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IMPACT OF THE UREA NITRATE CONTENT IN THE LEACHING SOLUTION ON THE GRANITE WEIGHT DECREASE AND THE FLUORIDE ION CONCENTRATION

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Abstract: The paper presents the results of the study on the impact of the initial concentration of urea nitrate and fluoride ion in the leaching solution on the weight decrease of granite mined at Prydniprovsk Specialized Quarry and the change in the fluoride ion concentration in the solution during intermittent and continuous agitation. During the experiments, we used urea nitrate with weight fraction of nitrate acid 41.5%, urea - 44.3%, water - 14.2%, and ammonium fluoride-bifluoride (fluorine content was 61.2%). Fluoride ion concentration was measured using a fluoride-selective electrode relatively a saturated silver chloride half-cell while the acidity of solutions was measured by titrimetry. Weight decrease was studied for a granite sample, grain fraction -2.0 + 1.0 mm, during intermittent stirring depending on the initial concentration of urea nitrate 0.25 g/dm^3, 0.5 g/dm^3, and 1.0 g/dm^3 and fluoride ion 2.81×10^{-2} g/dm^3 to 3.20×10^{-1} g/dm^3 with intermittent stirring at a temperature of 20±2 °C for 7 days. The data on the change in sample weight depending on the initial concentration of fluoride ion and addition of urea nitrate were received. It was revealed that the decrease in the fluoride ion concentration ambiguously depended on the initial concentration of both urea nitrate and fluoride ion. In our opinion, the fluoride ion concentration decrease occurred with adding urea nitrate due to the fact that nitric acid urea could form adducts with both sulfuric and fluoric acids resulting in the decrease of their reactivity. We have studied the decrease of the granite sample weight and the change in the fluoride ion concentration under continuous stirring and at a temperature of 30±2 °C for 4 days. It was found that the change in the sample weight and concentration of fluoride ion during continuous stirring differed from the similar data obtained during intermittent stirring due to more intensive formation of urea nitrate adducts with sulfuric and fluoride acids. The initial dissolution rate was calculated for a granite sample, its value was 2.384×10^{-7} s^{-1} after adding urea nitrate and 2.299×10^{-7} s^{-1} without its addition.

Keywords: granite, urea nitrate, ammonium bifluoride, weight decrease, fluoride ion.

1. Introduction

To intensify uranium leaching from refractory ores, ammonium fluoride-bifluoride is currently used ensuring the destruction of the crystal lattice of coherent uranium-containing minerals with high silica content. Silicon dioxide presents as feldspar, quartz and silicates that form solid structures with inclusions of uranium minerals: brannerite, pitch blende, etc. Therefore, standard methods for leaching such ores, even using oxidizing agents, do not provide complete uranium recovery [1].

This work is an integral part of the study of the impact of intensifying additives based on ammonium fluoride-bifluoride and urea nitrate on the destruction of the crystal lattice of refractory uranium-bearing ores [2, 3]. The effect of the initial concentration of fluoride ion and sulfuric acid in the leaching solution on the decrease of granite weight mined at Prydniprovsky Specialized Quarry was studied [2]. The data on the decrease in the granite sample weight and fluoride ion content in the leaching solution vs. the exposure time, the concentration of fluoride ion and sulfuric acid during intermittent stirring mode were given. It was defined that the fluoride ion concentration depended ambiguously on exposure time, the initial concentration of fluoride ion and sulfuric acid, and even resulted in its increase, which is probably due to the dissolution of fluoride-containing minerals (mica, fluorite, etc.) in samples. The results [3] on rock transformations were given for biotite granites (subway construction), amphibole-magnetite of biotite-quartz aposhale and granite mined at Prydniprovsk Specialized Quarry. Ammonium fluoride-bifluoride and urea nitrate were added to intensify the structural breakdown of resistant minerals contained uranium.

It is known [4, 5] that sulfuric acid is most commonly used for uranium leaching since it is the most common, cheapest, and low-volatile. Sulfuric acid leaches tetravalent uranium very slowly. To increase the leaching degree and rate, oxidizing agents are added: nitric acid, air oxygen, sodium chlorate, etc., which convert tetravalent uranium to hexavalent one.

Previously, we proposed to use urea adduct with nitric acid (urea nitrate) for uranium oxidation [6]. A method was designed to produce urea nitrate including zirconium production waste as a source material [7-9].

