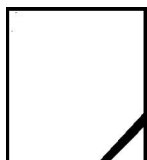


**THEORY AND PRACTICE OF UNDERGROUND  
LEACHING OF MINERAL RESOURCES**



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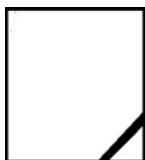
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### **Annotation**

The paper describes the vast experience of in-situ leaching in Kazakhstan, accumulated during 30 years of its application and improvement for mining, mainly uranium.

About half of the world's reliably explored uranium reserves are concentrated in the subsoil of Kazakhstan. A unique feature of the country's uranium reserves is that 75% of them are concentrated in deposits associated with regional zones of formation oxidation. This type of deposits is not widespread in the world. In Kazakhstan, these deposits are concentrated mainly in the Shu-Sarysu, Syrdarya and Ili uranium-ore provinces.

A number of deposits are currently being developed by the Stepny, Central and №6 ore departments of NAC Kazatomprom CJSC. Extraction is carried out by a relatively cheap and environmentally preferable method of in-situ leaching through a system of wells drilled from the surface underground borehole leaching (UBL).

For these purposes, a comprehensive research method is used, including: analysis and synthesis of practical and theoretical data in the field of uranium mining by underground leaching and the environmental problems arising in this case, mathematical modeling method, analytical calculations, analytical calculations, laboratory work and in-depth field experiments in production conditions, generalisation and transfer of the obtained scientific and practical data to design organisations and industrial enterprises dealing with uranium mining by in-situ leaching. The material from long-term observations of the process of aquifer self-regeneration is compelling and illustrative in the Irkol field of Syrdarya province in Kazakhstan.

The purpose of the work is to establish the patterns of natural demineralization of residual solutions of underground sulfuric acid leaching of uranium. For this purpose, at all operating UL enterprises, installations were designed and built to extract associated useful components from productive solutions.

In conclusion, it can be noted that the development and improvement, based on many theoretical and applied studies, of the method of borehole in-situ leaching of metals described in this work is the fruit of the creative efforts of a large number of specialists in various fields of knowledge both in the republic and abroad.

### **Introduction**

Underground leaching of metals is a method of development of ore deposits by selective conversion of useful component into liquid phase directly in the subsurface with subsequent processing of metal-containing (productive solutions). In this method the progressive technique of transferring one of the main hydrometallurgical processes - percolation - to the place of occurrence of ore material is successfully realised.

The scientific novelty is the establishment of theoretical and experimental substantiation of the regularities of the process of natural demineralization of residual solutions of underground leaching of

uranium and other components, the parameters of the formation and behavior over time of their halo under changing hydrodynamic conditions, as well as the scale of the demineralization zone.

Theoretical principles and methods for calculating the spreading parameters of technological solutions and their neutralization zones have been developed, and a general criterion for assessing the intensity of this process has been derived; a fundamentally new method has been created to intensify the process of natural demineralization of formation waters enriched with uranium leaching products, based on the displacement of the halo of residual solutions into rocks not affected by technogenesis.

The scientific significance of the work lies in the establishment by natural experiments of the basic laws of groundwater rehabilitation, the development of a theoretical method for predicting the spread of harmful new formations in waste horizons during uranium ISR.

The relevance of this study is that during underground borehole leaching (ISL) of uranium, the release of radioactivity into the atmosphere is significantly lower than with traditional mining methods of mining and processing uranium ore. Wells filled with liquid throughout the entire period of operation prevent the release of radon from the subsurface. During ISR, only about 20% of the main radioactive elements enter a mobile state in the subsurface and are brought to the surface, compared to 100% with traditional mining methods. There is also no need to build tailings dumps with a high level of radiation from the stored material. Solutions coming from leaching sites have a low level of radiation as a result of the poor solubility of radium and short-lived daughter products of the decay of U-238; only a very small part of Ra-226 and other radionuclides of the uranium-radium series is sorbed on the ion exchange resin simultaneously with uranium.

Moreover, it was in Kazakhstan that for the first time in the world the deepest deposits, with ore depths of more than 600 meters, were involved in mining using the UL method, and the profitability of their exploitation was proven primarily due to the production of richer productive solutions, the formation of which has a positive effect of natural autoclave - increased temperature and pressure in the area where the main leaching reactions occur.

It is difficult to overestimate the importance of the development and implementation of the UL method in Kazakhstan from an environmental and socio-economic point of view. Recently, one of the most pressing issues in mining production is its environmental assessment.

The idea of the work is to accelerate the process of natural demineralization and the depth of purification of residual uranium leaching solutions from harmful elements by forcibly shifting their halo from the zone of rocks disturbed by technogenesis to the zone with natural conditions.

The goal of the study is to mine uranium with the lowest content of radioactive substances. The fact is that during sulfuric acid leaching, as a result of the physicochemical interaction of the solvent with the host rocks and ores, in the process of multiple circulation of solutions between the above-ground and underground complexes, a complex anion-cation composition of technological solutions is formed, which far exceeds the maximum permissible concentrations for the waters used for drinking and household purposes. Significant amounts of sulfates, chlorides, bicarbonates, iron, aluminum, nitrates, radionuclides and other trace elements accumulate in EPS solutions. Contamination of groundwater with these solutions can occur in the event of their significant spreading beyond the boundaries of exhausted deposits or individual deposits along ore-bearing and adjacent aquifers. The ingress of hazardous listed and other components into drinking water can lead to serious environmental consequences.

### **1.1 Mineral resource base of uranium**

The material presented in this work allows us to get an idea of how large and diverse the uranium mineral resource base of Kazakhstan is. This is due to the peculiarities of the geotectonic position of the territory of the republic, the specifics of geological development, and the richness of geological and structural settings.

Industrial uranium deposits that make up the ore districts and provinces are found in deposits that are very different in age and structural and formational affiliation.

In the pre-Mesozoic formations of the Kazakh folded region and the spurs of the Tien Shan, the North Kazakhstan and Kendyktas-

Chu-Ili-Betpak-dala uranium provinces with a surprisingly diverse set of hydrothermal deposits are located, respectively.

Large soil-infiltration uranium-coal and bed-infiltration (sandstone) deposits of the Ili uranium province are localized in the coal-bearing terrigenous deposits of the Triassic-Jurassic depression structures.

The aquiferous sandy horizons of the Cretaceous-Paleogene host epigenetic reservoir-infiltration and uranium deposits of the regional zones of reservoir oxidation of the Chu-Sarysu and Syrdarya uranium-ore provinces, constituting one of the largest East Turanian megaprovinces in the world.

Finally, in the thickness of the Oligocene marine clays on the Mangystau Peninsula there is a uranium ore region of the same name with a unique phosphate-organogenic type of complex deposits associated with horizons of uranium-bearing fish and a variety of dinosaurs bone remains.

In addition to the noted uranium ore areas, a significant number of ore and uranium-bearing areas and individual objects (including other genetic types) that are currently in reserve have been identified, which in the future can be used to replenish the existing raw material base [1-2].

The evolution of the uranium raw material base in Kazakhstan is very indicative and interesting. From the 50s to the 70s, it was based on hydrothermal deposits localized in pre-Mesozoic formations, due to which its development and replenishment mainly took place.

Deposits of the organogenic-phosphate type on the Mangystau Peninsula also played a certain role. Other exogenous deposits (uranium-coal, reservoir-infiltration deposits in permeable aquifers of the Cretaceous and Paleogene) were not exploited due to the lack of acceptable technology.

Since the beginning of the 70s, with the introduction of a new progressive method of developing water-logged deposits - underground leaching, intensive searches, exploration and involvement in the exploitation of reservoir-infiltration deposits, large and unique in terms of the scale of distribution of raw materials, began.

It is difficult to overestimate the truly revolutionary role that the introduction of this method played in the creation of the mineral resource base of Kazakhstan.

In particular, the use of this method determined the amazing transformation of the unfavorable (for the mining method) features of epigenetic deposits, such as high water content and weak lithification of rocks and ores, into their main advantages, allowing the extraction of uranium and associated components without extracting the ore mass and host rocks at surface and thereby significantly reduce the negative impact on the natural environment. With the introduction of the UL method in the Mesozoic-Cenozoic depression structures of Kazakhstan, prospecting and evaluation work for uranium was again widely deployed, and the emphasis was placed on areas with already determined ore bearing Chu-Sarysu and Syrdarya uranium provinces.

As a result of the work carried out, the Chu-Sarysi depression by the end of the 70s took shape as the largest uranium ore province, representing a long-term mineral resource base for uranium mining using the underground leaching method. In this regard, it is advisable to note that the discovery of unique deposits of the Chu-Sarysu and Syrdarya ore provinces became possible only thanks to the development and prompt implementation into practice of the concept of regional ore-generating fronts of formation oxidation.

In particular, it was proven that the formation of epigenetic uranium deposits is associated not with individual Paleozoic uplifts, representing local areas of supply of oxygen-bearing uranium waters, as previously thought, but with the general development of the Tien Shan orogenic zone, which at the time of the latest tectonic activation caused the movement of formation waters immediately in all aquifers of the Cretaceous and Paleogene to the discharge centers. As already noted, in the initial period these deposits were explored for mining using the mining method (open pit or underground)

In terms of their industrial significance, they were considered monoelemental, where oxide uranium ores did not contain significant impurities of accompanying components. Accordingly, uranium was given the importance of the only metal capable of accumulating in industrial quantities at the boundaries of zones of formational limonitization.

The study of a number of elements localized together with uranium at the boundaries of the FOZ, in particular, selenium, molybdenum, and rhenium, was of a purely mineralogeochemical nature.

As a result of complex studies, the patterns of localization of uranium, selenium and molybdenum during the pinching out of the FOZ were outlined, and their place in epigenetic zoning was established.

However, when carrying out technical and economic calculations to determine the possibility of developing deposits and transferring them to industry for exploitation by mining, no practical interest arose in the accompanying elements, and these objects were still considered as monouranium, and not complex.

Again, the development by industry of the method of underground leaching at the location of ores through systems of geotechnological wells, made it possible to approach the problem of the possible use for the needs of the national economy of a number of useful components that are satellites of uranium in the exogenous epigenetic process from a fundamentally new position. It was shown for the first time that when implementing the IR method, when the working reagent (due to the specifics of the method) processes a larger volume of ore mass than necessary, the leaching processes should involve useful components contained not only in uranium ores, but also in the immediate vicinity of them in a single aquifer (rhenium, selenium, molybdenum, etc.).

Geological exploration work revealed, in addition to selenium, molybdenum, and rhenium, scandium, yttrium, lanthanides, and vanadium in the ores, and in the process of geotechnological research, the possibility of leaching the listed elements from ores of deposits of this type was in principle proven. By the beginning of the eighties, it became clear that the formation-infiltration deposits that were considered monouranium were polyelement deposits, and solving the problem of their detailed study, including complex geotechnological aspects, in preparation for industrial development in relation to the IW method is of great national economic importance.

Not only geological and operating organizations, but also industry and republican research institutes began to participate in the development of the problem

Thus, the structure of Kazakhstan's uranium raw material base began to steadily change in favor of deposits of this type, characterized by high competitiveness. By the beginning of the 90s, the basis of the uranium raw material base was formed by formation-infiltration deposits of regional 3POs. Hydrothermal deposits in pre-

Mesozoic formations are gradually being transferred to conservation for economic and especially environmental reasons. In addition, in recent years, the requirements for the profitability of deposits involved in development have sharply increased. In this regard, deposits of complex ores containing, in addition to uranium, other valuable associated components, began to attract maximum interest. The cost of uranium mined by the IR method in epigenetic reservoir-infiltration deposits is significantly lower than the cost of uranium mined by mining from most hydrothermal deposits.

The problem of negative technogenic impact on the environment as a result of the exploitation of deposits has now become of particular importance. In this regard, the UL method has a number of advantages over the mining method. Experts have clearly established that possible contamination of formation water during underground leaching can only occur as a result of a gross violation of the work technology. Existing methods of cleaning and reclamation of the natural environment, subject to compliance with all operating rules, ensure its environmental safety.

Currently, Kazakhstan has one of the world's largest uranium ore raw material bases, which not only makes it possible to fully meet domestic needs, even with maximum development programs for its own nuclear energy, but also makes the republic one of the largest potential suppliers of uranium to the world market.

In terms of total resources of natural uranium, the republic occupies one of the first places in the world, and in terms of resources and reliably explored reserves of uranium, suitable for mining uranium by underground leaching, it is a world leader. In the modern structure of Kazakhstan's uranium raw material base, the main place (about 73% in total resources and about 65% in reserves of categories B+C1+C2) belongs to deposits of reservoir oxidation zones, developed by the IW method. The explored reserves of soil-infiltration deposits account for 10%, of which 5.5% are complex molybdenum-uranium-coal deposits and 4.5% are deposits localized in sandy-clayey formations. About 3% are complex rare metal-uranium-phosphorus ores of organogenic-phosphate deposits of the Caspian region. The share of endogenous and polygenic deposits in pre-Mesozoic formations accounts for about 22%.



