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The Influence of the Physicochemical Characteristics of Ores on the Efficiency of Underground Well Leaching of Uranium Deposits in Kazakhstan

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Abstract: The features of uranium mining on Kazakhstan's enterprises have been examined, and uranium deposits located in the Syrdarya and Shu-Sarysu depressions have been described. Actual and projected data on the development of technological blocks in areas with complex geological structures have been analyzed and compared. Core samples were collected and, using X-ray diffraction analysis, quantitative and qualitative characteristics as well as mineral compositions of ores from various productive horizons of uranium deposits in the Syrdarya and Shu-Sarysu depressions were comparatively analyzed. It was determined that the ores in the Syrdarya depression are relatively homogeneous compared to those in the Shu-Sarysu depression, although in some places, clay minerals and gypsum are present, which hinder the uranium leaching processes. In the ores of the Shu-Sarysu depression, clay minerals that impede the uranium leaching processes are present in certain areas. Microscopic analysis of core material samples using a LEICA DM 2500 P microscope revealed particle sizes and shapes, as well as their distribution within the structure of host rocks in the productive horizon. Using X-ray diffraction analysis, mineral compositions of sediment-forming components during uranium well mining in the considered productive horizons were determined and comparatively analyzed. It was established that in the geotechnological wells of the Syrdarya depression, sediments of predominantly chemical origin, such as gypsum, are formed. However, in the geotechnological wells of the Shu-Sarysu depression, sediments of mechanical origin, consisting predominantly of quartz particles and clay minerals, are formed. Based on the obtained data, a method for intensifying underground uranium leaching in complex geological conditions has been developed, which involves dissolving sediment formations and increasing the oxidative–reductive potential of the leaching solution. The proposed and experimentally substantiated universal methodology for enhancing uranium well production involves the dissolution and prevention of precipitation using hydrofluoric acid solutions, as well as the oxidation of uranium dioxide with hydrogen peroxide.

Keywords: uranium; well mining; core; sedimentation; X-ray diffraction analysis; oxidative–reductive potential; uranium leaching

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1. Introduction

The consequences of climate change and the increasing demand for electricity in developing countries are driving greater interest in the further development of nuclear energy. Efforts to develop and deploy new modular nuclear power plants of small and large capacity with compact sizes and a low carbon footprint can have a significant impact on reducing CO_2 emissions worldwide (IAEA 2018; IPCC 2018). Uranium is a key component that underpins the nuclear industry and is a crucial element in the sustainable development of nuclear energy [1,2]. Kazakhstan's uranium mining industry, based on highly efficient in situ leaching technology, has the potential to make a significant contribution to meeting the growing demand for uranium resources.

In situ leach uranium mining [3,4] is the most economically viable and environmentally friendly method, especially when dealing with deep deposits below 300 m and low ore grades below 0.1%–0.2%. This technology is highly efficient and involves lower capital and operational costs during the deposit development process. In situ leach uranium mining involves the injection of a leaching solution (LS) containing sulfuric acid into the ore body through injection wells. Uranium-enriched productive solutions (PS) are then pumped from production wells using submersible electric pumps and transported through pipelines for processing in sorption–desorption columns [5,6]. Figure 1 illustrates the location of Shy-Sarysu and Syrdrya uranium basins, and in Figure 2, a layout of uranium deposits in the Syrdarya and Shu-Sarysu depressions is shown.

General confirmed industrial uranium reserves in the region are estimated at 1.3 million tons, of which 0.6 million tons are confirmed. Despite the low uranium content in the ore, ranging from 0.07 to 0.08%, the ore bodies are characterized by significant thickness and high productivity, ranging from 7 to 10 kg/m^2. However, during the extraction of technological blocks using the wellbore method, there are cases where the extraction of uranium from the deposits slows down due to a decrease in wellbore permeability and a substantial reduction in uranium content in productive solutions (PS). The decrease in geotechnological extraction parameters is attributed to changes in filtration rates within the ore due to the impact of process solutions on the structure of the host rocks of the productive horizon, changes in pH levels [7,8], dilution of productive solutions with formation water, as well as precipitation of various minerals. This results in an extended period for the extraction of technological blocks, an increase in operational and capital costs, a reduction in the profitability of extraction and processing of productive solutions [9,10].

To determine the actual deviations in uranium extraction from the projected values, the key geotechnological data of the block extraction were analyzed in areas with low filtration characteristics of ores, uranium deposits in the Syrdarya and Shu-Sarysu depressions. Based on the analysis and averaging of the results, curves of the actual block processing values were constructed for the Syrdarya region (green) and Shu-Sarysu depression (blue) areas (Figure 3).

