

PROMISING TECHNOLOGY FOR REPROCESSING COMPLEX URANIUM ORES FROM THE ELKON DEPOSIT

**K. M. Smirnov, T. V. Molchanova,
A. V. Anan'ev, I. D. Akimova,
E. V. Ovcharenko, and O. K. Krylova**

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The results of research on reprocessing of complex uranium ores from the Elkon deposit with recovery of uranium, gold, silver, and vanadium by methods of radiometric sorting, combining of autoclave and atmospheric leaching of ore followed by sorption and extraction recovery of valuable components, are presented. The capacity was 90 mg/g in sorption of uranium on strongly basic anionite and the uranium concentration ≤ 0.003 g/dm³ in sorption filtrates. The choice of eluent is determined by the formulation of the problem of obtaining the finished uranium product of the requisite form and quality. A fundamentally new composition of the extracting agent is proposed for direct extraction of uranium from nitrate-containing solutions. An iron-vanadium concentrate with vanadium and iron content 2.58 and 22.8%, respectively, suitable for subsequent reprocessing, was obtained. The anionite PuroGold S-992 is recommended for recovery of gold and silver. The gold and silver concentrations in the commercial desorbate were 270 and 380 mg/dm³, respectively; a gold-containing concentrate was obtained.

The concept for the development of the uranium industry in our country is based on nonstandard technologies that take account of the particularities of the raw ore material and the functional role of similar products in the extant structure of the nuclear industry.

The current interest in uranium extraction from refractory raw ore lies in bringing new capacity into production based on the largest reserved deposit in the Elkon ore field (342,000 tons, which comprises 53% of the reserves). The ores in the Elkon region of the Republic of Sakha (Yakutiya) belong to a single mineralogical-technological type – low-carbonate aluminum-silicate ores. The uranium is represented by brannerite. The uranium content equals, on average, about 0.2%. In addition, the ores contain gold in amounts 0.5–0.7 g/ton and silver 9–12 g/ton, which are associated with sulfides (pyrite, marcasite), as well as vanadium, whose content is at the level 0.08%. No mineral components of vanadium have been found in the ore. The vanadium could be present in titanium-magnetites FeTiO_3 as well as in the amphiboles $\text{Ca}_2\text{Na}(\text{MgFe}^{2+})_4(\text{AlFe}^{3+})[(\text{Si,Al})_4\text{O}_4]_2[\text{OH}]$ of hornblend. In the latter vanadium can replace di- and trivalent iron and have the same charge. The ores are difficult to open, which could be due to the low solubility of the concentrator mineral of the useful components and extremely small sizes of their precipitates, and possess high acid content, which is associated with the presence of chlorites and carbonates.

A commercial technology for processing complex uranium ores from the Elkon deposit with extraction of uranium, gold, silver, and vanadium has been investigated and developed (Fig. 1). The presence of several desirable elements and environmentally harmful components and the refractoriness of the minerals require the development of a multi-operation processing scheme. A series of studies was conducted under laboratory, experimental, and semi-commercial conditions using a technological scheme with preliminary radiometric sorting, autoclave and atmospheric leaching of ore, sorption, and extraction with recovery of uranium, vanadium, gold, and silver. The preliminary radiometric sorting makes it possible to separate the following products:

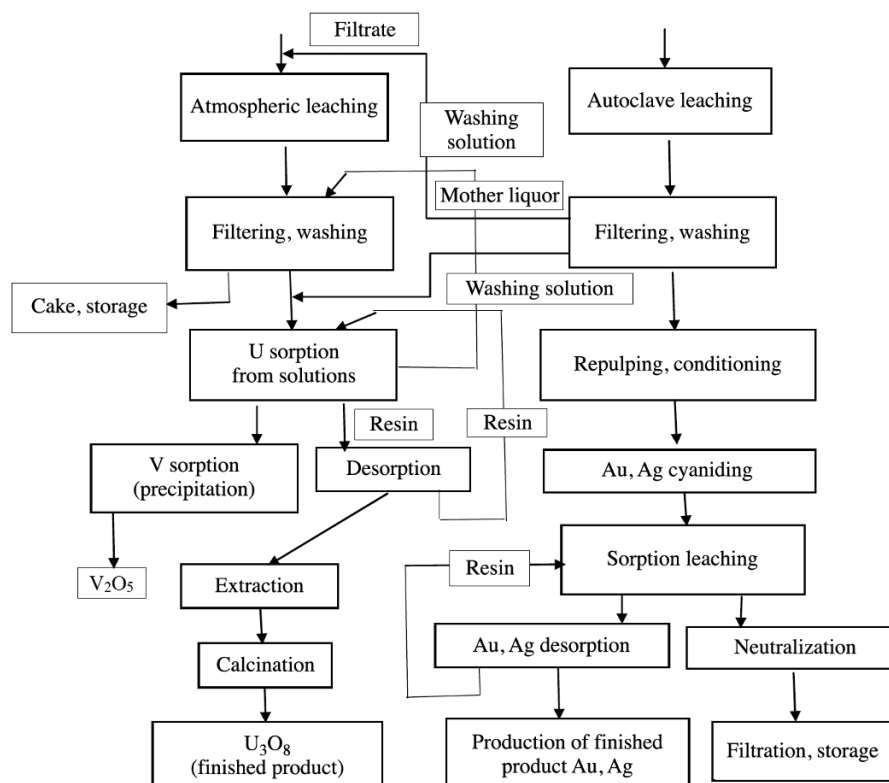


Fig. 1. Schematic diagram of hydrometallurgical processing of ore from the Elkon deposit.

rich concentrate in the amount 5.4% of the volume of the initial ore, containing a portion of uranium that is difficult to open (uranium extraction ~30% and vanadium and gold extraction 10–15%);
marketable product with yield 60.3% and uranium content 0.145%; and
dump cakes with yield 34.3% and uranium content 0.015%.

This operation increases the efficiency of the subsequent flotation enrichment as a result of a reduction of the required ore volume and reduction of the circulating load, and it promotes high recovery of valuable metals and acid-rich components into product going into autoclave leaching. The mineral and chemical compositions of the ore and products of the process stages are presented in Table 1.

The technological products are enriched compared with the initial product. The radiometric concentrate is enriched with uranium, gold, and silver; sulfide flotation concentrate by uranium, gold, silver, silver sulfide, carbonates, and chlorite and the carbonate flotation concentrate by uranium, carbonates, chlorite, and micas. The combined product of the enrichment cycle with the content U 0.288%, V 0.102%, Au 1.63 g/ton, Ag 16.79 g/ton as well as the bulk of the acid-rich components (acid content 165 kg/ton) go to autoclave leaching. Ore comprised of U 0.082%, V 0.018%, Au 0.11 g/ton, and Ag 1.7 g/ton goes to atmospheric leaching. The feeding of atmospheric leaching is represented primarily by feldspars and quartz (~90%) with low acid content (45 kg/ton).

Sulfuric-acid and carbonate autoclave leaching of uranium from products of flotation enrichment (sulfide and carbonate concentrates, pulp fraction) were studied in different regimes. Under the predetermined conditions (temperature 140°C, oxygen partial pressure $P_{O_2} = 0.3$ MPa, S:L = 1:1.5, leaching time 4 h), the recovery of the uranium in solution exceeded 93%, vanadium about 50% with 15% consumption of sulfuric acid and residual acidity ~15 g/dm³ (Fig. 2). Higher consumption of sulfuric acid is undesirable because of the very small (~1%) increment of uranium recovery. The consumption of sulfuric acid in this operation in terms of the initial ore equals 51 kg/ton. The low recovery of vanadium is associated with the fact that the mineralization is difficult to open in this ore sample.