It should be emphasized that the decisive role in the creation of the uranium raw material base of the republic belongs to the Volkov-geologiya enterprise; at least 70% of the uranium resources suitable for mining using the UL method have been identified and prepared by its specialists.

Despite the fact that the stock of uranium deposits located in favorable conditions and especially easily discovered has significantly decreased, the prospects for replenishing and increasing the uranium mineral resource base in Kazakhstan are quite large. This applies both to epigenetic reservoir-infiltration deposits exploited by the IW method, and to deposits of other genetic types [3].

### **1.2 Copper mineral resource base**

The largest object of the cuprous sandstone formation in Kazakhstan is the Zhezkazgan copper deposit, which in this work will be considered as the most promising raw material base for underground leaching.

According to K.I. Satpayev, mineralization here is confined to the sand-shale strata of the Upper Carboniferous. The ore-bearing strata is exposed in the direction from south to north at a distance of 70 km.

The Upper Carboniferous sequence and the underlying Devonian Lower Carboniferous rocks are folded into a large synclinal fold, complicated by brachyanticlines broken by normal faults. The thickness of the Upper Carboniferous sandy-shale sequence is 900 m; it is subject to seven horizons with mineralization confined to the crest of the chest-type brachinticline.

Mineralization is concentrated in layers of gray sandstones with carbonate cement and is absent or poorly developed in layers of red sandstones and conglomerates with clayey-ferruginous cement. Ore bodies have the form of sheet-like deposits and flat lenses, their number is small. The largest deposits can be traced at a length of 1.5-2.0 km and a dip of 800 m, with a thickness of 1.5-4.0 m to 18 m. In addition to the deposits, there are separate mineralized zones “veins with breccia”, for example, the so-called Peter and Paul fault, traced along the strike for 500 m.

Composition of the ores: chalcopyrite, bornite, pyrite, fahlores, sphalerite, galena, calcite, quartz, barite, chalcocite, covellite, oxides and hydrous carbonates of copper. Ore minerals are scattered in the form of small impregnations in the cement of sandstones and in the

form of veinlets composed of rock crystal, calcite and large crystals of chalcopyrite, bornite, chalcocite, and galena. The ores contain up to several percent Cu (on average), and in places are enriched in Pb, Zn and Ag.

A characteristic feature of the Zhezkazgan deposit is the unevenness of mineralization and the qualitative heterogeneity of the chemical and mineralogical composition. Therefore, as a rule, areas with high copper content alternate with poor ones, and poor ones with substandard ores.

In the Zhezkazgan mines over the past 15 years, the average copper content in ore has decreased by almost 40%. In the total ore flow, the share of ore with low content (close to cut-off content) reaches 25-30%. It is known that during the enrichment of depleted ores, the removal of useful components into the tailings sharply increases.

One of the methods that allows the extraction of low-grade ores is their leaching in situ. Therefore, at present, numerous research and experimental work is being carried out on this problem [4-5]. The widespread introduction of heap leaching and especially underground leaching methods will make it possible to increase the raw material base of the Zhezkazgan deposit by more than double, as well as reduce the operational losses already committed by 5-6 times.



Table 1

List of countries by fuel uranium production according to data

№	A country	2015, tons	2016, tons	2017, tons	2018, tons	2019, tons	2020, tons	2021, tons	Share in the world, 2020, %
1	Kazakhstan	23607	24689	23321	21705	22808	19477	21819	45,1 %
2	Namibia	2993	3654	4224	5525	5476	5413	5753	11,9 %
3	Canada	13325	14039	13116	7001	6938	3885	4693	9,7
4	Australia	5654	6315	5882	6517	6613	6203	4192	8,7 %
5	Uzbekistan	2385	3325	3400	3450	3500	3500	3500	7,2 %
6	Russia	3055	3004	2917	2904	2911	2846	2635	5,5 %
7	Niger	4116	3479	3449	2911	2983	2991	2248	4,7 %
8	China	1616	1616	1692	1885	1885	1885	1885	3,9 %
9	India	385	385	421	423	308	400	615	1,3 %
10	Ukraine	1200	808	707	790	800	744	455	0,9 %
11	South Africa	393	490	308	346	346	250	385	0,7 %

12	Iran	38	0	40	71	71	71	75	0,2 %
13	Iran	45	45	45	45	45	45	45	< 0,1 %
14	Pakistan	40	44	0	0	0	15	29	< 0,1 %
15	Brazil	1256	1125	940	582	58	6	8	< 0,1 %
16	Czech	155	138	0	0	0	0	0	0 %
17	Romania	77	50	0	0	0	0	0	0 %
18	France	2	0	0	0	0	0	0	0 %
19	Germany	0	0	0	0	0	0	0	0 %
20	Malawi	0	0	0	0	0	0	0	0 %
	Total in the world, tons	<b>60304</b>	<b>63207</b>	<b>60514</b>	<b>54154</b>	<b>54742</b>	<b>47731</b>	<b>48332</b>	<b>100 %</b>
	Production U <sub>3</sub> O <sub>8</sub>	71113	74357	71361	63861	64554	56287	56995	
	% of global demand	98 %	96 %	93 %	80 %	81 %	74 %	77%	

Table 2  
The largest uranium deposits and their developers as of 2019

Field	A country	Company	Extraction method	Production (tons)	Share in the world
Cigar Lake	Canada	Cameco / Orano	underground	6924	13 %
Khusab	Namibia	Swakop Uranium	open	3400	6 %
Olympic Dam	 Australia	<a href="#">BHP Billiton</a>		3364	6 %
Muyunkum and Tortkuduk	Kazakhstan	Kazatomprom (49 %)/Orano (51 %)	in-situ leaching	3252	6 %
Inkai	Kazakhstan	Kazatomprom (60 %) / Cameco (40 %)	in-situ leaching	3209	6 %
Budenovskoe	Kazakhstan	Kazatomprom (51 %) / Uranium One (49 %)	in-situ leaching	2600	5 %
Rössing	Namibia	Rio Tinto	open	2076	4 %
Arlit	 Niger	<a href="#">Orano</a>	open	1912	4 %
Central Mynkuduk	Kazakhstan	Kazatomprom	in-situ leaching	1964	4 %
South Inkai	Kazakhstan	Kazatomprom / <a href="#">Uranium One</a>	in-situ leaching	1601	3 %

### 1.3 Basics of geotechnologies for underground leaching of useful components

The optimal way to exploit uranium deposits is in-situ leaching (IL) at the ore site through systems of technological wells constructed from the surface. The industry currently has two technologies for underground uranium leaching: sulfuric acid, widely used in Kazakhstan and the CIS countries and mainly suitable for ores with a low content of bound carbon dioxide, and bicarbonate (carbonate) with an oxidizer, widely used in the USA.

The fairly high efficiency of the underground leaching method has led to a reduction in industry requirements for the quality of uranium raw materials (for example, the minimum cut-off content of uranium in ores for the IW method is usually taken to be 0.01% and, apparently, can be reduced to 0.005%, while for mining method it is 0.03%). The use of underground leaching has made it possible to take a fundamentally new approach to the problem of extracting from the subsoil a number of important minerals, in particular, scandium, rhenium, yttrium, a number of lanthanides, molybdenum and others associated with the wedging out of formation oxidation zones in aquifers shared with uranium and contained in ores in lower concentrations than those established by industry requirements for the mining method of their extraction [6].

Analysis of the materials shows that the geological and hydrogeological conditions for the localization of multi-element mineralization in exogenous epigenetic deposits of Kazakhstan are favorable for the extraction of useful components by underground leaching, which is primarily due to:

- the very specificity of exogenous epigenetic ore formation, during which oxygen-containing waters, along the path of filtration, extract useful components from the host rocks of the productive horizon or areas of nutrition and, in a certain sequence, precipitate (concentrate) them under changing geochemical conditions on reduction or neutralization geochemical barriers in a form favorable for leaching with aqueous solutions of acids or alkali metal salts. Thus, in the natural conditions of Southern Kazakhstan, the first unique cycle of hydrometallurgical processing takes place, preparing elements for the subsequent cycle of underground leaching;

- compact arrangement of epigenetic concentrations of uranium and associated useful components in a single aquifer, which deter-

mines the possibility of developing them mainly through unified systems of technological wells:

- the confinement of ore concentrations to horizons of highly permeable gravel-sandy, highly watered rocks, not suitable for mining.

#### **1.4 Underground leaching of metals from ores of polyelement deposits**

The studies performed have shown that the process of underground leaching of useful components from ores of polyelement infiltration deposits is in many ways similar to exogenous epigenetic ore formation, differing from it in the reverse direction, the concentration of leaching reagents in solutions, the rate of chemical reactions, the content of useful components in solutions, and the time factor. This conclusion is of great importance for the development of underground leaching technology for the sequence (stages) of extracting useful components from the subsoil.

Underground leaching of useful components from ores of exogenous epigenetic deposits is considered as a reverse process of transferring metals into a mobile state as a result of their reactions with oxygen-containing solutions of reagents rich in sulfate sulfur or carbonate ion, which are fed into the formation through a system of injection technological wells with subsequent movement within the volume leaching and pumping of productive solutions from pumping (discharge) wells. Thus, the commonality of exogenous epigenetic ore formation and underground leaching of epigenetic concentrations of metals in hydrogenous deposits lies in the very nature of the processes under consideration, their physicochemical essence.

The movement of aqueous solutions in both cases is carried out in a filtration mode in rocks with natural permeability (filtration coefficient is usually more than 1 m/day) due to a pressure gradient: during the epigenetic process - from areas of formation piezomaximum to areas of groundwater discharge, during underground leaching - from areas injection wells to unloading areas. Hydraulic slopes and natural speeds of movement of formation waters are 2-3 orders of magnitude lower than those of UL solutions.

Both processes can be defined as heterogeneous chemical interactions, from a physicochemical point of view, accompanied by changes in the concentrations of reacting substances in the liquid and solid

phases during the filtration movement of the first within the leaching volume. Both processes obey the same laws of diffusion kinetics and physicochemical hydrodynamics.

It is obvious that technogenic UL solutions, differing from natural ones in a higher concentration of leaching reagents (primarily sulfate or carbonate components and oxidizing agents), are more chemically active. Concentrations of ore elements in UL solutions vary widely, being 2 - 4 orders of magnitude higher than in ore-forming formation waters. Thus, for uranium, molybdenum, vanadium and selenium, in the technogenic process they are 10<sup>-2</sup>-10<sup>-1</sup> g/l, and in the natural ore-forming process - from 10<sup>-6</sup> 10<sup>-3</sup> g/l; for rhenium and scandium - 10<sup>-4</sup>-10<sup>-3</sup> and 10<sup>-7</sup>-10<sup>-5</sup> g/l, respectively.

The forms of migration of useful components with the carbonate (bicarbonate) IW method, in process solutions are the same as in formation waters with a near-neutral and moderately alkaline environment: these are anions represented by dissociations of acids - molybdic acid  $\text{M004}$ , rhenium  $\text{Re04}$ , orthovanadium  $\text{H}_2\text{VO}_4$ , selenite  $\text{HSeO}_3$ , hydrogen selenide  $\text{HSe}$  or carbonate complexes - uranyl  $\text{UO}_2(\text{CO}_3)_2$ ,  $\text{UO}_2(\text{CO}_3)_3$  and scandium  $\text{Sc}(\text{CO}_3)_2$ .

Precipitation (concentration) of useful components from ore-forming aqueous solutions is carried out on the wedging out of zones of formation oxidation (on reduction or neutralization geochemical barriers) in a certain sequence: on a barrier of the first type - in accordance with the natural decrease in Eh of the environment from +200 to -200 mV:  $\text{Sc} > \text{V} > \text{U} > \text{Re} > \text{Mo}$ ; on a barrier of the second type - in accordance with a decrease in pH from 7.0-8.5 to 6.5 and a subsequent increase to ~7.5 V  $\text{V} > \text{Sc}$ , TR. Exogenous epigenetic concentrations refer to mineral forms that are quite easily soluble in aqueous solutions of acids or alkalis - these are finely dispersed oxides, hydroxides, disulfides, and native forms. The production of useful components from productive solutions is carried out on the surface as a result of various technological operations (sorption, precipitation, etc.).

The process of UL of useful components is opposite in its direction to the process of epigenetic ore deposition. Thus, with the carbonate leaching method, as the Eh of the medium increases, according to thermodynamic calculations and experiments, Mo should be extracted from the ores first, then Re, U, V, and finally, in the pres-

ence of a strong oxidizing agent, Se. With the sulfuric acid method, according to the same data, this sequence is generally preserved, but here it reflects not so much an increase in the Eh of the medium as a decrease in pH as the L:T indicator increases - Mo (pH<7), Re (pH<6.5), Sc (pH<5), U (pH<4), V (pH<3), Se (pH<6 in the presence of a strong oxidizing agent).

