UDC 622.234.42

B. TOKTARULY[1], *Candidate for a Doctor's Degree, starbaha@yandex.ru*
A. BAYESHOV[2], *Doctor of Chemical Sciences*
Y. ABEN[1], *Assistant, Candidate of Engineering Sciences*
Sh. K. SULEIMENOV[1], *Student*

[1] *Satbayev University, Almaty, Kazakhstan*
[2] *Sokolskiy Institute of Fuel, Catalisys and Electrochemistry, Almaty, Kazakhstan*

EFFECT OF PROCESS SOLUTION SATURATION WITH OXYGEN ON URANIUM IN-SITU LEACHING PERFORMANCE

One of the effective methods of mining low-grade uranium deposits is the in-situ leaching technology. On the other hand, in difficult geological conditions, this technology fails to provide the desired effect and increases duration of mining, which, eventually, evaluates production costs.

Feasibility of increasing uranium content in pregnant solution and reducing production period is governed by ferric iron concentration in process solution. For increasing the ferric iron concentration and, thus, the content of uranium in pregnant solution in uranium in-situ leaching, it is proposed to saturate the leach solution with atmospheric oxygen using the Venturi tube. The lab-scale tests of core materials for determining dependence of the uranium content in the pregnant solution on the oxygen concentration in the leach solution prove the advantages of the proposed technology of uranium in-situ leaching.

According to many researchers, the uranium recovery in the pregnant solution in in-situ leaching depends on the degree of saturation of the leaching solutions with oxygen capable to oxidize ferrous iron (Fe_2) to ferric iron (Fe_3) and, thereby, to stimulate oxidizability of the leaching environment. The objective of the studies was to determine parameters of saturation of process solutions with oxygen.

Keywords: *deposit, geotechnology, mining, block, in-situ leaching, oxygen, air, uranium, leaching solution*
DOI: *10.17580/em.2022.02.12*

Introduction

Kazakhstan holds world's second largest uranium reserves and round 74% of uranium reserves suitable for in-situ leaching. The unique feature of Kazakhstan's uranium reserves is their occurrence nearby the regional zones of oxidation. Such deposits are rare in the world and are extracted using the advanced, comparatively cheap and environmentally preferable technology of in-situ leaching [1, 2]. In the in-situ leaching technology, ore at its resting place is pumped through with the leaching solutions. Accordingly, the soil mantle remains almost intact, and no waste dumps and tailings appear on ground surface. As compared with the conventional mineral mining, the in-situ leaching technology eases of the short-term and long-term impact on population, extremely reduces the radioactivity level with a very few radwaste and ends with no tailings at all [3].

The cost of the in-situ leaching is 2.5–3 times lower than the cost of underground mining, while the recovery efficiency of ISL ranges from 49% to 88% at the average value of 65% [4], and, for this reason, this technology remains the most promising.

Recently, the scope of ISL technology embraces geologically unfavorable reservoirs, with low uranium content, low permeability, high clay content and without ferric iron in rock mass and in reservoir water [5–7]. As a consequence, the uranium recovery efficiency in production blocks is round 50% at the sulfuric acid content of 10–15 g/l in leach solutions for easy compounds and round 80% at the solution acidity of 20–25 g/l for difficult uranium.

The uranium leaching practice shows that at the stages of ore acidification, it is observed that the useful component concentration in the pregnant solution increases together with the residual acidity. In transition to the stage of active leaching, uranium content in the pregnant solution achieves the peak value and then drops. This takes place for that chemically active hexavalent uranium almost totally goes to the pregnant solution by this moment, and only 4-valent uranium, which is more resistive to sulfuric acid, remains in ore [8].

For speeding up leaching, two additional requirements should be fulfilled, namely, the uniform injection of process solution at a general balance maintained and the minor deviation of borehole bottoms from their design positions (within 1–2 m). The nonobservance of these requirements complicates interpretation of check boring data and impairs accuracy of calculations.

For cutting the operation time of a leaching site until the wanted recovery efficiency is reached (85–90%), it is possible to decease the distance between the pumping-in and pumping-out wells, or to increase the well yield. The cold-technical difficulties exist in both cases. For example, at the depths of 400–700 m, it is impossible to drill holes without deviation of the filter by 3–5 m from the project position. For this reason, the minimal allowable distance between the pumping-in/out wells is to be 20–35 m per drilling depth. Furthermore, it is impossible to increase the yield of such wells as, alongside with the technical difficulty and elevated construction costs, the governing factor is the permeability of a pay horizon.