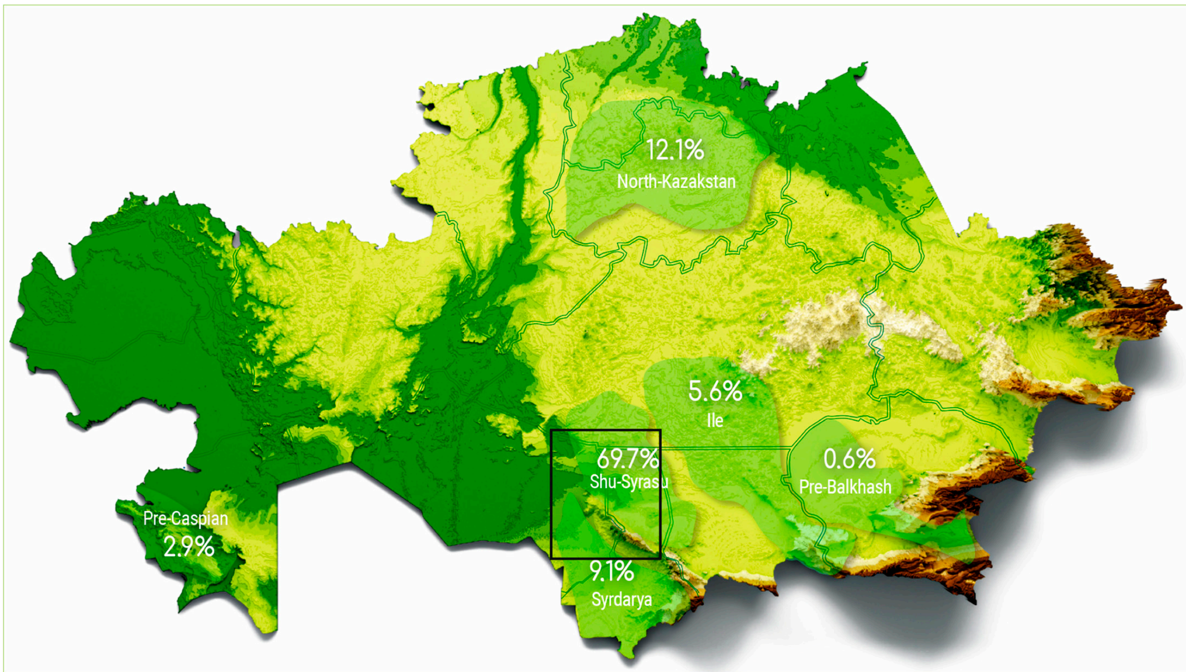


Figure 1. Location of uranium basins on Kazakhstan map.

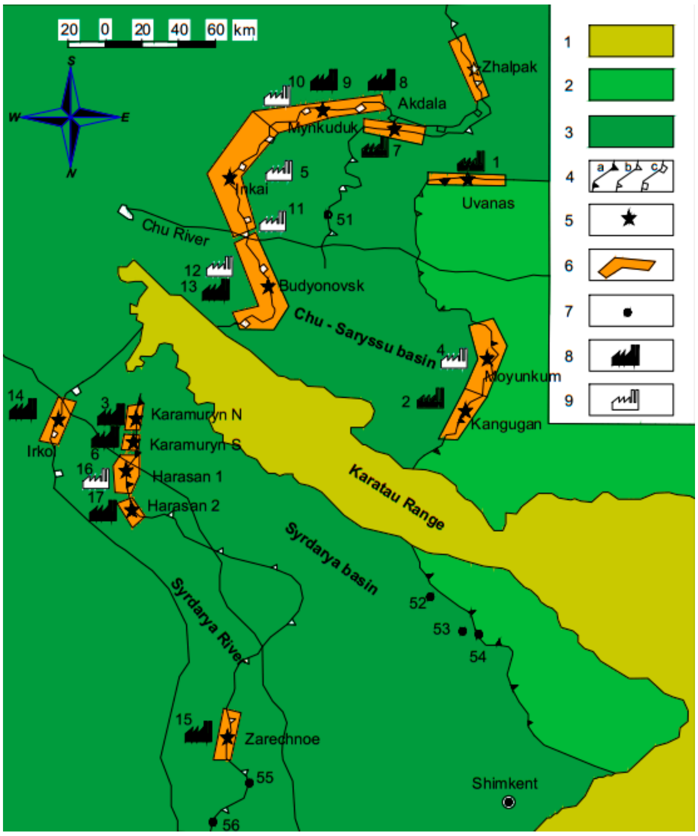


Figure 2. Location of uranium deposits in the Syrdarya and Shu-Sarysu depressions. 1—Karatau Mountains; 2—Hilly Terrain; 3—Plains; 4—Zone Dividing Boundaries; 5—Uranium Industrial Deposits; 6—Deposit Boundaries; 7—Prospective Areas; 8, 9—Developing Areas (1—Uvanas, 2—Kanjugan, 3, 6—North and South Karamurun, 4—Moinkum, 5, 11—North and South Inkay, 7—Akdala, 8, 9, 10—Eastern, Central, Western Myunkuduk; 12, 13—North and South Budenovskoye; 14—Irkol; 15—Zarechnoye; 16, 17—Kharasan 1,2).

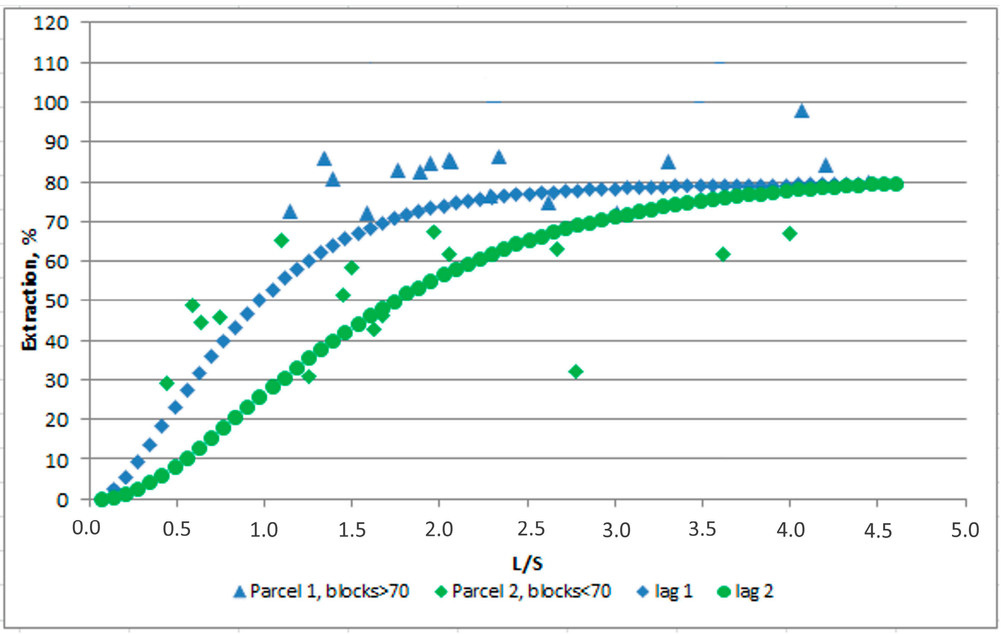


Figure 3. Projected and actual data for the extraction of technological blocks.