One of the features inherent in both the epigenetic process of ore formation and UL is the reprecipitation of useful components on mobile geochemical barriers along the path of filtration of ore-bearing solutions. For the conditions of natural ore formation, this effect is observed as long as there is a pressure gradient and the flow of oxygen uranium-bearing groundwater to geochemical barriers, and for the UL process - only during acidification of ore-bearing rocks or during the latent (hidden) period when preparing them for carbonate leaching. Responsible for the precipitation of useful components in natural conditions are mainly two types of geochemical barriers: for polyvalent elements - mainly reducing, for monovalent elements - neutralizing. Under technogenic conditions, two types of UL in the subsoil are also developed: with the acid method, the neutralization method predominates, and with the carbonate method, the reduction method predominates.

The intensity and duration of the processes of exogenous epigenetic ore formation and underground leaching are sharply different. If for the first it is millions and the first tens of millions of years, then for the second it is the first years. The relatively weak chemical activity and low degree of metal content of reservoir solutions when creating ore concentrations are compensated by the time factor - the duration of the ore formation process, and during operation (to achieve the design extraction of metals from the subsoil) its relatively short period is compensated by increased concentrations and chemical activity of working solutions, the creation of increased rates their movement within the mining volume and by other means.

Consequently, in the course of both natural ore-forming and technogenic processes of IR, one of the main cycles of hydrometallurgical processing is carried out directly in the subsoil, namely, the transfer of useful components into the liquid phase, and in the first, in addition, the concentration of elements in the solid phase at geochemical barriers in fairly easily soluble mineral form. The natural process

of exogenous epigenetic ore formation, as it were, prepares useful components for leaching and predetermines the possibility of using the IP method for the exploitation of multi-element deposits.

When developing geotechnological regimes of UL, the effect of precipitation of elements on the pinching out of formation oxidation zones in a certain paragenetic dependence is used. It is obvious that important for these regimes are the initial concentrations of the working reagent, the ratio of Liquid: Solid, the reagent capacity of the ore-hosting rocks and other factors that determine changes in the alkaline-acid index and the redox potential of the environment. It is recommended to extract useful components from polyelement ores in the reverse order of their deposition on geochemical barriers, according to the general scheme: Mo > Re > Sc, Y, TR, U > V > Se. Another important circumstance is the need to take into account the individual geochemical and mineralogical characteristics of useful components, which determines the choice of the environment and geotechnological conditions of the water supply, as well as environmental protection measures.

### **1.5 Thermodynamic prerequisites for the UL of useful components from ores**

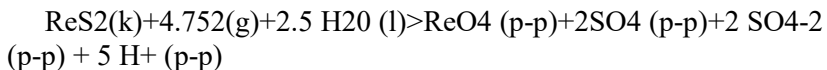
The theoretical basis of the physicochemical conditions of the process of IR of useful components (molybdenum, rhenium, uranium, selenium, vanadium, scandium, yttrium, some lanthanides) is based on thermodynamic calculations of the fields of predominance of compounds in the liquid and solid phases, highlighting areas of favorable geotechnological conditions for their leaching

### **1.6 Polyvalent elements**

It is necessary to take into account that their ore epigenetic concentrations are associated with a reducing geochemical barrier in choosing geotechnological regimes for leaching useful components of this group (molybdenum, rhenium, uranium, parts of vanadium, selenium).

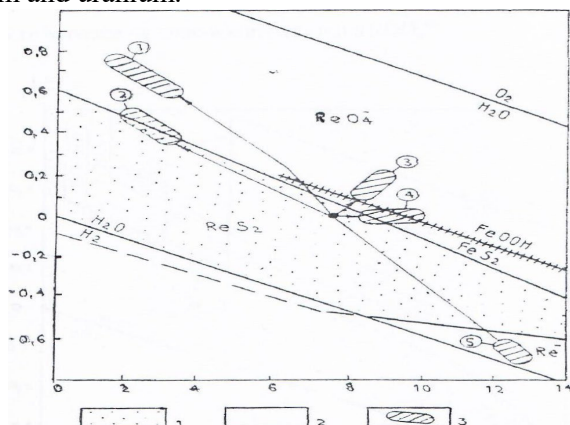
The assessment of geotechnological conditions for polyvalent elements is carried out in a sequence opposite to the order of their reductive precipitation, i.e., the sequence of their possible transition into the UL solution during oxidation. The interaction of leaching solutions with rhenium disulfide occurs according to the reaction equation:





Thermodynamically, this reaction, as in the leaching of molybdenum, does not depend on the alkalinity or acidity of the medium and for its implementation, in addition to the necessary kinetic factors, only the presence of oxygen or other oxidizing agents is required.

The most favorable geotechnological conditions for underground leaching of rhenium are mainly sulfuric acid and carbonate with an oxidizing agent, located in a vast field of perhenate ion  $\text{ReO}_4$ . Under these conditions, rhenium can be extracted from ores together with molybdenum and uranium.



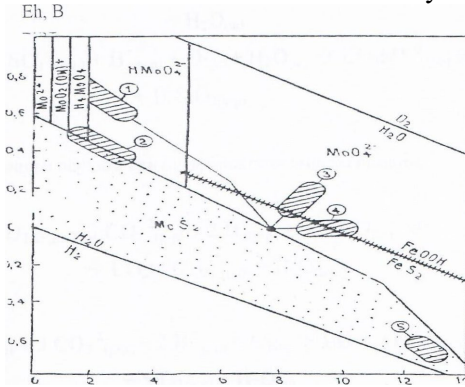
**Fig. 1.** Eh-pH diagram of the fields of dominance of the rhenium compound at = 25 °C and P = 1 bar. 1 - fields of liquid phases; 2 - fields of solid phases; 3 - geotechnological situation

The interaction of molybdenum leaching solutions occurs according to the reaction equations:



To implement these reactions, in addition to favorable kinetic factors, only the presence of an oxidizing agent is required. Favorable for underground leaching of molybdenum are mainly sulfuric acid and carbonate with an oxidizing geotechnological conditions, which

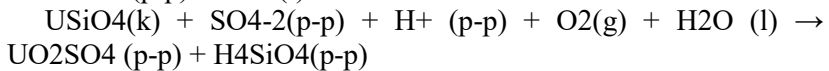
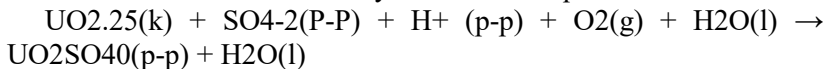
during the sulfuric acid method fall into the fields of liquid phases of hydromolybdate - ion  $\text{HMoO}_4^{2-}$  and molybdic acid  $\text{H}_2\text{MoO}_4$ , and for the carbonate method - into the field of molybdate - ion  $\text{MoO}_4^{2-}$ .



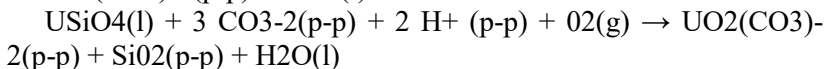
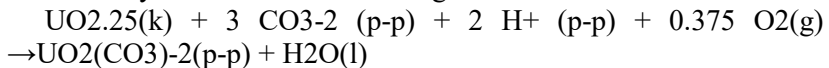
**Fig. 2.** Eh-pH - dominance field diagram molybdenum compounds at  $T = 25^\circ\text{C}$  and  $P = 1$  bar

Uranium is currently the main useful component in the deposits under consideration. The issues of geotechnology of underground leaching are the most developed for it. Depending on the mineral composition of the host rocks and the type of ore mineralization, acid (aqueous solutions of sulfuric acid) and carbonate, bicarbonate (aqueous solutions of sodium carbonate-bicarbonate, ammonium, etc.) methods are used for uranium leaching; Oxygen, hydrogen peroxide, and ferric iron are used as oxidizing agents.

The interaction of sulfuric acid working solutions with U (IV) oxides and silicates is described by the reaction equations:

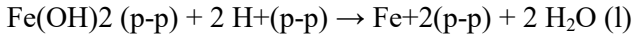
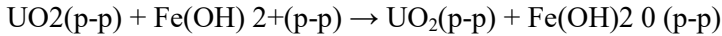
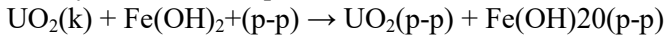


Similarly for bicarbonate leaching:



In an acidic environment, one of the oxidizing agents of U (IV) can be hydrolyzed forms of ferric iron:  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3$

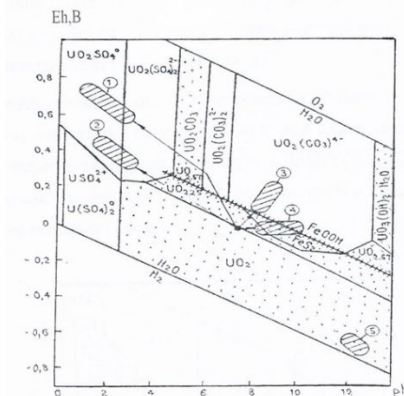
$\text{Fe}(\text{OH})_2^{2+}$  and, to a lesser extent,  $\text{Fe}^{3+}$  ions. The oxidation process of uranium oxides in an acidic environment is stepwise and is described by the reaction equations:



An additional oxidizing agent for uranium in a sulfuric acid environment is nitric acid, often supplied with sulfuric acid to passivate stainless steel materials and equipment.

Hexavalent uranium compounds are extracted from ores without an oxidizing agent in both acidic and carbonate environments.

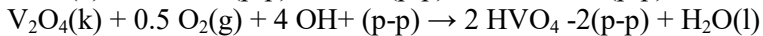
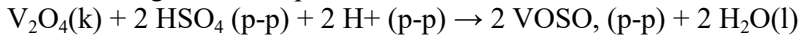
In general, three geotechnological conditions are thermodynamically favorable for uranium leaching: sulfuric acid with an oxidizer and sulfuric acid without an oxidizer, located in the fields of uranyl sulfate complexes  $\text{UO}_2\text{SO}_4 - \text{UO}_2(\text{SO}_4)_2^{2-}$  and carbonate with an oxidizer - in the field of tricarbonatouranyl  $\text{UO}_2(\text{CO}_3)_3$ , the position of the latter above the hydrogoethite-pyrite equilibrium line determines the need to use an oxidizing agent. The release of uranium into solution when using sulfuric acid with an oxidizing agent is thermodynamically possible in the range  $\text{pH}=6.5-5.7$ , where it is in the form of dicarbonatouranyl, and then at a  $\text{pH}$  below 5.0; and without an oxidizing agent - at a  $\text{pH}$  below 4.5-4.0. With the carbonate IR method, uranium is released into solution at  $\text{pH} = 7.8-8.5$ . In a highly alkaline reducing environment, uranium leaching is impossible [7-9].



**Fig. 3.** Eh-pH - diagram of the fields of predominance of uranium compounds at  $T=25\text{ }^\circ\text{C}$  and  $P=1\text{ bar}$

Increasing the temperature of the uranium leaching process to 50°C does not change the position of the regions of solid and liquid phases observed at 25°C (Fig. No. 4), i.e., it has a positive effect only on the kinetics of the UL process. Favorable geotechnological conditions for uranium UL are the same for the entire temperature range from 25 to 50°C.

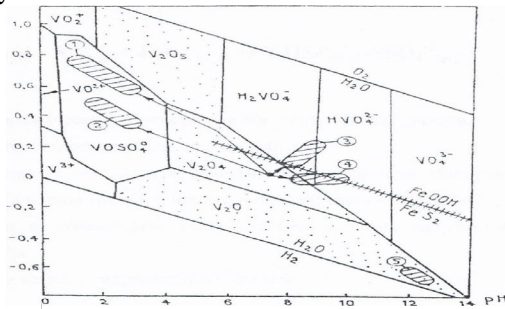
Leaching solutions react with vanadium compounds according to the following reaction equations:



Three geotechnological conditions are thermodynamically favorable for the leaching of vanadium: sulfuric acid with an oxidizing agent, sulfuric acid without an oxidizing agent, falling into the field of the monosulfate complex  $\text{VOSO}_4$ , and carbonate with an oxidizing agent - in the field of the dehydrogenate ion  $\text{H}_2\text{VO}_4^-$ . The through extraction of vanadium in sulfuric acid conditions at  $\text{pH} < 2$  is prevented by the  $\text{V}_2\text{O}_5$  field. In a carbonate environment without an oxidizer, leaching is unpromising due to the development of a field of solid phases  $\text{VO}_4$  and oxide  $\text{V}(\text{IV}+\text{V})$ .

The introduction of uranium into the calculation system leads to the disappearance of the field of soluble phases of vanadium in the alkaline region due to its displacement by the field of uranyl vanadates, for example, carnotite -  $\text{K}_2(\text{UO}_2)_2 \times (\text{VO}_4)_2 \times 3\text{H}_2\text{O}$ .

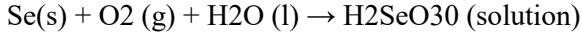
This limits the use of the UL method for the association of U and V, mainly by the sulfuric acid method.