In the rough, the operating time of ISL sites without central cell up to reaching the wanted recovery efficiency is round 3 years, or, with regard to mudding-induced decrease in the well flow rates, is 4–5 years.

On this basis, one of the ways of the in-situ leaching stimulation in uranium production is the use of various oxidizers.

Oxidation of U(IV) to U(VI) in carbonate media is possible using oxidizers, such as oxygen, ozone, hydrogen peroxide, thiosulfates of alkaline metals or ammonium, sodium hypochlorite etc., or using anode oxidation [9].

The study [10] experimentally proved very low efficiency of uranium leaching using return solutions without preliminary oxidation of iron. An increase in the concentration of sulfuric acid in the return solution somewhat increases uranium leaching efficiency. At the same time, the triple concentration of sulfuric acid raises the leaching efficiency only by 4–5%.

A serviceable bacterial oxidizer may be Ferrooxidans which can oxidize ferrous iron (Fe_2) up to ferric iron (Fe_3). When application of biological leaching to sulfide ore was better studied, the experiments were undertaken with uranium leaching. Biological leaching can be a good alternative in case of low-grade and rebellious ore which is uneconomic to treat using the conventional method [11].

The other oxidizer, often used to enhance uranium leaching efficiency, is nitrous acid or nitrites. It is known that in the presence of both iron and nitrite ions, uranium oxidation follows the catalytic mechanism (nitrite ions accelerate oxidation of iron which, in its turn, oxidizes uranium) [12]. Furthermore, ozone and hydrogen peroxide are applicable to stimulating leaching. It is common knowledge that hydrogen peroxide in leaching solution possesses high oxidation power relative to uranium [13, 14].

The above described methods to activate leaching solutions are by far attractive but also have some disadvantages.

The chemical methods (nitric acid and nitrites, pure oxygen, hydrogen peroxide) impose stringent requirements on the conditions of transport, storage and proportioning of chemical agents, on sophisticated equipment and, certainly, on safety [15].

The bacterial leaching needs special conditions for incubation and life maintenance of bacteria colonies [16].

The ozonation requires much power to generate high concentration of ozone.

Finally, different approaches to stimulating uranium production using various oxidizers involve essential operating and capital expenses, including the environmental protection.

Thus and so, it is proposed to use atmospheric oxygen as an oxidizer in the stimulated leaching processes.

Oxygen is poorly dissolvable in water. This gas solvability is directly proportional to the oxygen partial pressure and considerably depends on the temperature and composition of the water phase.

In the course of development of this technology, injection of compressed air in a reservoir as well as pre-saturation of process solutions with air were tested. For example, in test block 3 of ISL site 10 in the Uchkuduk deposit, air was injected under the pressure of 2–4 kg/cm^2 until the pay reservoir was saturated with oxygen at 0.1 kg/t, which agreed with the pore volume value [17]. In 30 days after actuation of pumping-out wells, uranium content of pregnant solutions reached the maximum value of 35 mg/l at the content of HCO_3 of 270 mg/l. For the comparison, in sulfuric leach blocks (without air feed), uranium content of pregnant solutions totals 10 mg/l at most.

The task of no less importance is the development of the technology for saturation of leaching solutions with atmospheric oxygen. At first sight, an evident way to this end is oxygen feed via an air supply hose from a compressor connected to a main pipe, but the problem is that the capacity of the main pipes in operating mines is from 60 m^3/h to 130 m^3/h. Alternatively, air can be fed directly to mother solution out of door, but, due to the relatively low pressure at the air feed place, oxygen escapes instantly, which nullifies the attempt to activate and stimulate the solution.

Research procedure

On the afore-listed grounds, it is suggested to use the Venturi tube for saturating leaching solutions with oxygen.

The Venturi tube is a short tube of a special design, with narrowing and with an air suction orifice in the middle portion. As the solution passes the isthmus of the Venturi tube, the flow velocity increases with simultaneous air suction [18]. According to Bernoulli's principle, the liquid volume or the leaching solution volume to flow along a large diameter tube is the same as the liquid volume to pass the narrow part per unit time. To ensure the same volume of liquid at two points, the liquid flow accelerates by Bernoulli's principle. In case of the higher flow velocity, the static pressure is lower. The liquid velocity/static pressure ratio is a direct proportion, i.e., by increasing the liquid flow velocity in a smaller diameter tube, it is possible to decrease the static pressure down to a value which enables air suction via the orifice in the narrow part of the tube.