As seen in Figure 3, achieving 90% recovery according to the project requires a significant amount of time for problematic blocks, with the liquid-to-solid (L/S) ratio averaging between 4.0 and 5.0. This increases operational costs for extraction and negatively impacts the economic indicators of the enterprise. In the challenging areas of the Syrdarya depression (green line), the extraction is flatter compared to the Shu-Sarysu depression (blue line). This is attributed to relatively lower ore filtration coefficients ranging from 2 to 5 m/day, deeper ore deposits exceeding 600 m, and mineralogical characteristics of productive horizons. This raises the coefficient of ore recovery on enterprises operating in the Syrdarya depression to ≥2.0, compared to ≤2.0 for enterprises engaged in the extraction of deposits in the Shu-Sarysu depression. Meanwhile, the total amount of processed productive solution, sulfuric acid consumption, and other chemical reagents are approximately the same due to different values of productivity and uranium content in the productive solution.

The L/S ratio is calculated as follows:

$$\mathrm{L/S} = \frac{\sum_{i=0}^{i=t} Q_{LS}}{\mathrm{MM}} \tag{1}$$

where Q_{LS} is the amount of leaching solution supplied to the block (cell, area) over time t in cubic meters m^3, and MM is the mining ore mass in tons.

$$\mathrm{MM} = S\ h_e\ \delta \tag{2}$$

where S is the leachable area of the block (cell, area) in square meters m^2; h_e is the effective thickness of the productive horizon in meters, and δ is the bulk density of ore-bearing rocks and ore in tons per cubic meter t/m^3.

The uranium extraction from the deposit is calculated as the ratio of the total extracted uranium from the block (cell, area) to the existing reserves in the block (cell, area), expressed as a percentage:

$$\varepsilon = \frac{\sum P_U}{\mathrm{P}} \tag{3}$$

where $\sum P_U$ is the sum of the extracted uranium from the block (cell, area) in kilograms kg, and P is the uranium reserves in the block (cell, area) in kilograms (kg).

The extracted uranium from the deposit P_U is determined as the amount of uranium obtained in productive solutions over a specific period, minus the uranium injected into the block with leaching solutions. It is calculated as follows:

$$P_U = Q_{PS}\ C_{U\ PS}\ - Q_{LS}\ C_{U\ LS} \tag{4}$$

where Q_{PS} and Q_{LS} are the volumes of productive solutions extracted from the block and leaching solutions supplied to the block over a certain period in cubic meters (m^3), and $C_{U\ PS}$ and $C_{U\ LS}$ are the concentrations of uranium in productive and leaching solutions, respectively, in grams per liter (g/L).

The sum of the extracted uranium from all blocks $\sum P_U$ should be equal to the sum of the shipped (packaged) uranium and the uranium in the processing complex apparatus. It is calculated as follows:

$$\sum P_U = U_{SH}\ U_{ED} \tag{5}$$

where U_{SH} is the uranium unloaded into containers in kilograms (kg), and U_{ED} is the uranium contained in the processing complex apparatus.

The significant reduction in geotechnological parameters is attributed to the rapid reaction kinetics of sulfuric acid with clayey and aluminosilicate minerals in the host rocks, leading to precipitation as a geochemical barrier that hinders the leaching process [11]. Studying the mineralogical and physicochemical characteristics of host rocks will help identify the reasons behind the precipitation and dilution of productive solutions, addressing the efficiency of the in situ uranium mining technology.

2. Materials and Methods

2.1. Mineralogy of Ores

To address the issues related to reduced well productivity and uranium content in productive solutions (PS) during ore leaching, it is essential to determine the mineralogical composition of the productive horizon and the structure of host rocks. The obtained data will help identify the reasons behind the decrease in uranium content in PS and determine the filtration rate of solutions in the reservoir, depending on the mineralogical and granulometric characteristics of ores in the Syrdarya and Shu-Sarysu depression deposits.

To compare the physicochemical characteristics of ores, core material samples were collected from various productive horizons of uranium deposits in the Shu-Sarysu and Syrdarya depressions.

X-ray analysis was performed using an automated DRON-3 diffractometer (Burevestnik S Peterburg, S Peterburg, Russia) with CuKα radiation and a β-filter. The data acquisition conditions for diffractograms were as follows: U = 35 kV; I = 20 mA; θ–2θ scan mode; detector speed of 2 degrees/min. Semi-quantitative X-ray phase analysis was carried out based on the diffractograms of powder samples using the method of equal loads and artificial mixtures. Quantitative ratios of crystalline phases were determined. Interpretation of the diffractograms was conducted using data from the ICDD database: the Powder Diffraction File (PDF2) and diffractograms of pure minerals [12,13].

2.2. X-ray Phase Studies of Sedimentation

The main goal of X-ray phase analysis is to quantitatively and qualitatively determine the characteristics of precipitates under laboratory conditions and compare them depending on the ore-bearing horizon of the Syrdarya and Shu-Sarysu depressions. Establishing the quantitative and qualitative characteristics of colloids will allow for the selection of effective approaches for their disruption, dispersion, removal, and long-term prevention of precipitation [14].

X-ray diffractometric analysis was conducted using the automated diffractometer DRON-3 with CuKα radiation and a β-filter. The conditions for taking diffractograms were as follows: U = 35 kV; I = 20 mA; θ–2θ scan; detector speed 2 degrees/min. X-ray phase analysis was performed on a semi-quantitative basis using the diffraction patterns of powder samples with the application of the equal weights method and artificial mixtures. The quantitative ratios of crystalline phases were determined [15].

The interpretation of the diffraction patterns was carried out using the ICDD database; the Powder Diffraction File (PDF2) and diffraction patterns of pure mineral phases were utilized. The content was calculated for the main phases.

2.3. Development of a Method for Chemical Treatment of Wells

The application of hydrofluoric acid and hydrogen peroxide solutions must be carried out according to a specially developed method using specialized technological equipment, while adhering to occupational safety requirements. The innovative method involves the direct treatment of the well's filtration area or near filter zone (NFZ) of wells with hydrofluoric acid solutions, ensuring maximum destruction and prevention of precipitation in the reservoir for an extended period. The method further involves the controlled delivery of hydrogen peroxide into the leaching solution through technological wells [16,17]. The introduction of hydrogen peroxide enhances the productivity of operational blocks and the overall metal extraction efficiency by increasing the uranium content in the productive solution. Additionally, it leads to a reduction in the specific consumption of sulfuric acid, electricity, labor, and other production costs in the process of uranium well extraction from diverse geological formations. Figure 4 illustrates the developed scheme encompassing the components of the intensification of uranium well extraction.