TABLE 1. Content of Uranium, Gold, Silver, Vanadium, and Acid-Rich Materials in the Initial Ore and Products of Process Stages

Technological product	U, %	Au, g/ton	Ag, g/ton	V, %	Pyrite, %	Carbonates, %	Chlorite, micas, %
Initial ore	0.129	0.79	9.08	0.055	3	11.3	18.5
Rich radiometric concentrate	0.723	1.57	14.26	0.12	4.7	20.6	21
Marketable product	0.145	0.84	9.08	0.054	3.4	10.3	15.3
Sulfide float-concentrate	0.215	3.85	40.2	0.175	15	25.8	21.4
Carbonate float-concentrate	0.226	1.44	13.78	0.109	5	40.9	23.5
Flotation tailings	0.082	0.11	1.3	0.066	0.7	4.7	–

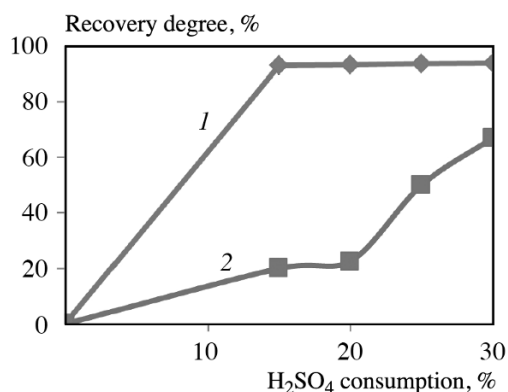


Fig. 2. Rate of recovery of uranium (1) and vanadium (2) into solution versus the sulfuric acid consumption.

The optimal conditions chosen for atmospheric sulfuri-acid leaching of uranium from the product of flotation (consumption of H₂SO₄ 15% and Mn₂O 1%, S:L = 1:0.8, temperature 75°C, duration 4 h) give uranium recovery above 95% (its residue in the cake is 0.0065%) and vanadium recovery 75% (0.005% in cake). The tested carbonate atmospheric leaching of flotation product does not give acceptable technological and economic performance – the uranium yield in solution does not exceed 75% with soda consumption 100 kg/ton.

The total recovery of metals into solution in autoclave and atmospheric leaching operations was equal to 93% for uranium and 54.3% for vanadium with sulfuric acid consumption 82.7 kg/ton in terms of the initial ore. The proposed, fundamentally new, technology for the recovery of uranium and accompanying valuable components makes it possible to reduce, compared with the technological arrangement using only autoclave leaching of the marketable product of enrichment, by more than a factor 2 the volume of the energy- and capital-intensive autoclave leaching and reduce the consumption of sulfuric acid by 28000 tons/yr with reprocessing of 5·10⁶ tons ore/yr. An additional advantage of the technology is a reduction in the amount of product going to re-extraction of noble metals, owing to the optimal distribution of the technological products of enrichment between the atmospheric and autoclave leaching operations.

In subsequent hydrometallurgical operations in the scheme of reprocessing of uranium ores from the Elkon region, ion exchange processes were used: sorption for recovery of metals and their concentration from solutions and pulps formed in the leaching of ores and different products of enrichment; extraction processes were used at the stages of purification by removal of impurities in obtaining the finished product.

Sorption recovery of uranium was conducted from combined solutions of autoclave and atmospheric leaching (Table 2). A comparative analysis of the sorbents showed a possibility of using for this purpose strongly basic anionites AMP from the

TABLE 2. Characteristics of Solutions from Leaching of Ore Samples

Component	Concentration, mg/dm ³
Uranium	600–900
Iron	3000–7000
Vanadium	150–400
Silicon (SiO ₂)	60–350
Calcium	400–700
Aluminum	400–1100
Manganese	200–500
Molybdenum	25–300
Nitrate Ion	800–3000
pH	0.9–2

Smoly company (Ukraine), Purolite A-500 and -600 (Great Britain), and Ambersep 910U and 920U (USA) as well as analogs of sorbents from China, which possess close technological and operating characteristics. The optimal parameters of sorption recovery of uranium were determined using perfected methods of the technological process: kinetics, statics, dynamics of sorption-desorption of uranium from solutions (pulpes). It was found that sorption of uranium is effective – ionite capacity reaches at least 90 mg/g; the uranium concentration in the sorption filtrates does not exceed 0.003 g/dm³. The choice of the eluent is made on the basis of the type and quality of the finished product [1]. A change over to the manufacture of product in the form of sodium or ammonium diuranate (yellowcake) and uranium peroxide increases the profitability of the product owing to production cost reduction. It was found that in the case of uranium desorption by a solution containing 100 g/dm³ NH₄NO₃ + 10 g/dm³ H₂SO₄ the uranium concentration in the marketable desorbate is 12–13 g/dm³ with its yield equal to two (volume) units per unit of ionite.

