարող է կիրառվել որպես էժան և հասանելի նյութ մետաղների, այդ թվում նաև ծանր, հոսքաջրերից կլանելու համար: Օլիվինի համեմատաբար ցածր կլանումային տարողությունը փոխհատուցվում է ցածր արժեքով և հասանելիությամբ: Օլիվինի մակերևույթին կլանման մեխանիզմը հնարավոր է նկարագրել որպես տարբեր մետաղների կատիոններով մագնեզիումի կատիոնների փոխանակում: Որոշակի միտում գոյություն ունի՝ մետաղների իոնային շառավղի մեծացման հետ մեկտեղ մեծանում է դրանց կլանումը: Սակայն ամեն բան իոնային շառավղի հետ կապելը հազիվ թե հնարավոր է: Իր դերն է խաղում նաև յուրաքանչյուր տարրի առանձնահատկությունը:

M. C. АЙРАПЕТАН, С. С. АЙРАПЕТАН, А. Г. ХАЧАТРИАН

ОЛИВИН-СОДЕРЖАЩИЕ СОРБЕНТЫ ДЛЯ УДАЛЕНИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ

Для изучения сорбционных свойств оливина использованы методы индуктивно-связанной плазмы–масс-спектрометрии (ISP-MS) и сканирующей микроскопии (SEM-XRF). Показано, что оливин может быть использован в качестве дешевого и доступного материала для сорбции металлов, в том числе и тяжелых, из сточных вод. Сравнительно небольшая сорбционная емкость оливина окупается его доступностью и дешевизной. Механизм адсорбции на поверхности оливина может быть описан как замещение катионов магния на катионы различных металлов. Есть некая тенденция – с увеличением ионного радиуса металлов их сорбция увеличивается. Однако связывать все с ионным радиусом металла вряд ли можно. Свою роль играет также специфичность каждого элемента.