The liquid flow in the narrow part is accompanied with dynamic cross stirring, then the air-saturated solution flows into the larger diameter zone, the flow velocity decreases, the flow mode becomes laminar again, and the static pressure increases proportionally. Practice shows that pressure has an essential influence on solubility of gases in water. As pressure increases, the solvability of atmospheric oxygen grows. The solvability of liquid and solid substances is almost independent of pressure. Thereupon, it can be stated that this technology allows saturation

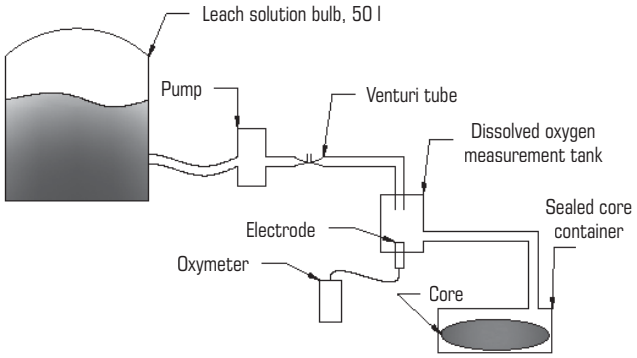

Fig. 1. Lab-scale modeling plant

of process solutions with oxygen at the least expenses and eliminates gas colmatage potential.

For the comparison, the reference and the proposed technologies with oxygen saturation were tested at a laboratory scale. The test core samples were taken on the eastern and western sides of the Central Mynkudyk deposit.

The core material was grey sand. The cores were sampled at different depths spaced at 20 cm, and each core was described. All in all, cores of total length of 6 m were taken on each side of the deposit. Aimed to determine the average uranium content of the cores, all cores were ground: the average uranium content of the eastern side and western side cores were 0.035% and 0.045%, respectively.

For the lab-scale tests, the ground core material was compacted in a special tube and placed in a transparent container.

The lab-scale modeling plant (**Fig. 1**) consists of a bulb with a leaching solution, container with core and a tank for the pregnant solution.

The plastic bulb with a volume of 50 l is connected with a flexible hose 60 cm long, equipped with a horizontal pump to ensure the required velocity of the liquid flow. Liquid is pumped through the Venturi tube at a high velocity. The solution saturated with atmospheric oxygen flows to tank for the dissolved oxygen concentration measurement. This tank has an air-proof lid on the top and an electrode on the bottom. The tank lid has an opening for the water-and-air mix to flow in, and the electrode serves to measure dissolved oxygen.

The acid concentration was 20 g/l, the redox potential was evaluated using pH meter IT-1101, and the content of uranium was measured at a mine laboratory. The leaching time was 9 hours, and the amount of the leach solution was 12 l. The pregnant solution was sampled every hour, and all in all 18 samples were taken, including 9 samples with from the eastern side of the deposit and 9 samples from the western side

Results and discussion

First, the reference technology was tested (**Tables 1** and **2**), and then the testing involved saturation of the leach solution with oxygen for determining the effect of the oxygen-rich solution on the concentration of ferrous and ferric iron, on the value of the redox potential and on the content of uranium in the pregnant solution. The acid concentration in the initial leach solution was 6.3 mg/l; after the solution was saturated with oxygen using the Venturi tube, the concentration of oxygen rises to 10.45 mg/l, i.e. by 66%.

As seen from Table 1, with increasing time of leaching, the value of the redox potential changes slightly, from 340 to 348 mV. In the meanwhile, the concentration of Fe(III) in the leach solution (LS) was 310 mg/l, then it increased to 324 mg/l in the further course of leaching but decreased to 320 mg/l afterwards. The concentration of Fe(II) grew from 270 mg/l to 368 mg/l but then lowered insignificantly to 354 mg/l.

