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Earth sciences



Gold and rare earth elements in enrichment products from the technogenic wastes of the Caspian Mining-Metallurgical Plant (Aktau, Kazakhstan)

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ABSTRACT

The paper presents the outcome of a comprehensive study at macro- to nanoscale levels of enrichment products from technogenic wastes. The products were obtained thanks to the experience of gravity enrichment during the treatment and preparation of the gold and REE sample material with preliminary mechanical and thermal activation. Thermal activation was applied for the first time. Native gold was identified in the form of single, micron-sized grains and, according to technological testing of enrichment products, there is a predominance of "invisible" dispersed gold. The gold content in the initial material was 2.93 g/t, which upon thermal activation of the sample increased to 6.37 g/t. According to the spectral analysis and electron probe microanalysis, the products of all enrichment stages are characterized by an increased content of yttrium and REEs. The REEs occurrence forms were determined. REEs are mainly found in micro- and nano-sized fluorine and fluorine-free phosphates (in apatite, by substitution of calcium), in REE-phosphates (in xenotime), and less often, possibly, in complex sulfo-phosphates and phosphate silicates. In thermal products consisting of inhomogeneous aggregates of nanosized phases, according to X-ray phase analysis, considering the elemental composition, REEs are included in the composition of phosphates: florensite and phases $Ce(P_5O_{14})$, $Ca_8MgSm(PO_4)_7$

Keywords: gold, REEs, micro- and nano-sized grains, technogenic wastes, Caspian Mining-Metallurgical Plant, Kazakhstan.

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Introduction

Accumulated for decades and occupying vast lands, technogenic wastes of large enrichment combines, factories, and plants, are rightly considered as technogenic deposits of valuable elements, and their study results may well comprise a separate section of metallogeny.

In the Mangistau oblast, the uranium-phosphorite deposits of Melovoe, Tomak, and others provided raw materials for the Caspian Mining and Metallurgical Plant (CMMP) [[1], [2], [3]]. According to open sources literature [[4], [5], [6], [7], [8], [9]], the CMMP ore process was as follows:

1. the clays were washed and classified, separating the washed phosphatized fish bones into large classes;

2. the washed bone detritus was sent to the plant's hydrometallurgical reprocessing for extraction of uranium and phosphorus, and the REEs were sent for storage in a sludge reservoir.

This way, two types of technogenic deposits were accumulated in Aktau:

- ore wash tailings: black, organically enriched clays, the most abundant;
- rare earth industrial sludge, limited by the sludge reservoir volume.

According to E.A. Pirmatov et al. [7], the content of rare-earth oxides in Aktau mineral technogenic formations comprises 3.67%, including 0.24% of the most valuable heavy group.

The research objective: a study of phase and mineral composition of enrichment products from technogenic wastes, that is phosphogypsum, formed as a result of reprocessing of uranium-phosphorus concentrates of fish bone detritus of Neogene-Paleogene marine clays. Of interest are gold and rare-earth phases (minerals) of micro- and nano-size.

Sample preparation and research methods

Material preparation and enrichment to obtain representative samples (enrichment products) for mineralogical, chemical, and other types of analyses were implemented according to the developed technological procedure for the enrichment of gold and rare earth element (REE) samples [[10], [11]]. The technology included additional operations for deep disintegration of sample material in a self-crushing mill and thermal activation (RK Patent No. 7613 [10]) of bulk analytical samples allowing approaching closely to the enrichment and quantitative determination of micro- and nano-components of ores.

Products of all reprocessing stages were analyzed in the Mineralogy Laboratory in K.I. Satbayev Institute of Geological Sciences (Almaty). To study the mineral and elemental composition, the samples were separated in heavy liquids into light and heavy fractions, followed by the separation of the heavy fraction into magnetic, electromagnetic, and non-magnetic. Grains of minerals, selected under a binocular, were studied by drop-microchemical, luminescent analyses, and electron probe microanalysis.

The following research methods were employed to identify micro- and nano-mineral components of

enrichment products from technogenic wastes: optical microscopy (LEICA DM2500P), X-ray phase (DRON-3 with PDF2 Release 2022), spectral (semi-quantitative) analyses, atomic absorption (Thermo ICE 3500 spectrometer) analyses, electron probe (JXA 733 with INCA ENERGY energy dispersive spectrometer). The chemical analyses were implemented in an accredited laboratory (NKZ.T03.1460 as of February 28, 2019) by EcoLux-As LLP (Stepnogorsk).