**Fig. 4.** Eh-pH - diagram of the fields of predominance of vanadium compounds at  $T = 22 \text{ }^\circ\text{C}$ ,  $P = 1 \text{ bar}$ .

The interaction of working solutions with mineral forms of selenium occurs according to the following reaction equation:

- during sulfuric acid leaching with an oxidizing agent;



$\text{FeSe}_2(\text{k}) + 2 \text{H}^+(\text{p-p}) + 2.5 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{SeO}_3(\text{solution}) + \text{Fe}^{2+}(\text{p-p})$

$\text{FeSe}_2(\text{k}) + 2.5 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{liquid}) \rightarrow 2\text{H}_2\text{SeO}_3(\text{solution}) + \text{Fe}^{2+}(\text{p-p})$

- during carbonate leaching with an oxidizing agent;



- during sulfide leaching;

$4 \text{Se}(\text{k}) + \text{S}_2(\text{p-p}) + 4\text{OH}^-(\text{solution}) \rightarrow 4 \text{HSe}^-(\text{solution}) + \text{SO}_4^{2-}(\text{solution})$

Three geotechnological conditions are thermodynamically favorable for selenium leaching:

-sulfuric acid with an oxidizing agent, falling into the field of undissociated selenous acid  $\text{H}_2\text{SeO}_3$  and partially hydroselenide - ion  $\text{HSeO}_3^-$ ;

-carbonate with an oxidizing agent, located in the fields of hydroselenide and selenide ion;

-sulfide - in the field of hydroselenide ion  $\text{HSe}^-$

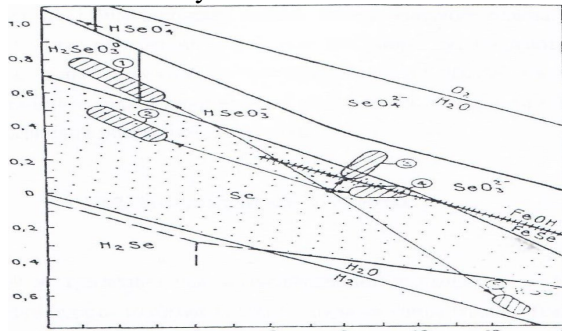
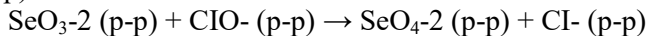
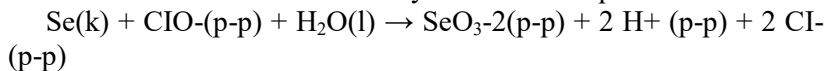


Fig. 5. Eh-pH - diagram of the fields of predominance of the selenium compound at T=25 degrees C and P=1bar.

Experiments have shown that oxidizing agents such as oxygen and hydrogen peroxide are not effective enough to completely convert selenium into the liquid phase from its elemental form. The pro-

cess proceeds more intensively when strong oxidizing agents are used, for example hypochloride, which is formed, in particular, in the presence of chlorine gas. The oxidation of selenium in an alkaline medium in this case is described by the reaction equations:



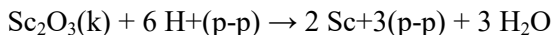
It can be seen that during the oxidation of selenium with hypochloride, both selenide and selenate-nones can be formed.

Sulfuric acid and carbonate environments without an oxidizing agent are unfavorable for the leaching of selenium. Leaching of selenium from ores of polyelement deposits using sulfuric acid and carbonate geotechnological conditions with a strong oxidizer can be carried out together with uranium, molybdenum, rhenium, vanadium, and in alkaline sulfide conditions - only with rhenium.

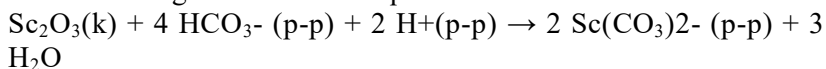
### 1.7 Monovalent elements

In choosing a geotechnology for leaching useful components of this group, it is necessary to take into account that their ore concentrations (scandium, yttrium, lanthanides, etc.) are associated primarily with the neutralization (alkaline) barrier. Consequently, the main role in extracting the elements under consideration from the subsoil should belong to the sulfuric acid UL method.

Thus, the solubility of scandium oxide increases sharply with a decrease in pH to less than 5.0-4.5, when the bicarbonate complex  $\text{Sc}(\text{CO}_3)_2$ , characteristic of near-neutral formation waters, and the monohydroxide ion  $\text{ScOH}^+$ , characteristic of weakly acidic environments, are replaced by the  $\text{Sc}^{3+}$  cation. According to thermodynamic calculations, the concentrations of this cation in equilibrium with crystalline  $\text{Sc}_2\text{O}_3$  are about 30 mg/l at pH=4, and more than 10 g/l at pH=3. The following reaction corresponds to the dissolution of the oxide:



In a near-neutral, weakly alkaline environment, the release of scandium into the process bicarbonate solution is fundamentally possible according to the reaction equation:



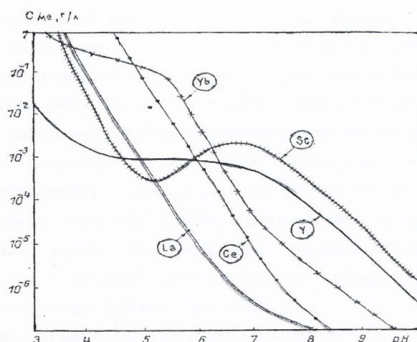
However, in this case, the maximum solubility of  $\text{Sc}_2\text{O}_3$  does not exceed -2.5 mg/l, and therefore the bicarbonate IR method for the

industrial extraction of scandium from multi-element formation-infiltration ores should be considered ineffective.

According to calculated data, the yield of scandium in both acidic and bicarbonate solutions will increase sharply if its mineral phase is represented by  $\text{Sc}(\text{OH})_3$  hydroxide, the solubility of which is 4 orders of magnitude higher than that of the anhydrous oxide. At the same time, if the metal in question enters the crystal lattice of apatite or other newly formed or syngenetic minerals, the efficiency of its extraction will sharply decrease [10].

Similarly, the sulfuric acid environment favors the effective leaching of yttrium and lanthanides from ores. All these rare earth metals, as mentioned above, form monosulfate complexes  $\text{MeSO}_4$ , the stability of which consistently increases with increasing acidity of the medium.

Thermodynamically, the most favorable for the UL of scandium, yttrium and lanthanides is the sulfuric acid geotechnological region. At the same time, according to the calculations performed, with an increase in the L:T ratio and a drop in the pH of the medium below 5.0-4.5, the first of the elements under consideration in significant concentrations can pass into solution cerium and ytterbium, then lanthanum, scandium and yttrium. At the same time, due to different levels of content of these metals and the initial solid phase - in ores and host rocks, they can change places, giving primacy to those elements that create the most significant epigenetic accumulations and, accordingly, are in easily soluble mineral forms and (or) have more high clarke.

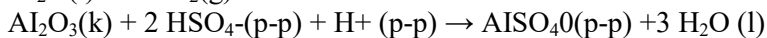
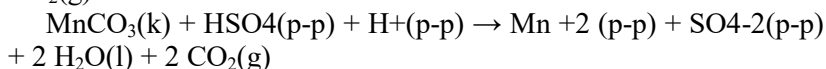
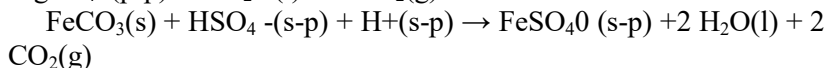
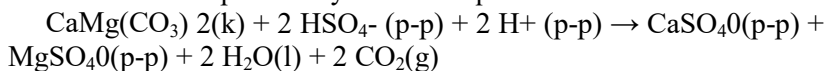


**Fig. 6.** Dependence on pH value of scandium concentrations and solutions (in the form of  $\text{Sc}_2\text{O}_3$ ,  $\text{Sc}(\text{OH})_3$  and  $\text{Sc}(\text{CO}_3)_2$ ); yttrium (in the form of  $\text{YSO}_4$ ); lanthanum (in the form of  $\text{LaSO}_4$  and  $\text{LaCO}_3$ ); cerium (in the form of  $\text{CeSO}_4$ ) and ytterbium (in the form of  $\text{YbSO}_4$ ) T-25 degrees C; P=1 bar

## 1.8 Possibilities for leaching of uranium associated components

In the process of underground leaching, working solutions react not only with ore concentrations of the elements discussed above, but also with a number of epigenetic and syngenetic accumulations, other metals, as well as with some rock-forming minerals. The largest amount of metals goes into solution with the acid UL method; the capabilities of the carbonate and sulfide methods in this regard are limited. A large group of elements is associated with the acidic migration environment, in addition to the Sc.Y described above. TR - aluminum, calcium, magnesium, manganese, nickel, cobalt, as well as iron, phosphorus, zinc, copper, partially lead, niobium, beryllium, cadmium, capable of participating in the formation-infiltration process during acidification of groundwater starting from pH = 7,0-6.5. If we take into account that under sulfuric acid AF conditions the scale of acidification of the environment becomes more significant (pH decrease to 1.0), then the above list should be supplemented with vanadium, indium, chromium, gallium, thorium, strontium, barium, radium. These metals in a strongly acidic environment with an excess of SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> ions form strong sulfate complexes, or are in the form of simple and hydroxide cations. Naturally, in the water-salt system under consideration, the concentrations of alkali metals - Na, K, Li, Rb, Cs - will also increase.

The concentrations of magnesium, calcium, iron, manganese, aluminum (in the form of MeSO<sub>4</sub>) in equilibrium with their mineral carbonate or oxide phases in sulfuric acid technological solutions become thermodynamically almost unlimited. Their transition into solution can be expressed by reaction equations:



The situation is similar with cobalt and nickel. According to thermodynamic calculations, in concentrations exceeding 1 mg/l, the following can pass into the sulfuric acid solution:



at pH<7.5 - zinc; at pH<6.4 - copper; at pH<4.8 - vanadium and niobium; at pH<4.4 indium,

at pH 2.9- gallium, at pH<6.8- cadmium; at pH<5.3\_ lead; at pH<4.5 - beryllium; at pH<3.3-chromium; at pH<2.0 – thorium.

Dependence of solubility on pH of the most stable mineral phases: chromium CrO<sub>3</sub> (eskolaite); indium In(OH)<sub>3</sub> (gilindite); cadmium CdSO<sub>4</sub>; zinc ZnSO<sub>4</sub> (morenosite); ZnCO<sub>3</sub> (smithsonite) and ZnO (zincite); T=25°C and P=1 bar, without taking into account the ionic strength of solutions (below the curves the limit of the predominance of the forms of occurrence of metals in solutions is shown).

It is clear that the intensity of the release of the listed metals into solution will be determined not only by the thermodynamic limits of solubility of their most stable mineral phases, but also by the contents of these metals in the host sand rocks, the presence of their easily leached epigenetic additive, the kinetics of the dissolution process of the initial mineral components, etc. .

According to calculations made on the basis of available thermodynamic constants, silver, tin, bismuth, antimony, tungsten, gold, platinum (the last two in the absence of organic acids), as well as the most important rock-forming component - silicic acid, practically do not react to a decrease in the pH of the environment. Elements that are relatively inert in the sulfuric acid treatment of formation-infiltration ores can also include germanium, zirconium, hafnium and, probably, tantalum, the solubility of their oxides increases at pH less than 1.0, i.e. in relatively concentrated acids.

In the case of the bicarbonate (carbonate) UB process, technological solutions can additionally extract from rocks those elements that (in addition to uranium and rare earths) form carbonate complexes: lead, copper, cadmium, beryllium, however, as calculations show, this enrichment will be negligible.

The introduction of an oxidizing agent into the working sulfuric acid or carbonate solution, which causes an increase in the Eh value of the aqueous medium, in all cases stimulates leaching from ores, in addition to Mo, Re, U, V, Se, tellurium, palladium, a complex of chalcophile elements that migrate well in oxygen conditions in favorable acidity ranges.

Thus, the main amount of metals is transferred into the liquid phase under sulfuric acid geotechnological conditions without an oxidizing agent.

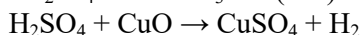
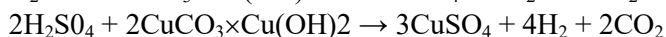
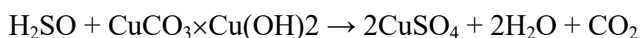
The use of a sulfuric acid environment with an oxidizer makes it possible to additionally extract tellurium, palladium, and a number of chalcophile elements from the subsurface. The carbonate geotechnological situation is generally unfavorable for the transfer of most metals into the liquid phase. The geotechnological conditions established during thermodynamic calculations that are favorable for each of the useful components are confirmed by the results of laboratory studies, field experiments at underground leaching sites and during the industrial exploitation of uranium deposits.

### **1.9 Obtaining copper-containing solutions from underground leaching**

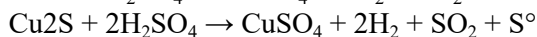
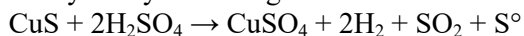
The conversion of natural insoluble copper compounds into a soluble (mobile) form occurs under the influence of chemical reagents.