Table 1. Uranium content, redox potential, and ferrous and ferric iron contents (eastern side, core 1)

Sample	Fe (+2), mg/l	Fe (+3), mg/l	Uranium content, mg/l	Redox potential, mV	Sampling time, h
LS1	270	310	2.10	340	0
PS1	300	318	18.40	340	1
PS2	290	318	18.40	344	2
PS3	362	322	18.60	345	3
PS4	365	324	19.30	346	4
PS5	368	324	18.70	345	5
PS6	362	320	19.60	346	6
PS7	360	322	20.00	346	7
PS8	356	326	18.90	348	8
PS9	354	320	18.80	346	9

Table 2. Uranium content, redox potential, and ferrous and ferric iron contents (western side, core 2)

Sample	Fe (+2), mg/l	Fe (+3), mg/l	Uranium content, mg/l	Redox potential, mV	Sampling time, h
LS2	288	312	1.90	334	0
PS1[1]	290	312	20.80	336	1
PS2[1]	290	310	21.25	338	2
PS3[1]	292	304	20.54	338	3
PS4[1]	289	315	20.58	340	4
PS5[1]	294	306	18.62	340	5
PS6[1]	290	304	18.22	342	6
PS7[1]	290	295	18.20	338	7
PS8[1]	288	305	18.00	340	8
PS9[1]	290	296	18.00	340	9

Table 3. Uranium content, redox potential, and ferrous and ferric iron contents (eastern side, core 1)

Sample	Fe (+2), mg/l	Fe (+3), mg/l	Uranium content, mg/l	Redox potential, mV	Sampling time, h
LS3	300	320	1.80	360.0	0
PS10	296	331	20.91	360.8	1
PS11	298	320	21.65	370.2	2
PS12	298	330	24.28	373.9	3
PS13	294	335	23.84	375.8	4
PS14	294	338	23.46	380.6	5
PS15	292	345	23.00	382.8	6
PS16	294	341	23.15	387.6	7
PS17	296	347	24.00	380.5	8
PS18	294	347	23.20	381.6	9

Table 4. Uranium content, redox potential, and ferrous and ferric iron contents (western side, core 2)

Sample	Fe (+2), mg/l	Fe (+3), mg/l	Uranium content, mg/l	Redox potential, mV	Sampling time, h
LS4	310	330	2.1	364.4	0
PS19	301	334	24.81	368.0	1
PS20	300	340	25.25	378.5	2
PS21	290	360	25.80	405.0	3
PS22	294	354	27.26	396.0	4
PS23	290	358	25.82	403.0	5
PS24	302	342	26.94	406.5	6
PS25	286	358	27.62	403.0	7
PS26	280	358	28.25	403.0	8
PS27	260	365	27.84	418.0	9

Within the preset leaching time, the uranium content in the pregnant solution (PS) changed in a minor way, in a range of 18.4–20.0 mg/l. On the whole, the content of uranium in PS totaled 18.63 mg/l, and the concentration of Fe(II) grew by 27%.

It is seen from Table 2 that before saturation of the leach solution with oxygen, the concentrations of Fe(II) and Fe(III) were, respectively, 288 and 312 mg/l, and the value of the redox potential ranged between 334 to 342 mV. During the assigned leaching time, the content of uranium in PS changed within a range of 18.0–21.25 mg/l. Generally, the average content of uranium in PS made up 19.35 mg/l.

The laboratory testing results on saturation of the leach solution with atmospheric oxygen are compiled in **Tables 3** and **4**.

As follows from Table 3, before saturation of the leach solution with oxygen, the concentrations of Fe(II) and Fe(III) were 300 and 320 mg/l, respectively, and after the saturation and with longer time of leaching, the value of the redox potential increased from 360 to 387 mV. The concentration of Fe(III) grew to 347 mg/l, and the concentration of Fe(II) slightly decreased to 292 mg/l. Within the preset leaching time, the content of uranium in PS changed in a minor way within a range of 20.9–24.2 mg/l. On the whole, the average uranium content in PS made up 23.05 mg/l, the concentration of Fe(III) grew by 5%, and the redox potential increased by 4.7%.

It is seen in **Table 4** that before the leach solution was saturated with oxygen, the concentrations of Fe(II) and Fe(III) equaled 310 and 330 mg/l, respectively, and after the saturation and longer time of leaching, the redox potential increased from 364 to 416 mV. The concentration of Fe(III) grew to 365 mg/l, and the concentration of Fe(II) lowered slightly to 260 mg/l. Within the time of leaching, the content of uranium in PS changed in a minor way in a range of 24.8–28.2 mg/l. Generally, the average uranium content in PS totaled 26.62 mg/l, the concentration of Fe(III) rose by 7%, and the redox potential increased by 14.0%.