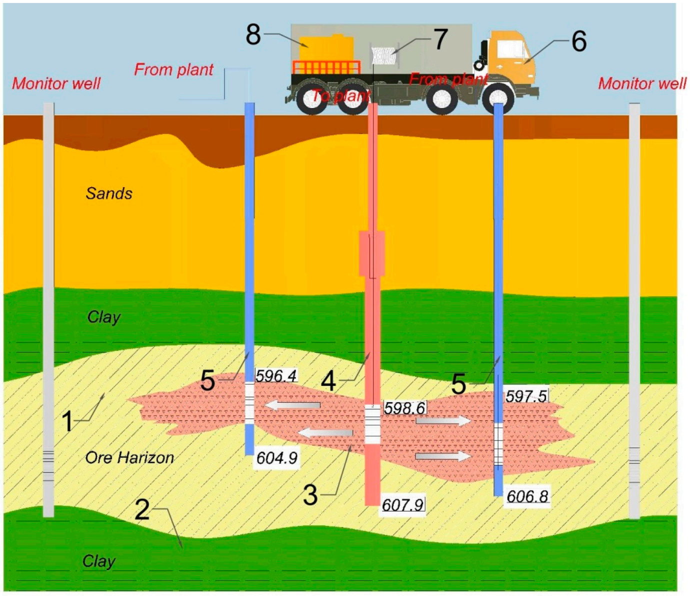


Figure 4. Scheme for the intensification of downhole uranium production 1—productive horizon; 2—impenetrable rocks; 3—sedimentation in the NFZ; 4—pumping wells; 5—injection wells; 6—equipment for chemical treatments; 7—pressure hose; 8—tank.

As seen in Figure 4, the main bulk of precipitates (3) occurs in the productive horizon (1), specifically in the solution unloading zone, and in the increase in solution velocity from injection wells (5) to production wells (4). The chemical treatment using a complex of chemical reagents involves preparing solutions on specialized equipment (6) and delivering them to the filtering part of the wells (4) through a pressure hose (7). The specially prepared solution is supplied from the tank container (8). The delivery of decolmatizing solutions based on hydrofluoric acid (10%) directly to the filtering part of technological wells reduces the consumption of chemical reagents and increases permeability for greater precipitation destruction and dispersion. The subsequent introduction of hydrogen peroxide into the productive horizon enhances the uranium content in the productive solution and shortens the processing period of technological blocks.

To organize experimental work in uranium well extraction, ensuring the leaching regime and calculating the required volume of acid and hydrogen peroxide solutions, it is necessary to calculate the following geotechnological parameters: liquid-to-solid ratio (L/S) and the calculated radius of dispersion.

The L:S ratio is calculated using the formula:

$$\mathrm{L:S} = \frac{\sum_{i=1}^{n} Q_{ls}}{S\, h_e\, \delta} \quad (6)$$

where Q_{ls} is the amount of leaching solution supplied to the subsurface during time t, m^3; S is leached area, m^2; h_e is effective capacity of the productive horizon, m; and δ is volume mass of ore-bearing rocks and ores, t/m^3.

The calculated area of spreading of solutions from the filter along the productive horizon was determined by the formula:

$$S = \frac{Q_D}{0.22 h_e} \quad (7)$$

where Q_D is the volume of decalcifying solutions supplied to the well, m^3; and 0.22 is the average porosity coefficient of the host rocks of the productive horizon.

The spreading radius of decolmating solutions was determined by the formula:

$$R = \left(\frac{S}{\pi}\right)^{\frac{1}{2}} \quad (8)$$

The proposed method involves the chemical treatment of wells using a synergistic action of a complex of chemical reagents for dissolving precipitates in the near-wellbore zone of the reservoir. This includes the use of hydrofluoric acid solutions to dissolve precipitates and the enhancement of the oxidizing capacity of the environment for the dissolution of uranium dioxide using hydrogen peroxide solutions. Depending on the contamination level of the productive horizon and the geological characteristics of the ore in the near-wellbore zone of the reservoir, the effective dispersion radius of chemical reagents is determined experimentally. The dispersion radius of the solutions from the well into the depth of the productive horizon affects the consumption of reagents (HF and H_2O_2).

2.4. Experimental Trials on Geotechnological Wells and Blocks

Experiments on intensifying uranium well extraction using decolmatizing solutions in combination with hydrogen peroxide were conducted at the Syrdarya depression deposit. Geotechnological wells were treated on a pre-selected technological block with low uranium content in the productive solution, reduced well productivity, and an extended operational period. A photograph of specially designed, manufactured, and implemented equipment for chemical well treatment is provided in Figure 5.

Figure 5. Technological equipment for intensifying uranium well extraction.

During the development, manufacturing, and adaptation of the installations, real geotechnological conditions of the Syrdarya and Shu-Sarysu depressions deposits were taken into account. Strict coordination with the developed and approved technological regulations was ensured during the implementation of production experiments. The equipment for preparing and delivering solutions of chemical reagents includes a storage tank for hydrofluoric acid, a transfer pump, a storage tank for hydrogen peroxide, and a dosing pump, all made of corrosion-resistant materials due to their contact with hydrofluoric acid and hydrogen peroxide solutions. The treatment was carried out according to the developed methodology using special solutions for intensifying uranium well extraction based on hydrofluoric acid, followed by the delivery of hydrogen peroxide solutions. Table 1 provides the parameters of the solutions for intensifying uranium well extraction.

Table 1. Parameters of Special Solutions.

Composition	Volume of Leaching Solution, m^3	H_2SO_4, kg	HF, kg	H_2O_2, kg	Average Inter-Repair Cycle, Days	Uranium Content in PS, mg/L
H_2SO_4 + HF	3	150	300	600	16	10

From Table 1, it can be seen that the solution for intensifying well extraction consists of a decolmatizing part based on hydrofluoric and sulfuric acids and hydrogen peroxide. The sequential delivery of these components ensures the dissolution of precipitates in the pre-filter zone of the productive horizon, leading to the restoration of the filtration characteristics of the ore, a decrease in the pH of the environment, and an increase in the oxidizing-reducing potential of leaching solutions.