These can be, first of all, acids - sulfuric, hydrochloric, nitric, alkaline reagents NaOH, Na<sub>2</sub>CO<sub>3</sub>, active gases, such as chlorine, chemical compounds of higher valence metals, such as ferric sulfate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, chlorine iron FeCl<sub>3</sub>, copper chloride CuCl<sub>2</sub>, etc. Without going into the advantages and disadvantages of this or that solvent, we note that currently the ubiquitous solvent in geotechnological processes for copper minerals is sulfuric acid [11].

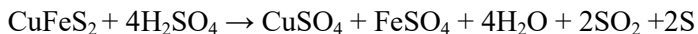
Not all copper minerals dissolve at the same rate. It has been established that copper oxides and carbonates dissolve at the highest speed, since the interaction of these compounds with sulfuric acid appears as a neutralization reaction that takes place with a large exothermic effect



The secondary copper sulfides covellite and chalcocite dissolve relatively easily according to the reactions:



Primary sulfides dissolve through complex multi-stage reactions:  
- chalcopyrite:



- bornite dissolves only in the presence of oxygen:



These equations characterize reactions from a qualitative point of view. For quantitative judgment, it is necessary to have data on the rate of dissolution of minerals, which are determined specifically for each mineral.

### **1.10 Socio-economic and environmental aspects of the UL method**

Over the past 30 years, in the mining of metals, the method of in-situ leaching (IF) has become widespread through a system of boreholes drilled from the surface or from underground mine workings.

The essence of underground leaching of minerals is the selective transfer of a useful component into the liquid phase by controlled movement of a solvent through the ore in its natural occurrence or through a pre-crushed ore mass, lifting a solution enriched with metal to the surface. And for this purpose, through wells drilled from the surface, a chemical reagent is supplied to the ore zone, capable of converting minerals of the mineral into a soluble form. The solution, having passed the path from the injection well to the pumping well, is lifted to the surface using technical means and then transported through pipelines to processing plants.

A necessary condition for using the UL method is the possibility of movement of the leaching reagent in the ore zone, i.e. ore-bearing rocks must have natural or artificially created permeability. Unlike the traditional scheme of ore mining and processing, the technological scheme of underground leaching from reservoir deposits, the productive horizon of which is flooded, does not require a complex set of structures for water supply and treatment of industrial wastewater, since the latter are absent in the process. From an environmental point of view, the UL method can be classified as a waste-free method of mining.

Water for preparing leaching solutions comes from the watered productive horizon through technological wells, and after extracting the metal from the productive solutions, they are further strengthened with a solvent reagent.

Injection of leaching solutions into the formation and lifting of productive solutions is carried out in a closed cycle, and the balance

of injected and pumped out solutions is maintained. Sometimes a slight imbalance in the operation of the system in the direction of increasing the pumped out solutions is planned in advance, which prevents the spreading of process solutions beyond the boundaries of the mining allotment contour.

In-situ leaching enterprises include two main complexes: a mining and processing plant.

A mining complex is a technology and technical means for extracting minerals from the subsoil in the form of solutions and delivering them to a processing plant. The mining complex consists of two parts: underground and surface.

The underground part includes technological wells and their equipment, with the help of which the opening of the productive horizon, preparation of the ore body for leaching, the leaching process itself and the rise of the productive solution are ensured (K.Ch. Kozhagulov et al., 2023)).

The equipment of the surface part of the mining complex includes technological pipelines for transporting leaching and productive solutions, reagents, air ducts, pumping stations for pumping solutions over long distances and settling tanks for cleaning solutions from mechanical suspensions.

### **1.11 Development system in aquiferous permeable rocks**

The method of underground leaching is most widely developed in the development of infiltration-type deposits with natural permeability of ores. The process is implemented through systems of technological wells constructed from the surface.

Wells are the main link in the technical equipment of underground leaching enterprises. The share of drilling costs in the cost of the final product is 15-30%, depending on the depth of the deposit.

With the help of wells, exploration is carried out and the reserves of the deposit are determined, the geometric shapes of ore bodies are specified, and ore deposits are opened and prepared for leaching.

In the technological process, a leaching solution is supplied into the formation through wells and productive metal-containing solutions are taken from the formation, the movement of technological solutions in the productive horizon and the completeness of mineral extraction are controlled. Various measures are also carried out through wells in order to protect the subsoil and the environment

from pollution. Deposit development by in-situ leaching, depending on its scale, requires the construction of several hundred to several thousand wells.

In recent years, the technical and economic indicators of well construction have improved significantly. Unified well designs using the same type of parts and assemblies have been developed. New pipe materials are being used that make it possible to equip wells up to 650 m deep and improve the quality of their operation (Zhalgasuly N. et al., 2023).

The following requirements are imposed on wells when extracting UL metal:

1. The location of wells and their operating mode must ensure maximum extraction of metal from ores with minimal unproductive losses of productive solutions and solvent.

2. Wells must be designed and operated with the highest possible productivity under the given natural conditions.

3. With the help of wells, a controlled process of movement of solutions in the subsurface must be ensured.

4. The service life of wells should not be less than the operating time of a cell (operational block or section).

5. When choosing the number of wells and determining their cost, it is necessary to proceed from the economic feasibility of mining using the UL method in order to obtain an acceptable cost of the metal deposit.

6. When constructing wells, the manufacturability of all operations performed must be ensured, using standard equipment and tools.

7. Wells should not be a source of environmental pollution.

All drilling wells used in opening and developing deposits using the UL method are, to one degree or another, involved in the technological process and are therefore called technological. Depending on their functional purpose, technological wells are divided into two groups: production and auxiliary.

Production wells are directly involved in the extraction of metal from the subsoil. Through them, solutions are transported and the hydrodynamic regime in the productive formation is regulated. Based on their purpose, production wells are divided into pumping and injection wells.

Pumping wells (sometimes called unloading wells) are designed to lift productive (metal-containing) solutions from the productive formation to the surface.

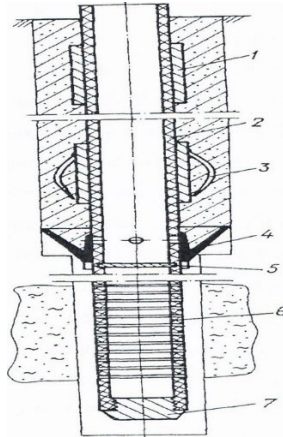
Injection wells are designed to supply leaching solutions (solvent) into the productive formation (ore deposit). The group of auxiliary wells does not directly participate in metal extraction. They play a large role in studying the deposit, preparing the formation for leaching, protecting and cleaning the subsoil from contamination, monitoring the water recovery process, etc.

Exploration wells are drilled for detailed exploration of a deposit or its individual deposits, clarifying mineral reserves, determining the shape of ore bodies in plan and section, and studying the properties of rocks along the IW process route.

Observation wells are intended for observation and control of the conditions for the formation of productive solutions within production blocks, the hydrodynamic state of the productive horizon, the spreading of technological solutions beyond the boundaries of production areas and their possible flow into higher or underlying horizons.

Monitoring wells are drilled in mined-out areas to monitor the completeness of extraction of useful components from the subsoil, as well as to solve other problems (studying changes in ore-bearing rocks, monitoring possible contamination of groundwater and the environment, etc.) .

Depending on their purpose, geotechnological wells have significant differences in design, drilling technology and technology, and equipment. They are also subject to various reliability and durability requirements.



**Fig. 7.** Typical design of a technological well (column layout):

- 1 - weighting agent; 2 - production string; 3 - centralizer; 4 - disconnecting cuff;  
5 - cement diaphragm; 6 - filter; 7 - plug

The borehole system is the most effective, as it allows you to sharply reduce the number of capital construction projects and reduce capital costs compared to the conventional mining method.

A borehole leaching enterprise can be created in successive stages, using a modular principle, when each stage includes a full set of necessary structures for mining the corresponding areas, and an increase in productivity is ensured by the parallel operation of several module blocks; the cost of production of such an enterprise is practically constant and does not depend on productivity.

In general, the cost of production at borehole leaching enterprises turns out to be 2-6 times less than at mining enterprises.

It is important to emphasize the significant difference not only in the magnitude, but also in the cost structure of the cost of a leaching enterprise and a mining enterprise with a traditional mining method. If at enterprises with a mining method of extraction the share of operating costs in the cost of production is 65-70%, and the depreciation of capital investments is 30-35%, then at borehole leaching enterprises the share of operating costs in the cost of production is always much higher and reaches 77-90% with a decrease the share of depreciation capital investments up to 23-10%. Moreover, the

amount of capital investment in the latter case is 2-4 times lower than in enterprises with a mining method of extraction.

The structure of operating costs of borehole leaching enterprises is also unique and consists of the costs of drilling and equipping wells with surface pipelines (17-23%), costs of reagents (30-45%) and energy (8-15%).

Downhole in-situ leaching systems also make it possible to sharply reduce the requirements for the content of useful components in ores and effectively involve poor and poor ore deposits in the development.

The nature of labor in production processes under the UL method has also changed significantly. All work on the preparation of ore bodies, drilling and casing wells, constructing simple trestles and laying pipelines, can easily be fully mechanized. All metal mining processes - injection and pumping out of solutions, their transportation, sorption and desorption - are easily automated.

With a significant reduction in tension and labor intensity compared to mining methods, the UL method makes it possible to increase labor productivity for the final product by 2-4 times. At the same time, the old problem of bringing production personnel directly to the surface of the earth has been solved.

Underground leaching is the most environmentally friendly, virtually waste-free production, since its use eliminates:

- delivery of ore and rock mass to the surface, creation of dumps and tailings of hydrometallurgical plants;
- release of contaminated drainage groundwater to the surface and discharge it into surface watercourses,
- air pollution with dust and harmful gases.

Essentially, the entire technogenic impact of this method is limited to ore-bearing aquifers, where natural waters are replaced by working solutions during operation. Both are distinguished by increased concentrations of uranium and a number of satellite elements (radium, selenium, vanadium, etc.). Technogenic impact on the ore-bearing horizon therefore does not create additional environmental hazards, since in areas of infiltration deposits, groundwater and in natural conditions are initially contaminated with the same complex of elements in concentrations significantly exceeding the MPC,



which makes them unsuitable for use for domestic and drinking purposes.

Recently, the issue of environmentally safe underground disposal of liquid industrial waste has become a problem; with underground leaching, the disposal of residual solutions at such objects is carried out as if automatically, which over time, according to numerous experiments, are actively self-cleaning.

### **1.12 Rock-based mining systems**

Deposits confined to rocks, under certain conditions, are also suitable for mining by underground leaching. Moreover, unlike reservoir infiltration deposits, they require the creation of mine or combined (underground mine workings plus wells) systems for development.

For underground leaching with a combined system, the most suitable sites are those where it is technically difficult to extract ore, where there has been a collapse, and finally where the content of the useful component is quite low. All of these objects can be defined as lost ores.

Let's consider some objects suitable for underground leaching at the Zhezkazgan copper deposit. The field has ten flexural zones located almost parallel at a distance of 200-300 and up to 800-1200 from each other, which can be traced from north to south from 2 to 9.5 km. The vertical amplitude of the displacement is from 15 to 200 m. Copper reserves in flexure zones account for about 6% of the total reserves of the deposit.

The stability of ores and rocks of the flexural part of the deposit is reduced due to large tectonic disturbances, therefore, mining of flexures using a room-and-pillar system, which is widely used in the deposit, is impossible due to the danger of working in an open mining space.

At the Kresto-Zapad mine in 1963, 4 blocks were mined in a steeply dipping flexure deposit using a forced block caving system.

This system is characterized by significant ore losses and dilution, and therefore the introduction of this system at the Zhezkazganok deposit was limited to the development of pilot blocks.

At present, when the preparation of the raw material base for the Zhezkazgan deposit lags behind the needs of metallurgical enterpris-

es, there is a need to develop reserves in flexural zones, which are classified as temporary reserves.

Currently, when the preparation of the raw material base for the Zhezkazgan deposit lags behind the needs of metallurgical enterprises, there is a need to develop reserves in flexure zones, which are classified as temporary reserves.

Based on the results of enlarged laboratory studies, the ZhezkazganNIPItsvetmet Institute compiled a technical and working design for the development of a pilot section of the 3-bis flexural mine, the "Cresto-Zapad" zone.

The site of the Western Krestovskaya flexure is located between the shaft of mine 3-bis and the failure of blocks No. 2 and No. 4. The steeply falling part of the flexure in the field of the site has access to the surface. Intense fracturing is widespread near and inside the flexure zone; the ores are destroyed by natural cracks of three separate systems with edge sizes not exceeding 0.8 m. In the oxidized zone there are sliding and secant cracks running at right angles to the rock bedding.

Ore-bearing gray sandstones are developed throughout the entire area of the site and almost everywhere contain copper mineralization with a content of 0.2%.