This paper present the results of the study regarding the impact of the initial concentration of fluoride ion and urea nitrate in the leaching solution on the weight decrease of granite mined at Pridniprovsk Specialized Quarry and decrease in the fluoride ion concentration in the leaching solution during intermittent and continuous stirring.

2. Experimental

The study was carried out using ground and sieved granite sample taken from Pridniprovsk Specialized Quarry, fraction -2.0 + 1.0 mm, sieved using MLW Thyr 2 laboratory vibrating sieve. Urea nitrate was used in experiments featured the following parameters: weight fraction was 41.5 % for nitric acid, 44.3 % for urea and 14.2 % for water. Ammonium fluoride-bifluoride (with 61.2 % fluoride content) and 40 % sulfuric acid, reagent grade, were used during the experiments. Reagent concentrations in solutions were selected based on technological processes used in the uranium industry [4]. Weight decrease for granite samples was measured using the procedure described earlier [2].

Fluoride ion concentration was measured using an ELIS-131F fluorine-selective electrode relatively EV1-1M3 saturated silver chloride half-cell by using an MV-88 pH-meter [10]. Reagents used during the measurement were at least reagent grade. The acidity of solutions was measured by titrimetry.

3. Results and discussion

Impact of urea nitrate and fluoride ion concentration on the granite weight decrease and the fluoride ion content under intermittent agitation. The decrease of the granite sample weight was studied under intermittent agitation at the solid-to-liquid phase ratio S:L=1:100 (sample weighed portion was ~10 g) depending upon the initial concentration of urea nitrate 0.25 g/dm^3, 0.5 g/dm^3 and 1.0 g/dm^3 and fluoride ion 2.81×10^{-2} g/dm^3 to 3.20×10^{-1} g/dm^3 at a temperature of 20 °C and intermittent agitation once per day during 7 days. Sulfate acid concentration was 18.8 g/dm^3 and typical [4, 11] to ensure maximum sorption capacity of anionites during further uranium recovery.

The decrease of granite sample weight (Δm, %) was calculated depending on initial concentration of fluoride ion ([F^-], g/dm^3) and urea nitrate using the equation:

$$\Delta m = \frac{m_1 - m_2}{m_1} \times 100 \quad (1)$$

where: m_1 is sample weight before treatment, g; m_2 is sample weight after treatment, g. Results are given in Table 1 and Figure 1.

Table 1 – Weight decrease of a granite sample

Fluoride ion initial concentration [F^-], g/dm^3	Sample weight before treatment m_1, g	Sample weight after treatment m_2, g	Weight decrease Δm, %
[$(NH_2)_2CO{\cdot}HNO_3$] = 0.25 g/dm^3			
3.31×10^{-2}	9.985	9.851	1.34
1.52×10^{-1}	9.987	9.787	2.00
3.20×10^{-1}	9.997	9.726	2.71
[$(NH_2)_2CO{\cdot}HNO_3$] = 0.5 g/dm^3			
2.81×10^{-2}	9.989	9.847	1.42
1.46×10^{-1}	9.986	9.771	2.15
3.18×10^{-1}	9.992	9.743	2.49
[$(NH_2)_2CO{\cdot}HNO_3$] = 1.0 g/dm^3			
3.18×10^{-2}	9.989	9.854	1.36
1.46×10^{-1}	9.991	9.798	1.93
3.18×10^{-1}	9.999	9.723	2.76

Experimental data were processed using the second-order polynomial, results are shown in Figure 1; polynomial equation is:

$$\Delta m = 1.685+6.386{\cdot}x+0.1288{\cdot}y-6.427{\cdot}x^2+0.5415{\cdot}x{\cdot}y-0.1599{\cdot}y^2 \quad (2)$$

where: x is urea nitrate concentration, g/dm^3, y is fluoride ion concentration, g/dm^3. Determination factor (R^2) was 0.9722.