Research results

The initial material was white with a yellowish tint homogenous sludge formed from the sulphuric acid processing of uranium-phosphate ores at the hydrometallurgical plant.

Thanks to our own technique of initial material pre-processing of mechanical and thermal activation (RK Patent No. 7613 [10]), it became possible to concentrate ore load in small weight mineralogical batches (finishing concentrates) and to obtain the technological parameters on gravitation enrichment of stockpiled tailings (sludge) after mechanical activation in a self-crushing mill. As the material is fine-grained and clumpy, manual disintegration was ineffective. The yield of non-disintegrated "lumps" was ~15 %, mechanical ~1.5 %. Therefore, enrichment was carried out after the mechanical activation of the initial material in the self-crushing mill.

Native gold in the form of single, micron-sized grains was detected in the gravity concentration products. In Figure 1, the gold particle is in phosphate-(Fe). The elemental composition according to electron probe microanalysis (%) is Cu 12.85, Ag 4.51, and Au 82.65.

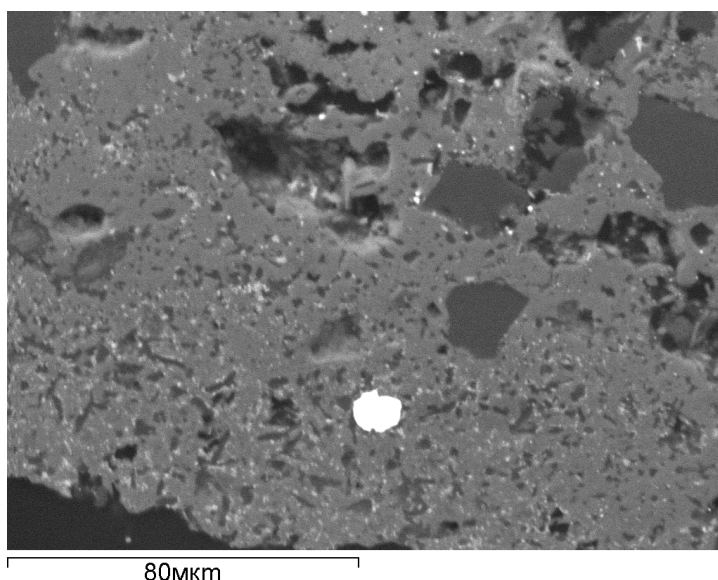
To study dispersed gold, samples were taken from the final tailings after their mechanical and thermal treatments (at 750-800°C) in a thermal activator [10]. It is assumed that heating causes the enlargement of dispersed gold nanoparticles up to micron size [[10], [11]] with their subsequent extraction into grave-concentrate (Table 2).

"Invisible" dispersed gold predominates in the technogenic wastes according to a study of enrichment products. The gold content in the initial material was 2.93 g/t, which after thermal activation of the sample increased to 6.37 g/t.

Table 1 - Results of gravity concentration of stockpiled tailings (sludge) after mechanical activation in the self-crushing mill

Enrichment products	Output		Gold content, g/t*	Gold recovery, %
	kg	%		
Vibratory screw separator concentrate re-processing concentrate (VCRC)	0.025	0.17	4.79	0.27
Vibratory screw separator concentrate re-processing tailings (VCRT)	0.092	0.62	2.36	0.50
Centrifugal apparatus concentrate (CAC)	0.031	0.21	6.74	0.47
The final tails	14.652	99.0	2.92	98.60
Source material: stockpiled sludge (sludge)	14.80	100	2.93	100

Note: *Protocol No.0003 of the Eco-Lux-As LLP dated 06.01.2022



The matrix material is phosphate-(Fe) (gray) in association with REE-bearing phosphate-Silicate-Fe nanoparticles (white dots), quartz (dark gray)

Figure 1 – Micron inclusion of gold (white). *BEI*

Table 2 - Results of gravity concentration of final tailings after their mechanical and thermal treatments with thermal activator coal

Enrichment products	Output		Gold content, g/t*	Gold recovery, %
	kg	%		
Thermal activator coal	130	34.12	2.25	12.09
Centrifugal apparatus concentrate (CAC)	30	7.88	5.06	6.38
Tails	221	58.0	8.97	81.63
Initial (Ini.) material (enrichment products + thermal activator coal)	381	100	6.37	100