There are two types of ores: oxidized (about 29%) and sulfide. The maximum oxidation depth reaches 40-65 m, the rocks are porous and the filtration coefficient varies over a fairly wide range. Near the daytime surface it is 3 m/day, at a depth of 80 m - 1.1 m/day and decreases to 0.1 m/day at a depth of 120 m.

When choosing in-situ leaching technology for the pilot site, two options were considered. The first option includes a combined system in which the ore of the oxidized zone, due to its intense fracturing, is leached without crushing, and the ore of the sulfide zone is crushed by drilling and blasting.

According to the method of breaking ores in the sulfide system of the zone in a combined zone, it can be associated with a system with staged breaking of ore in chambers. Its peculiarity is the creation of compensation spaces over the entire height of the floor, into which the ore mass is broken using deep wells in a compressed environment. The total height of the floor is equal to the height of the sulfide zone. The chamber is limited from above by the thickness of the oxi-

dized zone, and from the failure of previously mined blocks - by the whole between the blocks; an overcut pillar is left at the bottom of the chamber in order to preserve the chamber bed and drainage catching wells.

Separate saturation of the oxidized and sulfide zones with a leaching solution is provided. For the first, injection wells are drilled from the surface to a depth of H-45 m with a double-row arrangement at a distance of 20 m between their mouths, with a solution supplied to them under pressure of  $P=3$  atm. Due to pressure filtration of solutions through cracks, they saturate ore particles and enter into chemical reactions with ore minerals. The enriched solution, seeping through the thickness of the oxidized zone, flows into the ore stored in the chamber and, filtered, together with the solution supplied for leaching the crushed ore, exits through ore passes and ore outlets into the cross-cut. Some of the solution is drained through collection wells.

Along the groove, it moves into the settling tank of the pumping chamber and through the unloading well it is discharged to the surface into the main settling tank and then to the hydrometallurgical installation.

To irrigate the ores of the sulfide zone, wells are also drilled from the surface along a 5x5 m grid and go into the chamber. The solution supplied from the surface into cased wells through nozzles irrigates the crushed

Treatment work includes the preparation of compensation slots with the release of ore at the bottom of the crosscut 3-bis horizon 295 and the release of ore to the surface, breaking in a compressed environment of a volume of rock mass in the chamber and storing this volume for leaching.

The loosening coefficient of stored ore is Kr-1.2. The main amount of ore has a size of 200 mm. In order to preserve injection wells drilled from the surface, they are drilled after blasting in the chamber. To prevent unirrigated areas from remaining in the chamber, injection wells along the hanging side are located outside the contour of the flexure zone.

The advantages of the combined in-situ leaching system are as follows:

- a small volume of ore released to the surface when preparing chambers for leaching in the sulfide zone, amounting to 5% (with mining preparation and cutting operations) of the volume of ore in the chamber; efficiency of the process of leaching of crushed rock mass by infiltration flow.

However, the system has the following disadvantages: a significant amount of drilling work in preparing raw materials for leaching; the need to leave an inter-block and cross-cut pillar, which leads to the loss of a useful component in the subsoil, the need to supply a large amount of leaching solution for irrigation in order to cover the leached raw material in the chamber; significant costs for preliminary crushing of ore.

In order to reduce the cost of the system, a second option for underground leaching of naturally occurring ores has been developed.

Studies of the filtration properties of ore, carried out in laboratory conditions, for the first time using the method of electrohydrodynamic analogy, as well as the study of the mass transfer process in the "solid-liquid" system, where the solid denotes copper minerals, and the liquid. sulfuric acid solution showed that the experimental section of the flexure zone can be leached without preliminary crushing of the ores. To do this, the leaching solution under pressure is fed into injection wells to a depth of 100 m, where the filtration coefficient is 0.5 m/day and then until the crosscut, the solution will be filtered due to the pressure coming from the end of the wells.

During the leaching process, when the materials filling the cracks are largely destroyed as a result of chemical reactions, the filtration permeability of solutions along the cracks will increase.

The rate of filtration of sulfuric acid solutions through ore and ore materials - crack fillers is  $\sim 0.02$  m/day, with the solution diffusion rate for ore units being 0.016 m/day, solution concentration  $H_2SO_4 = 14$  g/l.

The advantages of this system are the following:

- a small number of workers - 25 people with a site productivity of 350 tons of cementation copper;
- there is no surface collapse;
- the minimum sufficient technical base for developing the site is: one drilling rig of the SBU-ZIF-300 m brand; polyethylene casing

pipes with a diameter of up to 100 mm; surface main pipeline (polyethylene);

- two chemical pumps (one of them is a backup);
- completeness of metal extraction;
- simplicity and convenience in organizing work; lack of mining preparation work during ore preparation.

The system has one serious drawback;

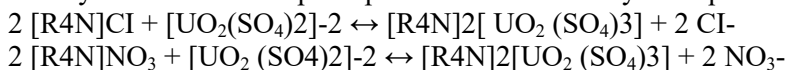
- Quite a long service life.

It will be possible to intensify and accelerate the leaching process by introducing ferric iron sulfate into the leaching solution.

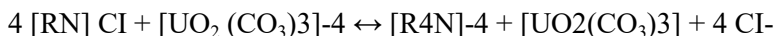
### **1.13 Technology for extracting uranium from UL solutions**

Currently, when processing sulfuric acid and bicarbonate (carbonate) UL solutions, preference is given to sorption methods.

In sulfuric acid solutions, uranium is in the form of uranyl-sulfate complexes, for example  $[\text{UO}_2(\text{SO}_4)_2]^{-2}$ , the pH of the medium is usually below 3. The sorption process is described by the equations:



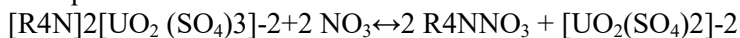
When using the carbonate UL method, the sorption process is reduced to the absorption of tricarbonatouranyl  $[\text{UO}_2(\text{CO}_3)_3]^{-4}$  by the resin



Depending on the salt composition of productive solutions, excess acidity or carbonate content, strongly basic anion exchangers are widely used. Competition for anionic forms of uranium during sorption consists of nitrate, fluoride, dihydrogen phosphate, sulfate and chloride ions. The depressant effect of a number of reagents is also used in the desorption of uranium from resin (in addition to sulfuric acid, nitric and hydrochloric, chloride and nitrate solutions, and in some cases some mixtures of them, are used).

When desorption of uranium by eluting, for example, uranyl sulfate ions absorbed during the processing of sulfuric acid solutions of PV, sulfuric acid eluents are effective. In this case, after desorption, the regenerated sorbent remains in the salt form used in the sorption processing of the solution. For desorption, 10-15% sulfuric acid solutions are used, the concentration of uranium in the commercial regenerate is 10-15 g/l. [14-15].

The best results are obtained by desorption of uranyl sulfate ions with nitrate solutions. The process of nitrate desorption is described by the equation:



After desorption, the treated ammonite must be converted into a working ionic form. Nitrate desorption is widely used at industrial water supply facilities of NAC Kazatomprom. The initial desorption solution usually consists of ammonium nitrate and nitric acid or melange.

Uranium is usually extracted from eluates using a precipitation method. This operation is determined by the type of solution used in the desorption step. Ammonia and alkaline precipitation are often used with finished products and in the form of polyuranates (diuranates).



The yellow cake is separated from the remaining solution by thickening and filtration. For transportation to further cleaning operations, the cake is dried or deoxidized in solutions (20-30 g/l) of sulfuric acid.

Thus, directly at the UL facilities, as a result of the redistribution of productive solutions, a significant concentration of uranium occurs in comparison with the initial one (10-500 mg/l); The finished products have a fairly high quality of uranium (30-40%).

#### **1.14 Methods for processing multicomponent productive solutions of UL**

The transfer of useful components into solution during underground leaching is carried out in the subsurface. Productive uranium solutions with a number of accompanying components (Re, Mo, V, S, Y, TR, etc.), depending on the recovery method, are pumped to the surface through a system of unloading (pumping) wells, settled and supplied to surface processing units to obtain marketable products (concentrates).

To process the combination of productive UL solutions, various methods are used - sorption, extraction, precipitation.

The main requirements for the implementation of individual technological schemes for the redistribution of productive solutions include: the most complete extraction of components converted into useful components; solution of technological schemes, the use of

methods and providing the minimum possible number of operations, reagents and modes for concentrating useful components to obtain enough (concentrates), as well as cost-effective, clean finished products, economically advantageous processing. The methods for extracting useful components existing in the Republic of Kazakhstan, near and far abroad countries are close to each other. Specific indicators and parameters of technological processes at different enterprises may vary due to the mineral and chemical composition of the ores, the IP method used and the conditions of the process, the set of useful components, etc.

Useful components from ores of polyelement deposits using sulfuric acid, productive solutions pumped to the surface may contain, in addition to uranium (10-500 mg/l), rhenium (0.1-0.3 mg/l), scandium (0.2-1.0 mg/l or more), yttrium (2-10 mg/l or more), lanthanides (fractions of milligrams and milligrams per liter), vanadium (up to 200 mg/l in the Zhutan type of ores), in a number of deposits molybdenum (3-10 mg/l). With a carbonate (bicarbonate) PV with an oxidizing agent, the amount of useful components in solutions is usually lower than with an acidic one: uranium - up to 200 mg/l, mainly 30-100 mg/t, rhenium 0.3-1.0 mg/l; yttrium, lanthanides and scandium are practically absent [12-13].

Productive sulfuric acid solutions have a total mineralization of 10-30 g/l, including concentrations (g/l): H<sub>2</sub>SO<sub>4</sub> - 8-22, free acid 1-5; Al - 0.2-1.5; Mn - 0.1-0.5; Fe - 0.7-2.0; Ca - 0.5-2.0; Mg - 0.2-1.0; H<sub>2</sub>SiO<sub>4</sub> -0.1-0.3; Cl - 0.1-1.5; R - up to 1.0. Na, K, Rb, Cs, Be, Sr, Ba, B, Ti, Nb, Co, Cu, Zn, Cd, Hg, As, Pb, NOg, Ni, etc. are present in various concentrations. pH value of productive sulfuric acid solutions 1,2-3.0. In productive bicarbonate solutions, the total mineralization is 3-7 g/l, rarely more, including concentrations (g/l): HCO<sub>3</sub> - 0.8-2.0; SO<sub>4</sub>-2-1-3; NH<sub>4</sub> - 0.4-0.6; Na+K - 0.5-1.0; Cl - 0.8-1.2; Cu - 0.6-1; Mg-0.1-0.3. The concentrations of F, Pb, Cu, Zn, Cd, Ga, Ge, H<sub>4</sub> SiO<sub>4</sub> are low.

In accordance with the complex chemical composition of productive UL solutions and the low content of useful components in them, their processing and initial concentration are based on sorption methods for extracting elements with subsequent use for greater concentration and purification from impurities of extraction, precipitation, and in some cases, again sorption methods .

### 1.15 Sorption methods

Sorption methods for the extraction of uranium and associated components are based on the use of the ion exchange process on ion exchange resins. Ion exchangers are solid, practically insoluble in aqueous solutions of acids, alkalis, and organic media, artificial (or natural) materials that ensure the extraction of metals in cationic or anionic forms from solutions. Horse exchange consists of two stages: saturation and desorption. At the first stage, the productive solution comes into contact with the sorbent, and useful components are quite selectively absorbed by the ion exchanger. Upon reaching equilibrium capacity for one or more metals, the sorbent is transferred to the desorption stage; during the latter, it comes into contact with a chemical solution, which removes metals from the ion exchanger, after which it returns to the saturation stage. The concentrated productive solution is sent for further processing. The volume of solutions of useful components after desorption is significantly less than the volume of the initial ones received for sorption, which, in turn, allows for their further concentration to be effectively carried out.

The process of sorption exchange obeys the law of mass action. One of the main requirements is selectivity for extracted metals and maximum resin capacity with fairly good kinetic parameters of sorption and regeneration. The efficiency of the sorption stage is assessed by the sorption capacity of the resin, the degree of metal extraction from UL solutions, the number of sorption stages, the one-time loading of the ion exchanger, the duration of contact of the solution with the ion exchanger, and the desorption conditions. All these parameters are usually interconnected and reflect the basic physical and chemical laws of sorption, and also depend on the instrumental design of the process. In modern processes of sorption extraction of uranium, rhenium, molybdenum, gold, rare and trace elements from acidic and carbonate solutions and ore pulps, strongly basic styrene-based dinonites are most widely used; AM, AMP, vinylpyridine anion exchanger BP-1 Ap, as well as macroporous anion exchanger AMI-25, which have increased selectivity and distribution coefficient of uranium, especially in the region of low concentrations (1-50 mg/l). This ensures a decrease in the uranium content in sorption mother liquors (to less than 1 mg/l) and an increase of 1.5-2 times in



eluates, with a corresponding increase in the efficiency of concentration and purification of uranium-containing compounds.

Of particular interest for the extraction and concentration of scandium and rhenium from PB solutions are 8H cation exchangers, in particular phosphorus-containing SF-3, SF-4, SF-5, sulfopolystyrene KU-2, KU-2-N, KMDR, etc., ampholytes of the Afl type.