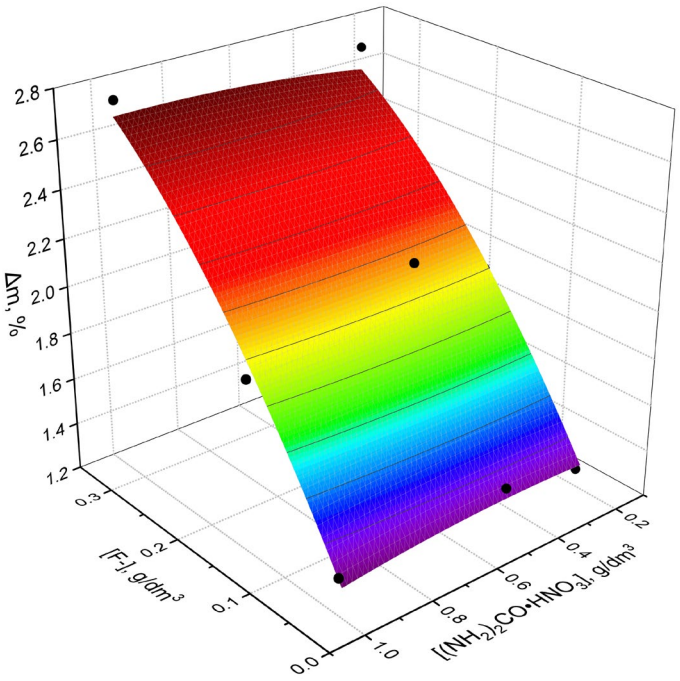


Figure 1 – Decrease of granite sample weight vs. the concentration of urea nitrate and fluoride ion

As it can be seen from the above data, Δm increased proportionally to the increase of the fluoride ion initial concentration and almost did not change when adding urea nitrate. Thus, urea nitrate addition to the solution with a variable fluoride ion content resulted in the Δm decrease in average by 1.37 % for the lowest initial fluoride ion concentration at all concentrations of urea nitrate, by 2.03 % for the average fluoride ion content, and by 2.65 % for the highest one. At the same time, the Δm value during the 7-day contact without adding urea nitrate [2] to solutions with similar content of sulfuric acid and fluoride ion was 1.80 %, 2.55 %, and 3.06 %, correspondingly.

Thus, adding urea nitrate resulted in the Δm decrease by 23.9 % for the minimum initial concentration of fluoride ion, by 20.4 % for its middle content and by 13.4 % for the maximum one.

Table 2 and Figure 2 contain the data on the decrease of fluoride ion concentration ($\Delta[F^-]$) depending on the initial concentration of fluoride ion ($[F^-]$) and urea nitrate in the intermittent stirring mode.

Experimental data were processed using the second-order polynomial, results are shown in Figure 2; the polynomial equation is:

$$\Delta[F^-] = 0.0169\text{-}0{,}0087 \cdot x\text{-}0{,}0357 \cdot y\text{-}0{,}07 \cdot x^2\ 0{,}0497 \cdot x \cdot y + 0{,}026 \cdot y^2 \qquad (3)$$

where: x is urea nitrate concentration, g/dm^3, y is fluoride ion concentration, g/dm^3. Determination factor (R^2) was 0.9364.

Table 2 – Decrease of fluoride ion concentration in the leaching solution during intermittent stirring

Initial concentration of fluoride ion $[F^-]$, g/dm^3	Residual concentration of fluoride ion $[F^-]_{res.}$ g/dm^3	Decrease of fluoride ion content $\Delta[F^-]$, g/dm^3
$[(NH_2)_2CO \cdot HNO_3]$ = 0.25 g/dm^3		
3.31×10^{-2}	2.29×10^{-2}	1.02×10^{-2}
1.52×10^{-1}	143×10^{-1}	9.1×10^{-3}
3.20×10^{-1}	3.17×10^{-1}	2.6×10^{-3}
$[(NH_2)_2CO \cdot HNO_3]$ = 0.5 g/dm^3		
2.81×10^{-2}	2.31×10^{-2}	4.9×10^{-3}
1.46×10^{-1}	1.40×10^{-1}	5.9×10^{-3}
3.18×10^{-1}	3.13×10^{-1}	5.2×10^{-3}
$[(NH_2)_2CO \cdot HNO_3]$ = 1.0 g/dm^3		
3.18×10^{-2}	2.29×10^{-2}	8.9×10^{-3}
1.46×10^{-1}	1.34×10^{-1}	1.15×10^{-2}
3.18×10^{-1}	3.05×10^{-1}	1.28×10^{-2}