3. Results and Discussion

3.1. Determination of Mineralogy of Ores and Sedimentation

This section highlights the importance of determining the structure and composition of ores in the productive horizons of uranium deposits in the Syrdarya and Shu-Sarysu depressions. This information is crucial for developing universal methods to intensify in-situ leaching of uranium. The new approaches involve the use of specialized solutions and oxidizers tailored to the specific composition of the ores and precipitates [18]. These methods can effectively disrupt and prevent deposits from forming in the productive horizons, thereby increasing the dissolution capacity of the leaching solutions in uranium in situ recovery. Table 2 presents the results of semi-quantitative mineralogical composition of core samples. Table 3 presents the results of semi-quantitative mineralogical composition of core samples.

Table 2. Results of Semi-Quantitative Mineralogical Composition of Core Samples, in mass. %.

Mineral	Formula	Syrdarya Depression			Shu-Sarysu Depression	
		Santonian Stage	Maastrichtian Stage	Campanian Stage	Inkuduk Stage	Mynkuduk Stage
Quartz	SiO_2	90.8	54.7	66.3	79	96
Smectite	$KAl_2(AlSi_3O_{10})(OH)_2$	-	27.0	-		
K-feldspar	$KAlSi_3O_8$	9.2	10.1	5.7	15	3
Kaolinite	$Al_2(Si_2O_5)(OH)_4$	-	6.7	11.6	6	
Gypsum	$CaSO_4\ 2(H_2O)$	-	-	16.4		
Albite	$NaAlSi_3O_8$					1
Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$					
Hematite	Fe_2O_3					

The results of X-ray phase analysis of core samples from various ore layers indicate a similarity in the mineralogical composition of ores from the productive horizons of the Syrdarya and Shu-Sarysu depressions. In samples from the Shu-Sarysu depression, the quartz content varies between 79% and 96%, feldspar ranges from 3% to 15%, and the presence of the mineral kaolinite in some ores fluctuates by around 6%. In contrast, ores from the Syrdarya depression are more diverse and include variations in the content of minerals over a wider range: quartz from 54.7% to 90.8%, feldspar from 5.7% to 10.1%, and kaolinite from 6.7% to 11.6%.

The presence of kaolinite (6.7%) and feldspar (15%) in the sample from the Inkuduk layer of the Shu-Sarysu depression suggests the formation of ion exchange and mechanical clogging due to the swelling of clay minerals resulting from interaction with sulfuric acid solutions. In contrast, ores from the Mynkuduk layer are more homogeneous without precipitation formations during underground ore leaching. The presence of feldspar (5.7% to 10.1%), kaolinite (11.6% to 6.7%), gypsum (16.4%) in samples from the Kampanian and Maastrichtian layers of the Syrdarya depression also indicates the formation of ion exchange, mechanical, and chemical precipitates, hindering the processes of well extraction. In contrast, ores from the Santonian layer are more homogeneous without precipitation formations during underground ore leaching. The swelling of clays and the precipitation of gypsum in the discharge zones result in the formation of impermeable areas in the productive horizon, altering the direction of leaching solution flow through non-ore zones, and reducing the uranium content in productive solutions (PS), thereby slowing down the extraction of uranium from the subsurface.

Table 3. Results of Semi-Quantitative Mineralogical Composition of Core Samples, in mass. %.

Mineral	Formula	Syrdarya Depression			Shu-Sarysu Depression	
		Santonian Stage	**Maastrichtian Stage**	**Campanian Stage**	**Inkuduk Stage**	**Mynkuduk Stage**
Quartz	SiO_2	-	-	35.6	78.2	89.9
Gypsum	$CaSO_4$ $2(H_2O)$	100	100	16.7		
Calcite	$Ca(CO_3)$	-	-	8.9		
Albite	$NaAlSi_3O_8$	-	-	33.9	6.3	4.4
Microcline	$KAlSi_3O_8$	-	-	4.9	15.4	5.7

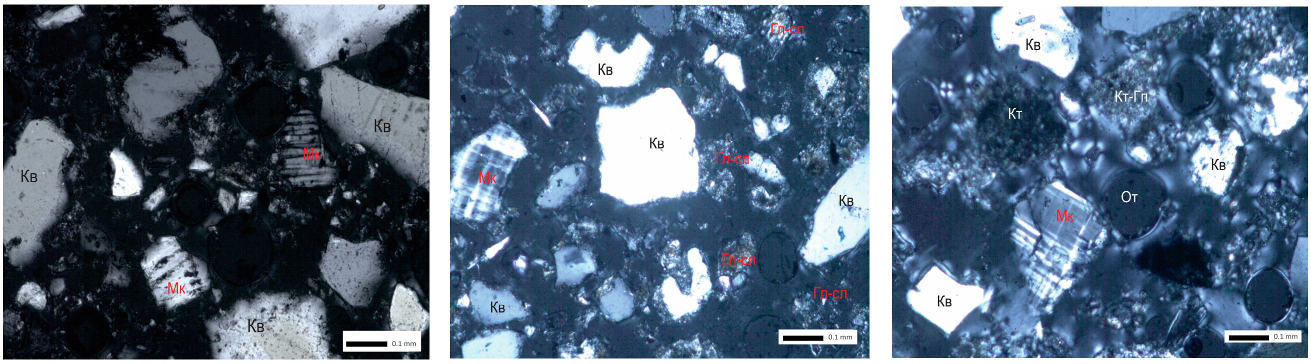
The results of X-ray phase analysis of precipitate samples from wells in the Santonian and Maastrichtian horizons of the Syrdarya depression indicate that the precipitates are single-components and consist of 100% gypsum, which is a product of chemical origin. Precipitates from the well in the Campanian horizon of the Syrdarya depression show that the precipitates are multi-componenst and have a complex structure. The presence of quartz (35.6%), albite (33.9%), and microcline (4.4%) confirms the predominance of mechanical clogging, while the presence of gypsum (16.7%) and calcite (8.9%) indicates the presence of chemically formed precipitates.

Precipitates from wells in the Inkuduk and Mynkuduk horizons of the Shu-Sarysu depression are similar in terms of quartz content (78.2% and 89.9%, respectively), albite (6.3% and 4.4%, respectively), and microcline (15.4% and 5.7%, respectively). The presence of these components in the Shu-Sarysu depression wells confirms the predominance of mechanically formed precipitates.