For the extraction of alkaline and alkaline earth elements, R3E and heavy metals, KMDF cation exchanger is intended, which is recommended for sorption of scandium and thorium from UL solutions. It has high chemical and osmotic stability and can be effectively used in processes involving alternating operations for treating the ion exchanger with solutions of acids and alkalis

Ampholytes with nitrogen-phosphorus-containing groups API-21 and API-22 are used for the sorption of uranium, scandium, rhenium, thorium from PV solutions, industrial waters and the capture of valuable components for the purification of natural components from industrial wastewater. In addition to being used for scandium sorption, ampholyte API-22 can be effectively used for the extraction of other metals. It has increased selectivity to vanadium, tungsten and platinum.

To extract uranium and rare metals (Re, Sc, Y) from productive UL solutions of complex salt composition, it is possible to use impregnated sorbents (C) created in recent years, the so-called productive solid extractants (TVEX).

Thus, a synthesis technology has now been developed, and the production of various sorbents - anion- and cation-exchange resins and ampholytes, solid extractants and various types of mitregnate resins for the sorption extraction of uranium, rare (Re, so, U). noble and most non-ferrous metals from solutions and remote control, including productive UL solutions. These sorbents have high exchange capacity, selectivity, mechanical and osmotic strength, chemical, thermal and radiation resistance, ensuring fairly effective extraction of useful components from solutions.

The sorbed metal from the ion exchanger is removed in the desorption stage; nitrate or chloride solutions, as well as acids (sulfuric, hydrochloric, nitric) are used for it. During desorption, the contents of useful components in the ion exchanger are gradually reduced to certain maximum permissible values, ensuring the production of

waste solutions containing valuable components. When filtrating eluting solutions through an ion exchanger layer, solutions with variable concentrations of metals are obtained, of which portions with the highest indicators are removed as a commercial fraction for further processing, and the remaining fractions with low concentrations of PC are used as recycled ones.

There are a number of methods for desorption of metals from ion exchangers: elution, displacement, conversion, extraction desorption. During elution, the metal is washed out from a saturated sorbent with a pure solvent (for example, uranyl sulfate complexes are eluted with 10–15% sulfuric acid solutions). As the eluent temperature increases, the amount of desorbed metal increases. Displacement occurs during desorption by a more sorbed ion or substance. The spent ion exchanger remains in the form of a desorbing ion and, therefore, requires special treatment to remove this tone from the ion exchanger in order to convert it into a working ionic form, which ensures the most effective extraction of the valuable component. For example, the displacement of uranyl sulfate complexes from anion exchangers by nitrates and chlorides is widely used. During conversion, a sorbed metal complex, for example, sulfate, in the ion exchanger phase is converted into a chloride or nitrate complex when the ion exchanger is treated with concentrated solutions of nitrates or chlorides. Extraction desorption is used to extract metal from anion exchangers, for which solutions of mineral acids with an extractant (tributyl phosphate, trialkylamine, etc.) are used.

Methods for extracting metal from commercial reclaims are different and depend on the composition of the desorbent used. For example, after nitrate desorption, fractional separation of metals from the solution is carried out by gradual neutralization with ammonia. If the metal is eluted with an acidic salt solution, then precipitation is performed by direct neutralization with ammonia. When used for desorption of alkali carbonate, acid additives are used to destroy it before uranium precipitation. The cake obtained after the remaining solution is thickened and settled is separated from the remaining solution by drying and filtering.

### **1.16 Extraction methods**

To process multicomponent productive solutions of PV, it is fundamentally possible to use extraction methods - the extraction of

metal compounds from aqueous solutions, where they are in the form of salts of inorganic acids into organic solutions that are immiscible with water. Compared to sorption technology, extraction has a number of advantages - simplicity of technology, high efficiency and selectivity. It allows you to selectively extract useful components with similar properties and effectively get rid of impurities.

In extraction processes, inert diluents of organic phases (kerosene, hexane, benzene, white spirit, etc.) are widely used. After this stage, the resulting extract (organic phase saturated with metal) is washed with water and subjected to stripping - extraction of the metal from the organic phase, followed by the return of the regenerated extractant to a new extraction cycle. Depending on the properties of the extractant and the stability of the resulting salt, ordinary water or water slightly acidified with nitric acid (hot), concentrated or diluted hydrochloric and fluoric acids, table salt, sodium and ammonium carbonate are used for re-extraction. Particularly pure final products are obtained when re-extraction is carried out in the solid-phase version.

Depending on the concentration of useful components and the required quality of the finished product, it is possible to combine sorption and extraction methods, as well as the use of several stages of sorption and extraction in the process of obtaining the finished product.

### **1.17 Precipitation methods**

Precipitation methods for processing productive solutions are usually implemented at the final stages of the technological process. The precipitation reagent must be cheap and available. Ammonia or alkaline precipitation methods are used to isolate components from purified acidic solutions, such as uranium. When a solution of  $\text{NH}_4\text{OH}$  or  $\text{NaOH}$  is added to a solution of uranyl salt, as the pH increases, hydroxouranyl complexes are formed with varying degrees of polymerization, which depends on the pH of the medium and uranium concentrations. When alkali or ammonia is added to a solution of uranyl sulfate, nitrate, or chloride, what usually precipitates is not uranyl hydroxide, but the corresponding salt of uranium acid (diuranate, more precisely polyuranate). This has certain advantages for further processing of the precipitate to obtain (by calcination) uranium oxide.

Uranium can be extracted from carbonate solutions by several precipitation methods, in particular: acid decomposition (acidification, precipitation of sodium diuranate with ammonia, calcination), decomposition of sodium uranyl carbonate salt with excess sodium hydroxide (the resulting precipitate of sodium diuranate is filtered off), etc.

### **1.18 Technology for extracting molybdenum from UL solutions**

Sorptive extraction of molybdenum from sulfuric acid media, including together with uranium, has been quite well studied and is successfully used in industrial practice.

It has been established that with a decrease in the concentration of sulfuric acid in the solution, the exchange capacity of anion exchangers for molybdenum increases, and the sorption front decreases.

According to the efficiency of ion exchange extraction of molybdenum from solutions

pH-1-2 (equilibrium concentration of molybdenum is about 0.1 g/l) known ion exchangers are arranged in a row:

BP-IAp		AM		
BP-Ip	>	MP	>	AFI-22
AM-p		BP-3Ap		
		AM-26		

Desorption of molybdenum can be effectively carried out with aqueous solutions of ammonia (30 g/l NH<sub>4</sub>OH), while the addition of NO<sub>3</sub> to eluents improves the process performance. Ammonia solutions containing ammonium sulfate can also be used for desorption of molybdenum. The finished product is obtained in the form of technical ammonium paramolybdate with a molybdenum content of more than 20%.

### **1.19 Technology for extracting rhenium from UL solutions**

Sorptive extraction of rhenium from UL solution is carried out using both ion-exchange resins and activated carbons. Sorption of perhenate ions is most effectively carried out by resins from solutions at pH=5-6. With an increase in the acidity of solutions to 5-15 g/l, their working capacity for rhenium decreases by 8-10 times, especially in the region of its low equilibrium concentrations. Sorbents based on the efficiency of rhenium extraction from solutions can be

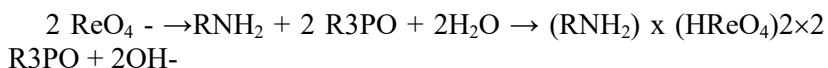
as follows: VP-1p>AM-3>AN-21>AM(AM-p)>activated carbons. One of the productive rhenium sorbents is the anion exchanger VTs-14KR, the elution of rhenium from which is carried out with ammonia.

With sufficiently high rates, rhenium can be extracted from acidic, alkaline and neutral solutions by extraction. The existence of rhenium in aqueous solutions only in the form of perrhenate ions determines the use of organic solvents for the extraction of anions (aliphatic, amines, quaternary ammonium bases and alkyl phosphates) for their extraction.

Rhenium is extracted from sulfuric acid solutions with aliphatic alcohols, ketones, amines, and TBP, depending on the ion concentration.

For the extraction of rhenium from carbonate media, a mixture of ANP -2 + FOR is widely used, and at pH = 11 - ANP -2 + TBP + FOR, which allows in one stage to double the extraction of rhenium in comparison with the mentioned double mixture of extractants, bringing it up to 92%.

In this case, rhenium extraction proceeds according to the equation:



Re-extraction of rhenium by approximately 90% can be accomplished in one stage with an ammonia solution. The finished rhenium product is ammonium perrhenate grade AR-O.

### **1.20 Technology for extracting vanadium from UL solutions**

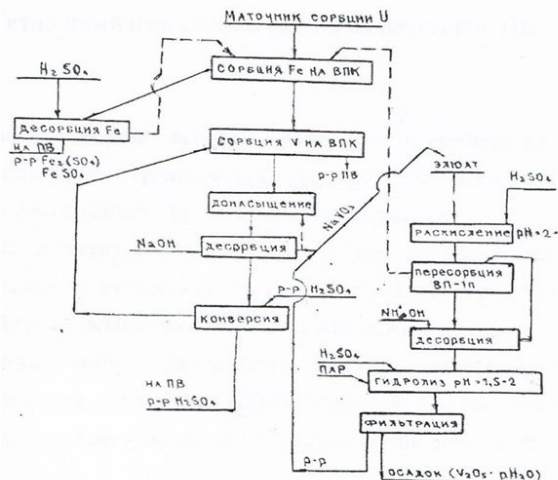
The extraction of vanadium from solutions to obtain its technical compounds is carried out by sorption, extraction and precipitation methods, and the last two are usually used when processing solutions that are relatively rich (10-200 g/l) in vanadium. When processing its poor (less than 1 g/l) solutions, sorption technology is preferable.

When extracting vanadium with anion exchangers VG1-1p and VG-1 Ap from sulfuric acid

media with a pH of 1.6-1.8 (after preliminary sorption of uranium from them), the degree of vanadium extraction is -90%. Its desorption with sufficient completeness can be carried out with aqueous solutions of ammonia.

The elution of vanadium from the VP-1Ap anion exchanger is improved by adding mineral salts, in particular  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaCl}$ , to desorbing ammonia solutions.

$\text{VO}^{+2}$  ions, which are stable in aqueous solutions, are sorbed from sulfate and chloride solutions by cation exchangers, for example KU-2.



**Fig. 8.** Schematic diagram of the associated extraction of vanadium from underground uranium leaching solutions

Cation exchangers practically do not sorb vanadium either from dilute alkaline media or from solutions obtained by acidification to relatively high concentrations due to the presence of vanadium, respectively, in the form of negatively charged particles.

### 1.21 Technology for selenium extraction from UL solutions

The main methods are physical and chemical. For the extraction of selenium from productive UL solutions, chemical methods are currently the most acceptable and tested.

The sorption of selenium from carbonate solutions is most effective if it is in an oxidation state of 6. The capacity of VP-1A resin in a carbonate environment is about 88 mg/l, in a neutral environment - 130 mg/l.

Selenium is also quite efficiently extracted from sulfuric acid solutions into resins:  $\text{AN} > \text{AN-2F} > \text{EDE-10P} > \text{AV-17x8}$ . For all anion exchangers, sorption for selenium (IV) reaches a maximum at pH-

3, and for selenium (VI) decreases at pH = 1-3 and remains constant at pH more than 3. The capacity of anion exchangers is high (170-700 mg/l).

Ampholytes may be of practical interest for selenium sorption. This direction is fundamentally possible for the redistribution of selenium solutions (Zhalgasuly et al., 2018).

For the desorption of sorbed selenium, acids (hydrochloric and sulfuric), anion exchangers AM, AMP, VP-1Ap, EDE-10P etc. are used; Selenium is well desorbed by alkali solutions.

When obtaining high-purity selenium from hydrochloric acid solutions, it is possible to use cation exchanger KU-2, Dauex-50 and anion exchanger AI-1, AV-17×8, Dauex-2.

### **1.22 Technology for extracting scandium, yttrium, lanthanides from UL solutions**

Scandium and rare earth elements are extracted from leaching solutions of ore concentrates by a combination of sorption and extraction methods: the elements are concentrated on a strong acid sulfation exchanger KU-2, and then separated and purified by extraction of TBP from nitric acid eluates.

The extraction of scandium from very poor (up to 1 mg/d) sulfuric acid productive solutions of UL is most effectively carried out according to a combined scheme using sorption and extraction methods.

To extract scandium from poor UL solutions, it is effective to use anion exchangers such as AMP, VP-Ap and VP-3Ap. Experiments have shown that during the sorption of scandium from sulfuric acid solutions (pH - 1.6-2.2), its 75% recovery can be achieved when the anion exchanger is saturated with AMP to 0.3-0.4 kg/t, and with subsequent desorption of scandium Using nitric-sulfate solutions, obtain eluates containing up to 40 mg/l.