It should be noted that the decrease in the fluoride ion concentration ambiguously depended on the initial concentration of both urea nitrate and fluoride ion. Thus, fluoride ion concentration decreased from 1.02×10^{-2} g/dm^3 to 2.6×10^{-3} g/dm^3 at the urea nitrate concentration 0.25 g/dm^3 and initial fluoride ion content 3.31×10^{-2} g/dm^3 to 3.20×10^{-1} g/dm^3,. The smallest decrease in the fluoride ion concentration from 4.9×10^{-3} g/dm^3 to 5.9×10^{-3} g/dm^3 was observed with an extreme area at initial fluo-

ride ion concentration 1.46×10^{-1} g/dm^3 at urea nitrate concentration 0.5 g/dm^3 and initial fluoride ion content 2.81×10^{-2} g/dm^3 to 3.18×10^{-1} g/dm^3.

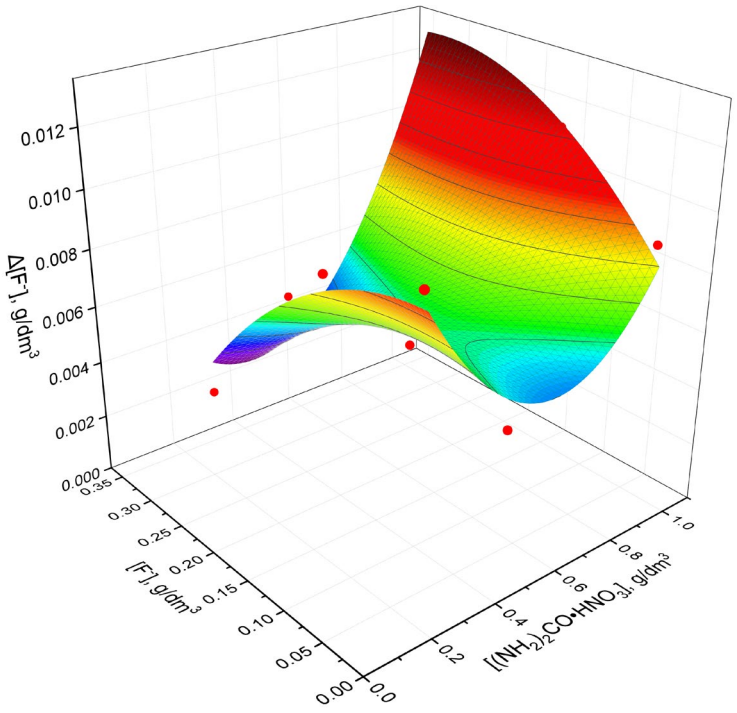


Figure 2 – Decrease of the fluoride ion content vs. the concentration of urea nitrate and fluoride ion

We observed a maximum decrease in the fluoride ion concentration from 8.9×10^{-3} g/dm^3 to 1.28×10^{-2} g/dm^3 for urea concentration 1 g/dm^3 and initial fluoride ion content 3.18×10^{-2} g/dm^3 to 3.18×10^{-1} g/dm^3.

Impact of urea nitrate and fluoride ion concentrations on granite weight decrease and the change of fluoride ion content under continuous agitation. The decrease in the granite sample weight and the change in the fluoride ion concentration were studied under continuous stirring at a temperature of 30±2 °C for 4 days with sampling every 24 hours. Samples were stirred using an MLW ER 10 propeller-type stirrer, the temperature was maintained by a MLW UH8 thermostat. Phase ratio was S:L=1:100 (sample weight was ~10 g), reagent concentration was 18.8 g/dm^3 for sulfuric acid and 0.25 g/dm^3 for urea nitrate. The initial concentration of fluoride ion was 3.14×10^{-2} g/dm^3 in the experiment with adding urea nitrate and 3.31×10^{-2} g/dm^3 without its addition.

Table 3 shows the decrease in the granite sample weight depending on the contact time without and with the urea nitrate addition.

The above data show that the sample weight decrease almost did not change after adding urea nitrate. Thus, after 4 days of contact, the difference between Δm values obtained after adding urea nitrate and without its addition was about 1 %.

It should be noted that this value significantly differed from Δm in the experiment with intermittent agitation, which was ~24 %. In our opinion, the results observed may be explained by the intensified formation of urea nitrate adducts with sulfuric and fluoric acids during continuous agitation.