Quartz, gypsum, and feldspar precipitates accumulate in the filter part of the wells, reducing the filtration characteristics of the productive horizon and hindering the flow paths of technological solutions, diverting them away from the ore-bearing areas.

3.2. Microscopic Studies of Ores

The aim of microscopic studies is to investigate the mineralogical composition of core samples and determine the spatial filling of core samples from the productive horizons of the Syrdarya and Shu-Sarysu depressions. Analyzing the obtained data will help identify the dependencies between the reduction in filtration characteristics and precipitation tendencies based on the composition and size of ore crystals in the host rocks of the productive horizon. Loose material from the samples was examined in immersion fluids, and transparent sections were prepared from it under a LEICA DM 2500 P microscope (Leica Microsystems, Wetzlar, Germany) [19,20]. Figure 6 shows images of the processed core samples from the Syrdarya depression: (a) Santonian, (b) Maastrichtian, and (c) Campanian stages.



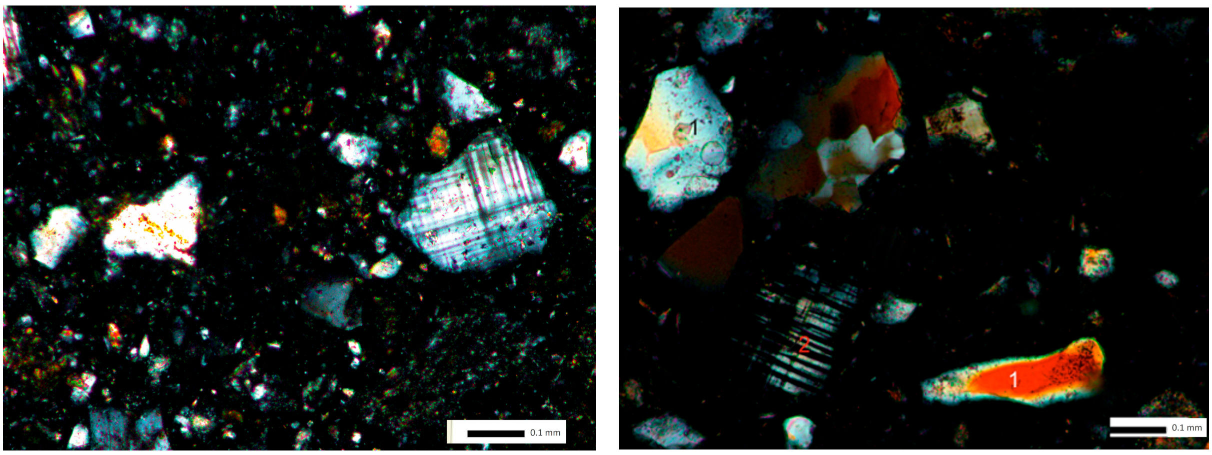
(**a**) (**b**) (**c**)

Figure 6. Images of the surface of core material samples from the Syrdarya depression, Nomarski interference contrast (**a**) Santonian, (**b**) Maastrichtian, (**c**) Campanian stages.

Sample (a, b, c) externally appear similar, having a light color with a faint grayish tint. Quartz is represented by irregularly shaped grain fragments, angular and rounded, with sizes up to 0.2–0.4 mm. Microcline is transparent with a characteristic microcline lattice. Orthoclase is heavily pelitized, semi-transparent to opaque, and brown. Refractive index values, determined in immersion liquids, correspond to standard minerals.

However, in the examined samples (a, b, c), there are significant distinctive features that have a substantial impact on the processes of uranium well extraction. In the plane of the transparent section of sample (a) from the Santonian layer, the following minerals were diagnosed: quartz, potassium feldspar, and cryptocrystalline rocks. The rock fragments are fine-grained, cryptocrystalline, transparent or semi-transparent, cloudy, pelitized, and composed of quartz and feldspar. In the plane of the transparent section of sample (b) from the Maastrichtian layer, the following minerals were identified: quartz, potassium feldspar, cryptocrystalline siliceous rocks, clayey-muscovitic rocks, and potassium feldspar rocks. The rock fragments are fine-grained, cryptocrystalline, transparent or cloudy, pelitized, and composed of quartz, feldspar, and clayey minerals. In the plane of the transparent section of sample (c) from the Campanian layer, there are quartz, potassium feldspar (microcline and orthoclase), kaolinite, and fine-grained aggregates of kaolinite with gypsum. The aggregates of kaolinite and gypsum are fine-grained, cryptocrystalline, difficult to diagnose, cloudy, and pelitized.

The images of the processed core samples from the Shu-Sarysu depression are presented in Figure 7: (a) from the Inkuduk layer and (b) from the Mynkuduk layer.



(**a**) (**b**)

Figure 7. Images of the surface of core material samples from the Shu-Sarysu depression, nickel staining. (**a**) Inukduk layer, (**b**) Mynkuduk layer.

The material of samples (a, b) appears similar externally, featuring minerals of quartz with a light color and a grayish tint. Quartz is represented by fragments of grains with various shapes: angular, rounded, oval, anhedral with winding irregular boundaries, typically free, without intergrowths, sometimes in the form of grain aggregates or with inclusions of fine-grained rocks.

However, there are significant distinctive features. In sample (a), the size of the quartz grains ranges from fractions to 0.3 mm, and potassium feldspars are represented by microcline and orthoclase. Microcline is transparent with a characteristic microcline lattice. Orthoclase is heavily pelitized, cloudy, with characteristic polysynthetic twins, and occasional individual crystals. In sample (b), the quartz grain sizes range from 0.2 to 0.3 mm. The grains are free, occasionally in aggregate clusters with mosaic structure. Potassium feldspars (K-feldspar) are similar to those described above in optical properties and sizes, ranging from 0.1 to 0.3 mm.

3.3. The Mechanism of Intensification of the Uranium Leaching Process

This technology has the potential to enhance uranium content in the productive solutions and restore the filtration characteristics of the ore in the productive horizon at deposits in the Syrdarya and Shu-Sarysu depressions. It can also reduce labor, energy, and other operational costs associated with uranium mining.