At the laboratory scale, the solution feed velocity was set to equal to the industrial conditions, i.e. 0.7 m/s. After suction of air via the Venturi tube, the oxygen concentration in the leaching solution was 10.45 mg/l. Such concentration of oxygen made it possible to increase Fe(III) concentration in the treated solution as against the initial solution and, accordingly, to maintain that higher concentration of Fe(III) in the productive solution (see Tables 1–4).

After processing of the testing data, the contents of uranium in PS were plotted as functions of the leaching time in the reference technology and with LS saturated with oxygen (**Figs. 2**).

The comparison of the laboratory test data shows that in the reference technology of leaching, the average uranium content in the pregnant solution is 18.63 mg/l and 19.36 mg/l in the core samples from the eastern and western sides of the test deposit, respectively. After saturation of the leach solution with oxygen, the average uranium content is 23.05 mg/l and 26.62 mg/l, respectively. It is possible to state that as against the reference leaching technology, the proposed approach has enabled the increased uranium contents by 23.7% and 37.5% in leaching of the core samples from the eastern and western sides of the test deposit, respectively.

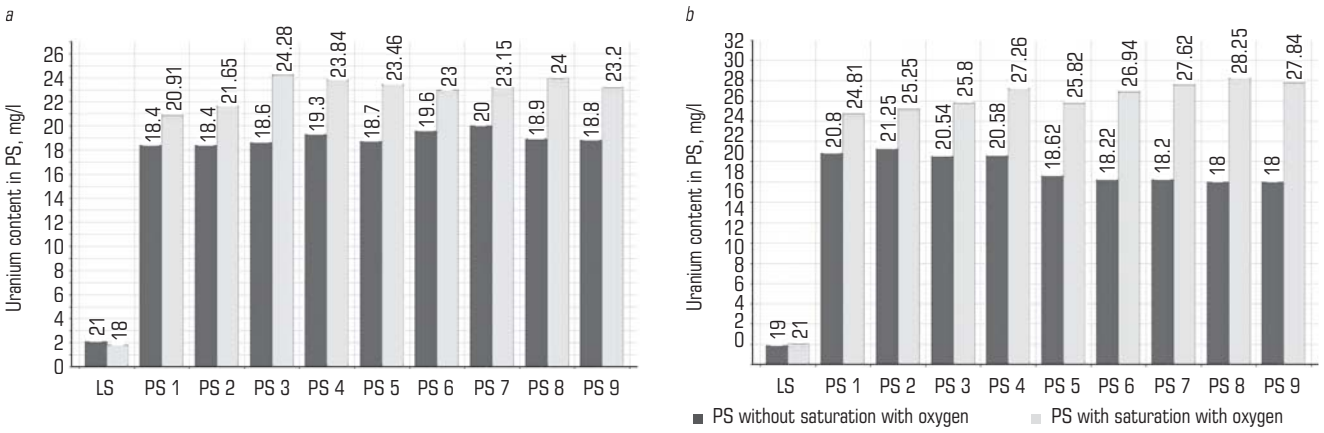

Fig. 2. Uranium content in PS versus leaching time in reference technology and with LS saturated with oxygen:
1–core 1; *2*–core 2

Conclusions

The lab-scale studies allow drawing some conclusions as follows:

• the proposed technology of saturating the leaching solution with oxygen using the Venturi tube provides air suction and active mixing of air with the solution as it passes the isthmus in the tube and promotes effective transition of oxygen from air to the solution owing the change in the solution pressure;

• the technology is advantageous for the low capital and operating cost, simple arrangement and maintenance and elimination of chemical additive;

• the saturation of the leach solution with oxygen ensures oxidation of ferrous iron up to ferric iron, which promotes the increase in the content of uranium in the pregnant solution and shortens the treatment time of uranium leaching in production blocks.

Acknowledgement

The authors express their sincere gratitude to Doctor of Engineering, Professor of the Mining Department at the Satbayev Kazakh National Technical University and Corresponding Member of the National Academy of Sciences of Kazakhstan Kh. A. Yusupov for the auspices and fruitful advice in the course of this research.