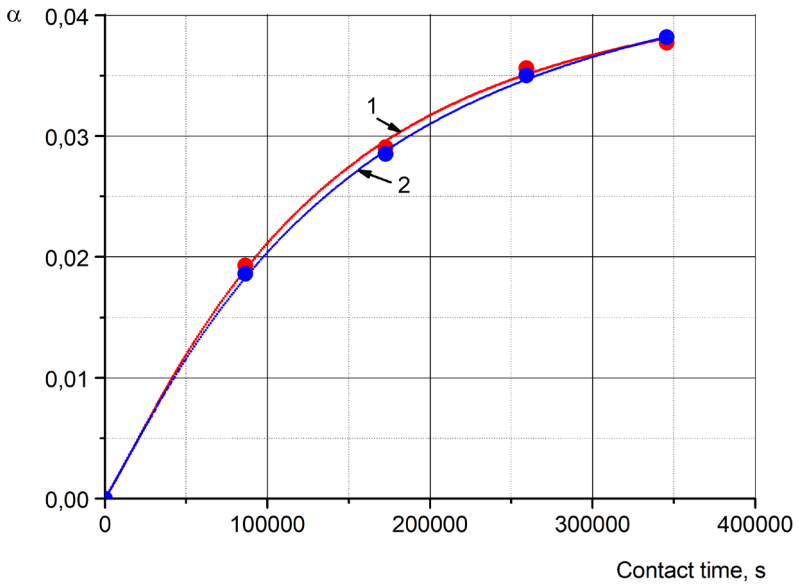
Table 3 – Weight decrease for granite samples

Contact time, days	Sample weight before treatment m_1, g	Sample weight after treatment m_2, g	Weight decrease Δm, %
Without adding urea nitrate			
1	9.992	9.806	1.86
2	9.992	9.707	2.85
3	9.992	9.642	3.50
4	9.992	9.610	3.82
$[(NH_2)_2CO \cdot HNO_3]$ = 0.25 g/dm^3			
1	10.000	9.807	1.93
2	10.000	9.709	2.91
3	10.000	9.644	3.56
4	10.000	9.623	3.77

Figure 3 illustrates the dissolution degree of a granite sample depending on the contact time (in seconds). The dilution degree (α) was calculated using the formula:

$$\alpha = \frac{m_1 - m_2}{m_1} \quad (4)$$

where: m_1 is sample weight before treatment, g; m_2 is sample weight after treatment, g.



1 – with adding urea nitrate, 2 – without adding urea nitrate

Figure 3 – Dilution degree of a granite sample vs. the contact time

The initial dissolution rate (k_0) of the granite sample [12] was calculated by the slope ratio of the tangent line to the dissolution curve (Figure 3), which started from the origin. It should be noted that $k_0 = 2.384 \times 10^{-7}$ s^{-1} when adding urea nitrate is almost the same as $k_0 = 2.299 \times 10^{-7}$ s^{-1} without adding urea nitrate.

Table 4 contains data on the $\Delta[F^-]$ change in the leaching solution during intermittent agitation.

Table 4 – Decrease of fluoride ion concentration during intermittent stirring

Exposure time, days	Initial concentration of fluoride ion $[F^-]$, g/dm^3	Residual concentration of fluoride ion $[F^-]_{res}$, g/dm^3	Decrease of fluoride ion content $\Delta[F^-]$, g/dm^3
Without adding urea nitrate			
1	3.31×10^{-2}	2.69×10^{-2}	6.2×10^{-3}
2	3.31×10^{-2}	2.59×10^{-2}	7.2×10^{-3}
3	3.31×10^{-2}	2.48×10^{-2}	8.3×10^{-3}
4	3.31×10^{-2}	2.45×10^{-2}	8.6×10^{-3}
$[(NH_2)_2CO\cdot HNO_3] = 0.25$ g/dm^3			
1	3.14×10^{-2}	2.75×10^{-2}	3.9×10^{-3}
2	3.14×10^{-2}	2.66×10^{-2}	4.8×10^{-3}
3	3.14×10^{-2}	2.58×10^{-2}	5.6×10^{-3}
4	3.14×10^{-2}	2.54×10^{-2}	5.9×10^{-3}

It may be seen from the data above that the addition of urea nitrate resulted in the $\Delta[F^-]$ decrease in the leaching solution. Thus, this value was 8.6×10^{-3} g/dm^3 without adding urea nitrate and 5.9×10^{-3} g/dm^3 with adding urea nitrate, even though the initial concentration of fluoride ion in the solution without adding urea nitrate was higher than in the initial solution with its addition.