Note: *Protocol No.0013 of Eco-Lux-As LLP dated 20.01.2022

Table 3 – Bulk chemical composition (normalized to 100%) (wt.) of heavy fraction sample from enrichment products (average for 3 analyses)

Analysis components	1	2	3	4	5	6	7	8	9
O	43.50	38.00	41.57	39.44	40.06	40.73	38.74	45.06	39.64
F	0.00	0.00	9.18	9.39	9.06	9.65	8.78	0.00	0.00
Na	1.07	1.12	0.48	0.61	0.80	0.80	0.57	2.14	0.94
Mg	1.59	1.67	3.43	3.72	1.7	3.75	4.12	1.84	1.66
Al	3.22	3.39	3.95	3.89	2.35	4.16	4.20	5.07	3.57
Si	9.22	8.47	1.21	0.51	4.58	1.59	0.85	12.40	11.52
P	10.75	10.31	19.49	21.97	10.28	18.69	22.17	7.88	8.92
S	0.37	0.41	0.59	0.32	2.50	0.84	0.53	0.82	0.66
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27	0.15
K	0.61	0.69	0.19	0.04	0.29	0.18	0.10	1.47	0.81
Ca	5.09	2.36	5.53	3.83	14.29	6.20	3.56	6.16	5.30
Ti	0.00	0.36	0.00	0.00	0.00	0.00	0.00	0.29	0.47
Cr	0.85	4.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	21.2	24.29	11.62	12.26	11.27	11.70	12.84	15.88	25.32
Ni	0.83	2.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	2.01	0.39	0.00	0.00	0.00
La	0.27	0.67	0.55	0.73	0.15	0.41	0.66	0.34	0.38
Ce	0.68	0.94	1.01	1.45	0.67	0.92	1.26	0.37	0.64
Pr	0.17	0.00	0.27	0.41	0.00	0.00	0.28	0.00	0.00
Nd	0.32	0.00	0.56	0.68	0.00	0.00	0.75	0.00	0.00
Sm	0.23	0.00	0.26	0.26	0.00	0.00	0.31	0.00	0.00
Eu	0.21	0.00	0.00	0.20	0.00	0.00	0.12	0.00	0.00
Gd	0.12	0.00	0.2	0.29	0.00	0.00	0.26	0.00	0.00
Σ	100	100	100	100	100	100	100	100	100

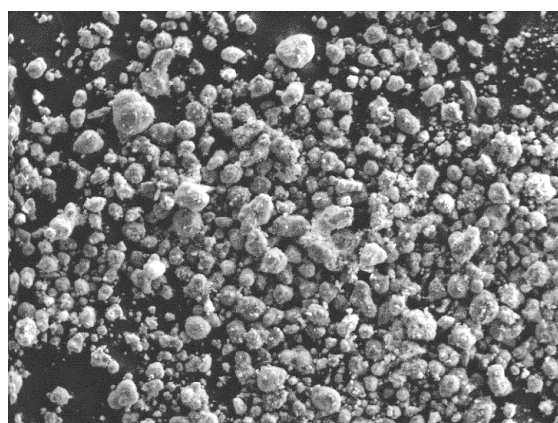
Note: 1 - REE-1 Fc (finishing concentrate) of technogenic mineral formations (TMF) concentrate sample, 2 - REE-2 Fc of TMF concentrate sample, 3 – REE VCRT sample, 4 –REE tailing sample, 5 – REE CAC sample, 6 – REE VCRC sample, 7 – REE VCRT sample, 8 – REE-1 Ini. Fc of VCRC sample, 9 – REE-1 Ini. Fc of VCRC sample

During the study of the material composition of samples for REE, the refined products were divided into light, magnetic, electromagnetic, and non-magnetic fractions. The light fraction was found to contain gypsum, quartz, feldspar, hydromica, chlorite, phosphates, and rarely carbonates. The magnetic fraction contained mainly dark brown iron ochre in the form of crusts and rarely magnetite in the form of rounded formations. The electromagnetic fraction contained the main mass in the form of phosphates, less often hematite, ilmenite, iron hydroxides, limonite on pyrite, amphibole, epidote-zoisite, light pink garnet, dark green pyroxene, and extremely rare single