References

1. Sukhodolov A. P. World's supply of uranium: prospects for primary provision of atomic energy industry. *Izvestiya IGEA*. 2010. No. 4. pp. 166–169.
2. Boytsov A. Worldwide ISL Uranium Mining Outlook : Presentation. *Proceedings of the International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle: Exploration, Mining, Production, Supply and Demand, Economics and Environmental Issues (URAM-2014)*. Vienna : IAEA, 2014. pp. 1–23.
3. Mark S. Pelizza, Craig S. Bartels. Introduction to uranium in situ recovery technology. Uranium for Nuclear Power. London : Woodhead Publishing, 2016. pp. 157–213. DOI: 10.1016/B978-0-08-100307-7.00007-7
4. Golik V. I., Stradanchenko S. G., Maslennikov S. A. The concept of obtaining metals by leaching. *Bulletin of Kemerovo State University. Series: Biological, engineering and earth sciences*. 2018. No. 1. pp. 49–60.
5. Omarbekov Y., Yussupov Kh. Improving the technology of uranium mining under the conditions of high groundwater pressure. *Mining of Mineral Deposits*. 2020. Vol.14, Iss. 3. pp. 112–118.
6. Filippov A. P., Nesterov Yu. V. Redox processes and stimulation of metal leaching. Moscow : Ore and Metals, 2009. 543 p.
7. Yusupov Kh. A., Aliev S. B., Dzhakupov D. A. et al. Application of ammonium bifluoride for chemical treatment of wells in underground uranium leaching. *Gorniy Zhurnal*. 2017. No. 4. pp. 57–60. DOI: 10.17580/gzh.2017.04.11
8. Ovseychuk V. A., Zozulya A. M. Reduction of process losses of uranium during underground leaching due to the dissolution of uranyl hydroxide. *Vestnik Zabaykalskogo Gosudarstvennogo Universiteta*. 2019. Vol. 25, No. 4. pp. 4–12.
9. Chervyakov N. M., Andreev A. V., Boyarintsev A. V. et al. Kinetic study of the oxidative dissolution of uo2 and u3o8 in aqueous sodium carbonate solutions. *Uspehi v himii i himicheskoy tehnologii*. 2020. Vol. 34, No. 9. pp. 34–36.
10. Pastukhov A. M. Application of synthetic oxidants for intensification of uranium in-situ leaching process: Final R&D report. Yekaterinburg : UrFU, 2013. 34 p.
11. Kaksonen A. H., Lakaniemi A.-M., Tuovinen O. H. Acid and ferric sulfate bioleaching of uranium ores. *Journal of Cleaner Production*. 2020. Vol. 264. DOI:10.1016/j.jclepro.2020.121586
12. Koltunov V. S., Marchenko V. I. Kinetics of U(IV) oxidation with nitric acid with catalytical treatment by ions of ferric iron. *Radiohimia*. 1973. Vol. 15. No. 1. pp. 78–84.
13. Hodjiev S. K., Nazarov Kh. M., Ermatov K. A. et al. Effectiveness of hydrogen peroxide action as an oxidizer of uranium dioxide depending on the pH state. *Doklady Akademii Nauk Respubliki Tadzhikistan*. 2018. Vol. 61, No. 3. pp. 281–285.
14. Yusupov Kh. A., Aleshin A. P., Bashilova E. S. et al. Application of hydrogen peroxide to intensify in-situ leaching of uranium *Obogashchenie rud*. 2021. No. 2. pp. 21–26. DOI: 10.17580/or.2021.02.04
15. Draft Federal Law N 584587-5 dated 10 October 2011 : Amendment of some statutes of the Russian Federation in terms of rate setting improvement. Available at: https://sozd.duma.gov.ru/bill/584587-5 (accessed: 02.03.2022).
16. Turaev N. S., Zherin I. I. Chemistry and technology of uranium. Moscow : Ore and Metals, 2006. 396 p. ISBN 5-98191-019-4
17. Tolstov E. A. Physicochemical geotechnologies of uranium and gold production in the Kyzylkum region. Moscow : MGU, 1999. 312 p.
18. Khalidilla Yussupov, Yerbolat Aben, Armanbek Omirgali, Azamat Rakhmanberdiy. Analyzing a denitration process in the context of underground well uranium leaching. *Mining of Mineral Deposits*. 2021. Vol. 15, Iss. 1. pp. 127–133. EM