The principle scheme for extracting useful components from complex UL solutions involves first removing uranium (according to one of the known methods), then scandium, and then yttrium and lanthanides.

As experiments show, the sorption of scandium from sulfuric acid solutions of UL containing only 0.1 - 0.7 mg/l Sc should be carried out on apholytes of the API type (API-21 and API-22). At pH 1.2-2.5, the capacity of ampholyte API-22 for scandium reaches 0.2-0.5

kg/ton of sorbent. Carbonate ( $\text{Na}_2\text{CO}_3$ ) desorption of scandium and its subsequent resorption onto API-22 from deoxidized eluates makes it possible to concentrate up to 30-40 mg/l. which is sufficient for subsequent effective extraction and purification of scandium from impurities.

Primary scandium concentrate with a  $\text{Sc}_2\text{O}_3$  content of 1 to 5% can be obtained directly at IP facilities. Its further processing is recommended under stationary conditions at any of the processing plants in the industry, where, depending on the requirements for the finished product and using existing extraction, precipitation and sorption methods, scandium oxide corresponding to the SKO-3, OS-1, SKI-3 grades is obtained.

Available technical and economic studies allow a minimum on-board concentration of scandium in productive UL solutions at the level of 0.1 mg/l.

The concentrations of the sum of rare earth elements and yttrium in UL solutions are usually low and amount to 5-25 mg/l, less often - 55-60 mg/l.

For the sorption of rare earth elements from ISL solutions from the available set of sorbents, cation exchangers KU-2 are preferred; KU-2 x 8N; KU-23.

Desorption of lanthanides is carried out with a sulfate-nitric acid solution. The extraction cycle of solutions is carried out using synthetic fatty acids, dioctyl methylphosphonate in hydrocarbons and other extractants to concentrate the amount of P3E and remove impurities. Re-extraction is carried out with solutions of nitric acid, nitric acid, technical water. An ammonia solution is used to precipitate divalent metals from the strip extract.

The finished product is obtained in the form of a hydrate cake with a total lanthanide and yttrium content of about 20-28%. Subsequently, at one of the hydrometallurgical enterprises, the hydrate cake is dissolved in nitric acid, followed by complex extraction purification of rare-earth metal nitrates and the separation of individual lanthanides, and then the production of rare-earth metal concentrate of the cerium group, neodymium oxide (NOK-1), concentrate P3M of the yttrium group, neodymium oxide (ItO-Lum), samarium and europium concentrate, gadolinium and lutetium, samarium oxide (SMO-M), europium oxide (EvO-Zh). The most important indicator



of the profitability of hydrate cake production and especially its further processing is the concentration of the amount of P3E in UL solutions (usually not lower than 15-20 mg/l) and individual elements.

### **1.23 Technology for extracting copper from UL solutions**

Sorption technology for extracting copper from solutions is best carried out using an ion exchanger and extraordinary sorption-desorption equipment, developed and tested in industrial conditions by specialists of the Tselinny Mining and Chemical Combine at the KV and UL facilities. The results of desorption of various metals obtained on an SDK column are several times higher than their concentrations in commercial reclaims achieved on traditional desorption columns.

The main operations of the technological scheme for processing productive solutions of heap or underground leaching can be called the following.

Sorption of copper from productive solutions is carried out on ampholyte ANBK-35 in columns of the SVNK-2400 type and, partially, in SDK-1500 columns. The copper sorption capacity of the ion exchanger is 40-50 g/kg, the copper content in the sorption mother liquor is 35-45 mg/l. It is planned to saturate the sorbent with copper in one of the branches of the SDK-1500 column.

Desorption of the fully saturated ion exchanger is carried out with a sulfuric acid solution, which makes it possible to obtain a sulphate regenerate rich in copper, suitable for subsequent extraction of copper by electrolysis or cementation, or separation of copper sulfate.

The technological scheme for processing productive solutions does not have liquid and solid discharges. All solutions are in circulation and do not enter the environment. To ensure the cleanliness of the air basin, the scheme excludes airlift pumping of ion exchanger with sulfuric acid solutions.

### **1.24 Practical results**

The fundamental basis of the method of geotechnological extraction of metals in Kazakhstan was the sulfuric acid method of uranium extraction by borehole systems, developed and implemented in the late 70s and early 80s.

As already indicated, it is difficult to overestimate its revolutionary role both in the development and dramatic expansion of the republic's mineral resource base, and in the creation of a technologi-

cally new, science-based progressive direction in the development of scientific and technological progress.

The first, not entirely successful, experimental work on underground leaching of uranium was undertaken in 1973-1975. at small uranium deposits of the South Kazakhstan region of Kyzylkol and Chayan by the Leninabad Mining and Chemical Combine and the Krasnokholm expedition. The complex geological conditions of these deposits, the lack of necessary experience, the lack of specific equipment and materials in the mining industry of those years, etc. became the reason that the results of the experimental work were not very promising.

However, the undoubted attractiveness of the IP method and certain successes of these studies achieved in neighboring Uzbekistan served as the basis for the launch in 1977 of full-scale, methodically developed pilot work at two large deposits in Kazakhstan - Uvanas and Northern Karamurun.

The Uvanas deposit had ideal geological and technical features for the underground leaching method, and Northern Karamurun was then the deepest deposit in the world where uranium geotechnology was tested.

Upon completion of more than successful pilot tests, both of these deposits were involved in industrial development and a few years later, on their basis, the first large UL mines were built - Stepnoye in the Suzak region of the South Kazakhstan region and Mining Department No. 6 in the Kyzylorda region. These enterprises are successfully operating to this day.

During these same years, the Volkov expedition, together with the Kyrgyz Mining Combine, successfully carried out a full-scale experiment on underground leaching of uranium in the Eastern section of the Mynkuduk deposit, which is unique in terms of reserves, which since 1985 has become the second operational mine of the Steppe RU.

The large Kanzhugan deposit, discovered in the 70s by the Volkov expedition, became the raw material base for the organization of another mining operation in the UL - Central.

Thus, by the mid-80s in Kazakhstan, as part of a fairly powerful, previously created uranium mining sub-industry, a fundamentally new industrial type of enterprises was formed that successfully ex-

tracted uranium using the underground leaching method. Until the beginning of the 90s, production volumes at these mines were constantly increasing and already accounted for about 50% of the total uranium production in the republic.

The introduction of a new progressive method of uranium mining and the creation of a large and long-term raw material base for it constantly reduced the competitiveness of both other types of uranium deposits and existing mining operations, which were significantly inferior in profitability to underground leaching. With the fall in uranium prices around the world in recent years, the profitability of developing a number of deposits using the traditional mining method has sharply decreased, and as the economy of Kazakhstan transitioned to market relations, most of the mines and mines here were mothballed.

To date, almost all of the uranium produced in the republic is mined by underground leaching. Since the organization of the first, quite modest in terms of production volumes, pilot tests of this method, to this day Kazakhstan is one of the leaders in uranium mining.

In this regard, it is very indicative to compare the role of underground uranium leaching in the overall production of uranium in the republic and in the world as a whole. As can be seen from Fig. No. 2, its share in the world does not exceed 15% of total production and does not yet have a noticeable tendency to increase. This situation is, first of all, evidence of the uniqueness of the republic's mineral resource base, where, as stated earlier, about 10% of all available uranium reserves are suitable for mining using this method, as well as a fairly developed production infrastructure that carries out the IR process.

In some years, Kazakhstan ranked first in the world in terms of uranium mining volumes using the UL method and retains its leadership to this day; moreover, NAC Kazatomprom's immediate plans provide for a sharp increase in production volumes based on the modernization of existing and the creation of new in-situ leaching facilities.

Over the past two decades of intensive development of the uranium irradiation method, mining and geological exploration organizations of the republic have accumulated enormous practical and theoretical experience in this area.

In addition to improving the geotechnological uranium theme, already at the first stages of operational and experimental work it was established that in productive solutions, together with uranium, industrially significant concentrations form some valuable rare elements: rhenium, scandium, vanadium, lanthanides, selenium, yttrium, etc., which caused In life, a whole area of research is the selection of geotechnological techniques and methods that provide the possibility of the most comprehensive extraction, the development and implementation of methods for obtaining commercial concentrates of associated components for uranium processing plants, and much more related to this problem.

All this, naturally, could only be carried out on the basis of a thorough study of the complex geochemical transformations occurring both at the stage of complex uranium ore formation, and directly during the process of active leaching itself. The basic testing grounds for these studies were numerous experiments carried out in dozens of deposits at the stage of geological exploration, as well as during the exploitation of such elements as rhenium scandium, vanadium and rare earth metals that had already been produced on an industrial scale.

For this purpose, at all operating UL enterprises, installations were designed and built to extract associated useful components from productive solutions. In some fields in the south of Kazakhstan, extraction was organized by borehole leaching, for example, of lanthanides and vanadium, where uranium was already regarded as an associated component. For the first time in world UL practice, pilot industrial production of selenium, etc., was carried out at the Northern Karamurun deposit.

At each stage of the enterprise's scientific and technical activities, the latest achievements of world and domestic science and technology were used when choosing directions and methods of work. This became possible thanks to the high qualifications and professionalism of the majority of specialists, many of whom defended dissertations on this topic, made dozens of inventions, received patents, and wrote numerous scientific publications.

The authors of this work were direct participants in this long process, holding various positions at the level of chief specialists in scientific institutions since the early 70s.

The destruction of the entire economic system and the severance of scientific and practical ties, with the collapse of the Soviet Union, sharply reduced interest and demand for many rare useful components, and the general global drop in prices for non-ferrous metals in recent years has made their extraction, even incidentally the main production of uranium, unprofitable. Recently, however, there has been a tendency for world prices to increase for such metals as rhenium and vanadium, therefore NAC Kazatomprom does not include in its plans for the coming years, given favorable market conditions, the continuation of their associated production.

Significant volumes of solutions productive in uranium and other components at operating UL enterprises, despite their relatively low concentrations, make it possible to extract hundreds of tons of uranium, hundreds of kilograms of rhenium and scandium, the first tens of tons of yttrium and lanthanides, tens and hundreds of tons of vanadium per year from each developed multi-element deposit. The profit from extracting from the subsoil the entire possible complex of useful components at just one UL enterprise can amount to millions of dollars.

The use of the leaching process as one of the most currently developed geotechnological methods for mining minerals can significantly improve the technical and economic performance of existing mining enterprises.

The relevance of underground leaching, for example, of Zhezkazgan ores using various technological schemes described in this work, is confirmed by a number of patents issued recently in Kazakhstan.

Thus, in one of the latest technical solutions, based on an optimal combination of means, methods and processes that ensure resource-saving use of mineral raw materials, a new technology for selective mining and processing of ore mass using traditional and geotechnological methods has been developed in relation to the conditions of the Zhezkazgan deposit.

The essence of the developed technology is to separate the broken ore in the working face into two ore flows:

One with a low metal content (0.4-0.6%) and the other with a higher one. In this case, sorted higher-grade ore is transported to the surface for subsequent beneficiation, and ore with a low metal con-

tent is subjected to leaching in underground conditions, followed by processing of the solutions using hydrometallurgical methods.

The authors' calculations show that processing ore with low copper content that has already been crushed and left in the mine workings by leaching will increase the total profit of LPA "Kazakhmys" by no less than 3-5%.

### **Conclusion**

The development and improvement, based on many theoretical and applied studies, of the method of borehole underground leaching and metals described in this work is the result of the creative efforts of a large number of specialists in various fields of knowledge both in the republic and abroad.

Over the past two decades, specialists from the mining institutes named after D.A. Kunaev, NAC Kazatomprom of Kazakhstan, geological prospectors, operators, representatives of fundamental and applied science have made perhaps the most significant contribution to the development of this progressive direction of scientific and technical improvement.

The result of this was a radical restructuring of the uranium mining industry of the republic and Kazakhstan becoming a world leader in the use of geotechnological methods of mining in mining. Over the years, no other country in the world has produced as much uranium and its accompanying useful components using the UL method as Kazakhstan.

In recent, difficult times for all metallurgists in the world, when prices for almost all non-ferrous and rare metals have fallen and there is a widespread decline in mining production, the basis for maintaining and even increasing the volume of production of uranium, copper and rare metals for the republic will be the widely introduced highly profitable geotechnological method of IR.

In 1998, NAC Kazatomprom, together with the Academy of Sciences of the Republic of Kazakhstan and other scientific and production organizations, developed the "State Program for the Develop-

ment of Nuclear Energy and Industry of the Republic of Kazakhstan until 2030,” which received approval from the Government.

The basis for the development of the uranium industry, laid down in the program, is the systematic expansion of natural uranium production, using underground leaching methods, which will allow the country in a few years to take one of the first places in the world in the production of uranium compounds.

The widespread introduction of borehole underground leaching methods in general at the Zhezkazgan ore field will significantly improve the main technical and economic indicators of this important industrial facility for the republic.

All this, along with the purely scientific value of the research presented in the work, will help accelerate the economic and social development of Kazakhstan in accordance with the strategy of the 2030 Program.

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