The required quality of commercial eluates is secured by using a combination of technological devices including preliminary selective washing of impurities from the anionite by weak sulfuric acid solutions and its additional saturation with uranium, which makes it possible to reduce the iron content on the sorbent, increase the capacity in terms of uranium, and obtain directly from commercial desorbates finished product meeting the quality standards ASTM C 967-13 [1, 2].

Direct extraction recovery was tested together with the sorption method of separating uranium from solutions after leaching. This is a new trend in the domestic practice of reprocessing uranium ores. Abroad, the reprocessing of decantation solutions after sulfuric acid leaching of ores is performed by a solution of tri-alkyl amine in a mixture of high-molecular alcohols in a hydrocarbon diluent; this is due to the exceptionally high selectivity of trialkyl amine with respect to uranium. The drawbacks of this reagent are low capacity in terms of uranium (~4 g/dm³ uranium for 0.1 mol/dm³ of tri-alkyl amine solution), possibility of using only in sulfuric acid concentration range 10–30 g/dm³, and negative impact on the extraction of the nitrate ion.

In extraction recovery of uranium by a mixture of 0.2 M trialkyl amine + 0.2 M decyl alcohol in kerosene from a solution containing (g/dm³) U 1.6, Fe³⁺ 6, H₂SO₄ 20, and different NO₃ concentration, it was found that upon saturation of the extracting agent by uranium the capacity decreases sharply as a result of the predominant recovery of nitrates in the form of nitric acid and displacement of uranium from the organic phase (Fig. 3). For nitrate-containing solutions, a fundamentally new composition was proposed for the extracting agent based on a mixture of tri-alkylamine, di-2-ethylhexylphosphoric acid (D2EHPA) and tri-butyl phosphate (TBP) in kerosene [3]. The optimal composition was determined for the mixture of extracting agents in equimolar ratio with content of each component 0.05–0.07 mol/dm³. High efficiency and selectivity of uranium recovery were attained by means of direct extraction of uranium from combined leaching solutions. The uranium saturation of the extracting agent was equal to 7.1–7.9 g/dm³ with Fe³⁺ concentration in the saturated extracting agent not exceeding 8 mg/dm³.

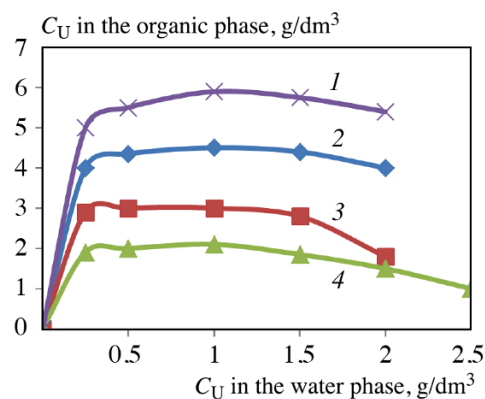


Fig. 3. Impact of the content of the nitrate ion 0 (1), 3.33 (2), 5 (3), and 7 g/dm³ (4) on uranium recovery.

The technology of the precipitation of yellowcake in the form of uranium peroxide was investigated and the factors influencing selectivity and increasing selection efficiency were determined. The precipitation of uranium peroxide from carbonate re-extracts with the chosen parameters (pH 3.6–4.2, mixing time 1–1.5 h, settling time at least 1 h, 50–100% excess of hydrogen peroxide from stoichiometry) gives 99.98% uranium extraction in the precipitate and uranium concentration in the filtrate not exceeding 10 mg/dm³. The mass fraction of the primary impurities with respect to uranium in U₃O₈ is much lower than provided by the international quality standards ASTM C 967-13 for uranium ore concentrate (%):

U	84.6	Sm	1·10 ⁻⁵
P	0.009	Eu	1·10 ⁻⁵
V	2·10 ⁻⁴	B	1·10 ⁻⁵
Cd	5·10 ⁻⁵	Mn	1·10 ⁻⁴
Cu	1·10 ⁻⁴	Th	5·10 ⁻⁴
Fe	0.003	S	0.014
Mo	7·10 ⁻⁴	Al	0.018
Si	0.002	Ni	1·10 ⁻⁵
Na + K	0.001		