In our opinion, granite weight and fluoride ion concentration decreased after adding urea nitrate because urea nitrate could form adducts both with sulfuric and fluoric acids.

4. Conclusions

The impact of the initial concentration of fluoride ion and urea nitrate on the decrease of the granite sample weight and fluoride ion concentration in the leaching solution during intermittent and continuous agitation was studied. It was found that the decrease in sample weight increased proportionally to the increase of the initial concentration of fluoride ion and almost did not change after adding urea nitrate.

It was established that the decrease in the fluoride ion concentration depended ambiguously on the initial concentration of both urea nitrate and fluoride ion. The decrease in fluoride ion concentration occurred after adding urea nitrate due to possible formation of urea nitrate adducts with both sulfuric and fluoric acids resulting in their reactivity decrease.

The values of the decrease in granite weight and fluoride ion concentration during continuous agitation differed from those for intermittent one due to the intensified formation of urea adducts with sulfuric and fluoric acids.

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REFERENCES

1. Gulyuta, M.A., Andreev, V.A., Buinovskiy, A.S., Makaseev, Yu.N., Molokov, P.B., Sofronov, V.L., and Ivanov, Z.S. (2014), "Research of Activation of Persistent Uranium Ores by Ammonium Fluoride Solutions", *Bulletin of the Tomsk Polytechnical University,* vol. 324, no. 3, pp. 53–59.

2. V.Yu. Korovin, Yu.M. Pohorielov, Yu.G. Shestak, and O.M. Valiaiev (2022), "Impact of the Fluoride Ion and Sulfuric Acid Content in Leaching Solution on the Granite Weight Decrease", *Geo-Technical Mechanics*, no. 160, pp. 142–153. https://doi.org/10.15407/geotm2022.160.141

3. Baranov, V.A., Mametova, L.F., and Korovin, V.Yu. (2020), "Modelling of Metasomatosis in Radiogenic Rocks as a Factor of Transformation of Their Properties", *Geophysical Journal*, vol. 42, no. 1, pp. 86–95. https://doi.org/10.24028/gzh.0203-3100.v42i1.2020.195478

4. Babak, M.I., Koshik, Yu.I., Avdeev, O.K., Bezrodnyi, S.A. and Saveliev, Yu. Ya. (2001), *"Dobycha I Pererabotka Uranovykh Rud v Ukraine"* [Uranium Ore Mining and Processing in Ukraine], in Chernov, A.P.(ed.), ADEF-Ukraina, Kyiv, Ukraine.

5. Verkhovtsev, V.G., Lisichenko, G.V., Zabulonov, Yu.L., and Vozniak, D.K. (2014), "*Perspektivy rozvytku uranovoyi syrovynnoyi bazy yadernoyi energetyky Ukrayiny"* [Prospects for the Development of Uranium Resource Base of Nuclear Power of Ukraine], Scientific Book Project. Naukova Dumka, Kyiv, Ukraine.

6. Skrypko, M.M., Korovin, Yu.F., Korovin. V.Yu., Pohorielov Yu.M., Merkulov V.A. and Rozhkov, E.M. «Rekord LLC» (2010), *Sposib vyluchennia uranu* [Uranium recovery method], State Register of Patents of Ukraine, Kiev, UA, Pat. № 49189.

7. Skrypko, M.M., Korovin, Yu.F., Korovin. V.Yu., Ivanov, A.Zh. and Pohorielov Yu.M., «Rekord LLC» (2005), *Sposib oderzhannia vazhkozaimystogo azontokyslogo karbamidu* [Production method for highly flammable urea nitrate], State Register of Patents of Ukraine, Kiev, UA, Pat. № 7700.

8. Skrypko, M.M., Korovin, Yu.F. and Korovin. V.Yu. «Rekord LLC» (2007), *Sposib utylizatsii azotnokyslykh rozchiniv I filtrativ* [Utilization method for nitric solutions and filtrates], State Register of Patents of Ukraine, Kiev, UA, Pat. № 77721.