The dissolution of gypsum, aluminosilicate, and siliceous deposits in the productive horizon is achieved through the application of hydrofluoric acid (HF) in accordance with Reactions (9)–(11) [21].

$$CaSO_4\ 2(H_2O) + 2HF = CaF_2 + H_2SO_4 + 2H_2O \tag{9}$$

$$NaAlSi_3O_8 + 25HF = NaF + H_3AlF_6 + 3H_2SiF_6 + 8H_2O \tag{10}$$

$$SiO_2 + 6HF = SiF_4 + 2HF + 2H_2O \tag{11}$$

As evident from Equations (9)–(11), complete dissolution of gypsum, aluminosilicate, and siliceous precipitates in the near-wellbore zone of the wells is achieved by using a 10% hydrofluoric acid (HF) solution in a volume sufficient to penetrate the solution from 0.5 to 1.0 m along the entire length of the well filter and creating an acid bath. This will allow the restoration of filtration characteristics in the near-wellbore zone of the reservoir and increase the productivity of geotechnological wells.

Experiments on dissolving precipitates have allowed for the determination of optimal concentrations and volumes of the supplied chemical reagents to enhance the productivity of mining wells. The uranium content in the productive solution (PR) varies depending on various geological factors such as ore and host rock productivity, the presence of clay and carbonate minerals, acid consumption of rocks, and technical factors such as sulfuric acid concentration in the leaching solution, pH, eH of the environment, and others. While geological factors are beyond human control, we can modify technical factors that influence the intensity of uranium extraction from ores.

To increase the oxidative-reductive potential (ORP) of the leaching solution, hydrogen peroxide is added in small volumes ranging from 1 to 5 g/L. This raises the oxidative capacity of the leaching solution to approximately 450–500 mV, facilitating the oxidation of uranium dioxide (UO_2) from U IV (U^{4+}) to U VI (U^{6+}) as indicated by Reactions (12)–(14) [22].

$$2FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O \tag{12}$$

$$UO_2 + Fe_2(SO_4)_3 = (UO_2)SO_4 + 2FeSO_4 \tag{13}$$

$$UO_2 + H_2O_2 = UO_3 + H_2O \tag{14}$$

As evident from the interaction Equations (12)–(14), the oxidation of UO_2 to UO_3 is achieved through the oxidation of iron by hydrogen peroxide, transforming Fe II (Fe^{2+}) to Fe III (Fe^{3+}). Effective iron oxidation by hydrogen peroxide occurs at a pH range of

1.5 to 2.0. Intermittent hydrogen peroxide injection into the leaching solution to increase the Oxidation-Reduction Potential (ORP) will enhance uranium content in the PR and reduce sulfuric acid consumption in uranium leaching, thus intensifying the well mining process. The use of a complexing agent and pH reduction with sulfamic acid is permissible to increase the reactivity of hydrogen peroxide and form complexes with Fe III (Fe^{3+}). The application of hydrofluoric acid and hydrogen peroxide will lead to reduced labor, energy, and operational costs in uranium extraction [22].

Subsequent analysis of geotechnological parameters of the technological block before and after experimental works allows for the construction of graphs depicting uranium extraction from the subsurface, demonstrating the effectiveness of the chemical well treatment using the innovative method. Figure 8 shows a diagram of uranium extraction from the subsurface of the block before and after experimental works.

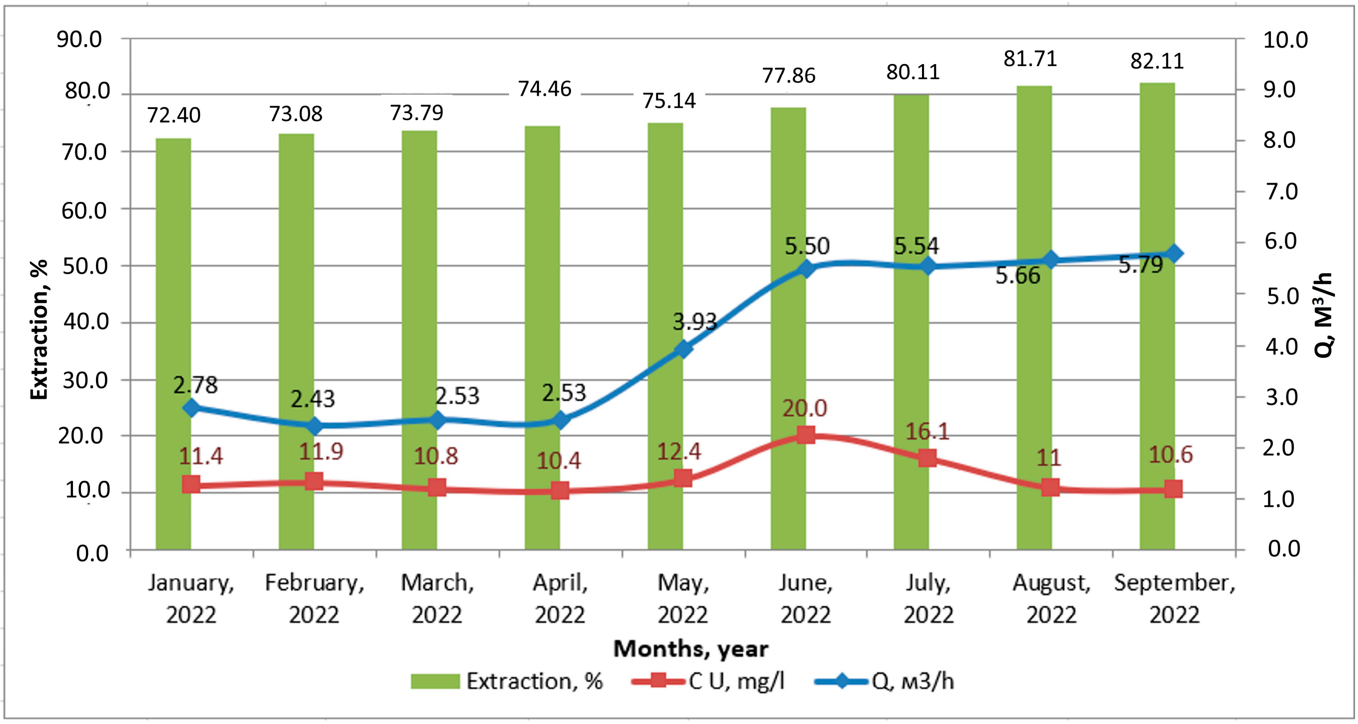


Figure 8. Monitoring of geotechnological parameters in the block.