Additional reduction of the production cost of uranium is obtained by increasing the throughout recovery of gold, silver, and vanadium. Vanadium is an exceedingly valuable metal, widely used in different industries. At the same time, it is a highly toxic element, so that discharges of vanadium-containing solutions into the environment make it necessary to detoxify the solutions. During leaching of uranium, significant amounts of vanadium enter the solution; the vanadium content in solutions depends on the S:L ratio and equals 200–400 mg/dm³. Therefore, in reprocessing, for example, 4.5·10⁶ tons of ore per year, it is possible to obtain 6.4·10³ tons of V₂O₅ together with uranium. For comparison, the largest specialized vanadium producer in the world Vindimurra (Western Australia) produces 6.8·10³ tons per year, which is about 12% of the world market [2].

It was found that in the case of sorption-extraction recovery of uranium almost all of the vanadium is concentrated in the sorption filtrates (96%). Since the redox potential in solutions equals 450–500 mV, the vanadium is in a quadrivalent state in the form of the vanadyl ion VO²⁺, but the presence of a significant number of Fe³⁺ ions in solutions permits simultaneous presence of pentavalent vanadium.

The sorption recovery of vanadium from the filtrates of uranium sorption was checked in different strongly basic (Ambersep-920U, AMP, Rossion-62) and weakly basic (AMN-2, ALX-220, Purolite A-100) ionites. Under optimal conditions (redox potential 500 mV, pH 2, and temperature 70°C), the best result was obtained for the anionite AMP (working capacity >58 mg/g), but in this case, elevated vanadium content was observed in the discharge solutions. An oxidation-sorption recovery

TABLE 3. Sorption Characteristics of Anionites in Sorption from Silver-Gold-Containing Cyanide Solutions

Parameter	PuroGold S-992	AM-2B
Capacity, mg/g		
Au	5.1	6.5
Ag	4.4	7.7
Fe	1	1.2
Cu	0.1	3
Zn	1.7	4.3
Ni	0.4	1.7
Co	0.2	0.1
Capacity in terms of total impurities $a_{\Sigma\text{imp}}$, mg/g	3.4	10.3
Selectivity, $a_{\text{Au}}/a_{\Sigma\text{imp}}$	2.8	1.37

was proposed in order to remove it from the solutions; this decreases the concentration in the wastes and simultaneously yields an iron-vanadium concentrate with vanadium content 2.58% and iron content 22.8%, which is suitable for subsequent reprocessing by the known calcination-sorption scheme. The recovery of vanadium into the finished product equals 52%.

Gold is recovered from cyanide solutions and pulps by means of activated carbon (domestic brands AG-2000, MeKS, and VSK-400), strongly basic anionites (AM, AV-17), mixed-basicity anionites (AM-2B, Purolite A-100/2412), and weakly basic anionites represented by domestic products (Rossion-25/2, Rossion-26/2, ANS, Rossion-15) as well as PuroGold S-992 from the Purolite firm (Great Britain) [4, 5]. Weakly basic anionites sorb $\text{Au}(\text{CN})_2^-$ more effectively, since they have active amino groups with higher degree of ionization and are characterized by simple desorption of gold with simultaneous purification by removal of impurities.

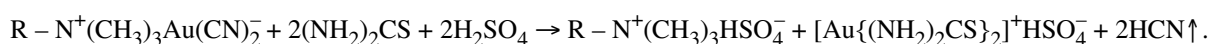
In application to the proposed scheme, the recovery of gold and silver on the anionites PuroGold S-992 and AM-2B from cyanide solutions obtained from autoclave leaching cakes was investigated. A solution with the following composition was used in the experiments (mg/dm³): Au 3, Ag 29, Fe 2.8, Cu 9.5, Zn 3.2, Ni 1.1, Co 1, NaCN 280; pH 10.2.