9. Valyaeva, E.V., Korovin Yu.,F., Pogorelov, Yu.G., Korovin, V.Yu., Shestak, Yu.G., Barkova, V.V. and Skripko, N.N. (2011), "The Study into the Laws Governing the Nitrate Carbamide Recovery from Nitric Acid Solutions Used in the Zirconium Production Process", *Cooperation to Solve the Waste Problems: VIII International Conference, Kharkov, Ukraine, February 23–24, 201, Conference proceedings*, https://waste.ua/cooperation/2011/theses/index.html

10. Midgley, D., and Torrans, K. (1980), *Potentsiometricheskiy Analiz Wody* [Potentiometric Water Analysis], Translated by Kahan, B.B., in Mairanovskiy, S.G. (ed.), Mir Publ., Moscow, USSR.

11. Korovin, V.,Valiaiev, O, Zontov, O., Zontona, L., Pilchyk, V. and Pysmennyi, B (2019), "Uranium (VI) Sorption from Sulphuric Solutions by AM-p-2 Anionite", *Essays of Mining Science and Practice 2019, E3S Web of Conferences*, Dnipro, Ukraine, 09 July 2019, pp.1–8. https://doi.org/10.1051/e3sconf/201910900039

12. Zelikman, A.N., Voldman, G.M., and Beliaevaksya, L.V. (1983), "*Teoriia gidrometallurgicheskikh protsessov"* [Hydrometallurgical Process Theory], Metallurgiia, Moscow, USSR.

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ВПЛИВ ВМІСТУ АЗОТНОКИСЛОГО КАРБАМІДУ У РОЗЧИНІ ДЛЯ ВИЛУГОВУВАННЯ НА ЗНИЖЕННЯ МАСИ ГРАНІТУ ТА КОНЦЕНТРАЦІЮ ФЛУОРИД-ІОНУ

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Анотація. В роботі наведені результати дослідження впливу початкової концентрації нітрату карбаміду та фторид-іону у розчині для вилуговування на зменшення маси граніту, що видобувається на Придніпровському спеціалізованому кар'єрі, та зміну концентрації фторид-іону у розчині при періодичному та безперервному перемішуванні. В експериментах використовували азотнокислий карбамід з масовою часткою нітратної кислоти 41,5 %, сечовини - 44,3 %, води - 14,2% та фторид-біфторид амонію (вміст фтору - 61,2%). Концентрацію фторид-іонів вимірювали за допомогою фторид-селективного електрода відносно насиченого хлор-срібного електроду, а кислотність розчинів визначали титриметричним методом. Зменшення маси досліджували для зразка граніту з фракцією -2,0 + 1,0 мм при періодичному перемішуванні залежно від початкової концентрації азотнокислого карбаміду 0,25 г/дм^3, 0,5 г/дм^3 та 1,0 г/дм^3 та іонів фтору від 2,81×10^{-2} г/дм^3 до 3,20×10^{-1} г/дм^3 при періодичному перемішуванні при температурі 20±2 °С протягом 7 діб. Отримані дані про зміну маси зразка залежно від початкової концентрації фторид-іону та додавання азотнокислого карбаміду. Виявлено, що зменшення концентрації фторид-іону неоднозначно залежало від початкової концентрації як азотнокислого карбаміду, так і фторид-іону. На

нашу думку, зниження концентрації фторид-іону при додаванні азотнокислого карбаміду пов'язане з тим, що азотнокислий карбамід може утворювати адукти як з сульфатною, так і з фтористоводневою кислотами, що призводить до зниження їх реакційної здатності. Досліджено зменшення маси зразка граніту та зміну концентрації фторид-іону при безперервному перемішуванні та температурі 30±2 °С протягом 4 діб. Встановлено, що зміна маси зразка і концентрації фторид-іонів при безперервному перемішуванні відрізняється від аналогічних даних, отриманих при періодичному перемішуванні, за рахунок більш інтенсивного утворення адуктів нітрату сечовини з сірчаною і фтористою кислотами. Початкова швидкість розчинення була розрахована для зразка граніту, її значення склало 2,384×10-7 с-1 після додавання нітрату сечовини і 2,299×10-7 $с^{-1}$ без його додавання.

Ключові слова: граніт, азотнокислий кабамід, біфлуорид амонію, зниження маси, флуорид-іон.