As seen in Figure 8, at the time of the experiments, uranium extraction from the block reached 75%, with an average monthly increase of 0.68%, compared to the projected growth rates of 2.5% per month. The low extraction rates are attributed to the low uranium content in the Productive Solution (PS), which does not exceed 12 mg/L, and the insufficient productivity of wells, averaging no more than 2.53 m^3/h. However, after conducting experimental work on production wells in the technological block, a significant increase in well productivity is evident, from 2.53 to projected values of 5.50 m^3/h. Additionally, the uranium content in the PS increased from 11 to 20 mg/L, with a subsequent gradual decrease from 16 to 11 mg/L.

The increase in well productivity indicates the dissolution of precipitates in the pre-filtration zone of the wells and an improvement in well filtration characteristics. The increase in uranium content in the PS from 11 to 20 mg/L and its subsequent decrease to 11 mg/L over a period of 2 months indicates oxidation from Fe^{2+} to Fe^{3+}, consequently oxidizing U^{4+} to U^{6+}, which has high solubility. The extraction rate increased from 0.68% to 2.18% per month, totaling 82.11%. The subsequent decrease in uranium content in the PS and the restoration of initial values indicate the completion of chemical oxidation processes of uranium dioxide with the supplied hydrogen peroxide.

The obtained results are significant and confirm the undeniable effectiveness of the innovative method for intensifying uranium well extraction using dekolmating solutions based on hydrofluoric and sulfuric acid, followed by the injection of hydrogen peroxide into deposits with low ore filtration characteristics.

4. Conclusions

The conducted comparative quantitative and qualitative studies of samples indicate the similarity in the mineralogical composition of ore intervals in the Syrdarya and Shu-Sarysu provinces. X-ray phase analysis results show the prevalence of quartz in the Santonian (90.8%), Maastrichtian (54.7%), and Campanian (66.3%) ore intervals of the Syrdarya depression. The dominance of quartz in the Includuk (58.6%) and Mynkuduk (94%) ore intervals of the Shu-Sarysu depression is similar to the previous values. The second most abundant mineral in the ore intervals is potassium feldspar (K-feldspar), constituting 9.2%, 10.1%, and 5.7% in the Santonian, Maastrichtian, and Campanian horizons of the Syrdarya depression, respectively. The content of K-feldspar in the ore intervals is 14.3% for Includuk and 6% for Mynkuduk in the Shu-Sarysu depression. Gypsum in the ore intervals is found only in the Campanian horizon (16.4%) of the Syrdarya depression and the Includuk horizon (7.5%) of the Shu-Sarysu depression. The presence of gypsum and clay minerals in the ore intervals indicates challenging geological conditions for well extraction.

The results of comparative analysis of microscopic studies of core samples from productive horizons of the Syrdarya and Shu-Sarysu depressions visually show the sizes of crystal grains and other minerals in host rocks, allowing the identification of reasons for the decrease in ore filtration characteristics. Samples from the Santonian horizon are characterized as homogeneous, with fragments of irregularly shaped quartz grains, ranging in size up to 0.2–0.3 mm, transparent microcline, and pelitized orthoclase. Results from the Maastrichtian horizon samples are less homogeneous, with irregularly shaped quartz grain fragments up to 0.2–0.4 mm, the presence of potassium feldspar, and clayey-muscovite minerals. Core samples from the Campanian horizon are characterized as non-homogeneous, containing fragments of irregularly shaped quartz grains with average sizes up to 0.2–0.3 mm and the presence of potassium feldspar, microcline, orthoclase, kaolinite, and fine-grained aggregates of kaolinite with gypsum. Core samples from the Includuk and Mynkuduk horizons are homogeneous, containing quartz and feldspar. However, in Includuk horizon samples, the quartz grain sizes are 0.3–0.4 mm, with a predominance of fine-grained fraction, while in Mynkuduk horizon samples, the sizes are 0.3–0.5 mm, with a predominance of medium fine-grained fraction. The presence of fine-grained particles in the ore intervals of the Campanian horizon of the Syrdarya depression and the Includuk horizon of the Shu-Sarysu depression reduces ore filtration characteristics and increases the block processing period.

Comparatively analyzed compositions, quantitative–qualitative characteristics of precipitate-forming materials in technological wells of the yrdarya and Shu-Sarysu depressions were studied.

The results of X-ray phase analysis of samples from wells in the Syrdarya depression indicate the prevalence of chemically originated precipitates, primarily gypsum and calcite. However, in the Campanian horizon, the precipitates are multi-component, with a complex structure. The presence of quartz (35.6%), albite (33.9%), and microcline (4.9%) suggests the dominance of mechanically formed precipitates.

In the ore intervals of the Shu-Sarysu depression, precipitates are predominantly mechanically formed due to the presence of quartz, albite, and microcline.

Based on the obtained data, the effectiveness of the innovative method for intensifying underground uranium leaching has been developed and experimentally substantiated. This method involves the use of a universal precipitate solvent and a uranium dioxide oxidizer. Experiments on treating technological wells in the selected block resulted in averaged values for well productivity and uranium content in the productive solution (PS).

The monitoring results showed an increase in well productivity from an average of 2.5 to 5.5 m^3/h and an increase in uranium content in PS from 11 to 20 mg/L, with subsequent gradual reduction to the initial 11 mg/L. This allowed for increasing the intensity of uranium extraction from the depths from 0.6 to 2.5% per month over an extended period.

Hydrofluoric acid serves as a universal precipitate solvent, helping to restore the filtration characteristics of the productive horizon and increasing the productivity of technological wells. Hydrogen peroxide serves as a uranium dioxide oxidizer, enabling the oxidation of uranium dioxide and increasing uranium content in PS. The well treatment method reduces the specific consumption of chemical reagents and increases the efficiency of the underground well leaching of uranium.

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