The results of these investigations (Table 3) show that the anionite PuroGold S-992 exhibits gold capacity 5.1 mg/g, AM-2B – 6.5 mg/g; the capacity in terms of silver is 4.4 and 7.7 mg/g, respectively. However, the capacity in terms of impurities for the anionite PuroGold S-992 is 3–3.2 times less than for AM-2B. The presence of silver in amounts significantly exceeding the concentration of gold (by factor of 10 or more) results in lower capacity of sorbents for gold.

These sorption isotherms of gold-cyanide complex $\text{Au}(\text{CN})_2^-$ are more convex than sorption isotherms of the silver-cyanide complex $\text{Ag}(\text{CN})_2^-$, which has lower affinity to anionites and is displaced from sorbents by gold (Fig. 4). The differences of the initial sections of the isotherms for gold and silver attest for deep recovery, especially from lean solutions, predominance of gold sorption (the waste concentration <0.01 mg/dm³) over silver (waste concentration <0.5 mg/dm³).

The study of the kinetics of sorption recovery of gold, silver, and impurity metals showed that cyanide complex anions of metals are sorbed in order of increasing charge in the following sequence of their anionite affinity: $[\text{Au}(\text{CN})_2]^- > [\text{Zn}(\text{CN})_4]^{2-} > [\text{Ni}(\text{CN})_4]^{2-} > [\text{Ag}(\text{CN})_3]^{2-} > [\text{Cu}(\text{CN})_4]^{3-} > [\text{Fe}(\text{CN})_6]^{4-}$. As the ionite saturates, the ions of gold, zinc, and nickel displace from the sorbent phase the copper, silver, and iron anions already present there.

The desorption of gold from the anionite AM-2B proceeds efficiently with the use of acid solutions of thiourea, which forms complex cationic compounds with gold, silver, and copper:



The desorption of gold from saturated weakly basic anionite PuroGold S-992 proceeds easily during processing by solutions of alkali (principle of acid-base hydrolysis), which is explained by the lower content of strongly basic groups and

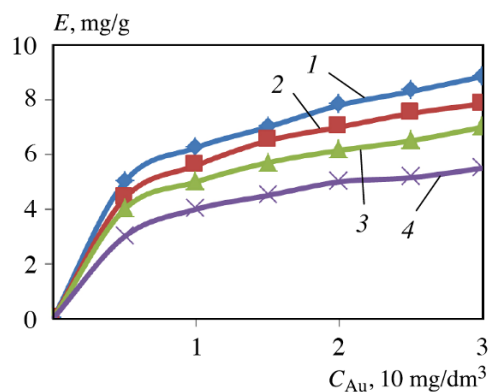


Fig. 4. Sorption isotherms of gold on AM-2B (1), PuroGold S-992 (2) and silver on AM-2B (3), PuroGold S-992 (4).

the presence of undissociated weakly basic active groups. The degree of sorption of gold from resin exceeded 95%; the concentration of gold and silver in the commercial desorbate was 270 and 380 mg/dm³, respectively. In terms of technological properties, the anionite PuroGold S-992 is no worse than the anionite AM-2B, so that it can be regarded as an alternative in the conventional sorption processes of recovery of gold (silver) from cyanide pulps and solutions. In the reprocessing of commercial desorbates, the finished product of the technological scheme is a gold-containing concentrate – ligature gold or the alloy Dore. The throughout recovery of gold and silver equals 55 and 24%, respectively.

The reprocessing of 4.8 million tons of ore per year will yield 5000 tons of U₃O₈ and 12.5 tons of Au–Ag alloy; the approximate consumption of the primary reagents will be as follows:

H ₂ SO ₄ , kg/ton	104
NaCN, kg/ton	0.29
AMP, g/ton	120
AM-2B, g/ton	4.5
D2EHPA, g/ton	12
TBF, g/ton	9.8
UVS, g/ton	119

On the basis of these investigations, including laboratory, trial, and semi-commercial tests, a promising hydrometallurgical technology for reprocessing ores from the Elkon deposit was developed. It has a practical advantage owing to the complex recovery of uranium, gold, silver, and vanadium with final yield 90, 55, 24, and 52%, respectively. The initial data for design work were developed to validate investments in the construction of a mining-metallurgical combine in the Elkon uranium-ore region.

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