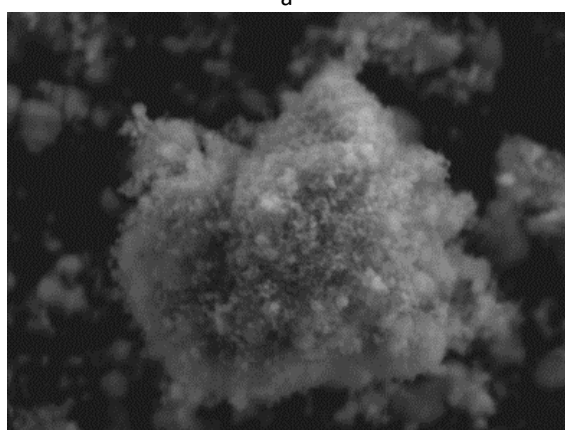
occurrences of tourmaline, titanite, mica (biotite). The non-magnetic fraction of samples has mainly white, light gray spherical, and columnar aggregates of phosphates and sulfates, transparent apatite; less often zircon, pyrite, rutile, white barite, and carbonates.

According to the spectral analysis, products of all stages of enrichment are characterized by high content (g/t) of yttrium up to 500, light and heavy REEs: lanthanum up to 500, cerium up to 1500, praseodymium up to 10 000, neodymium up to 3 000, samarium up to 1 500, gadolinium up to 1 500, terbium up to 1 000, dysprosium up to 1 000, erbium up to 300, ytterbium up to 1 000. According to

electron-probe microanalysis, the bulk elemental composition of products mainly contains light REEs, with high values (%) for cerium up to 1.49; lanthanum up to 0.88; praseodymium up to 0.86; neodymium up to 1.03 (Table 3). The grains of heavy fraction samples selected and preliminary studied on pucks (semi-quantitative analysis) in SEI mode are mainly lumpy loose rounded macroaggregates (Figure 2 a) made of nano-sized grains (Figure 2 b).



a



b

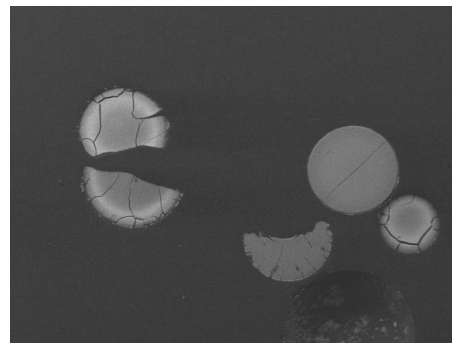
Figure 2 – Micro-aggregates from heavy fraction sample. *SEI*. General view of rounded lumpy micro-aggregates – a, shape and size of a rounded micro-aggregate consisting of nano-sized grains of Fe phosphates and REE-bearing apatites – b.

To determine elemental composition and forms of REEs occurrence in *BEI* mode (compo), grains of samples, i.e. concentrates of different reprocessing stages from the non-magnetic fraction were placed on polished sections. In the detailed figure, the grains turned out to be inhomogeneous aggregates consisting of many nano-sized phases. In finishing concentrate (sample REE-2 Fc of TMF concentrates) light and heavy REEs were revealed in heterogeneous xenotime phase (Table 4, analysis 1);

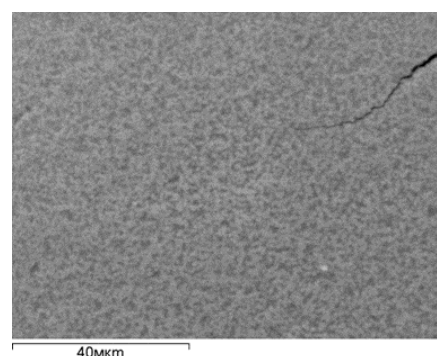
light REEs and yttrium are part of fluorine-free apatite (Table 4, analyses 2-5).

In analysis 2-5, the remaining iron, aluminum, magnesium, and chromium, according to X-ray phase analysis (Table 3), can enter lipscombite $\text{Fe}_{2.95}(\text{PO}_4)_2(\text{OH})_2$, iron and aluminum phosphate $\text{Al}_{0.67}\text{Fe}_{0.33}(\text{PO}_4)$, magnetite $\text{Mg}_{0.04}\text{Fe}_{2.96}\text{O}_4$, Mg-bearing hercynite $\text{Fe}_{0.77}\text{Mg}_{0.29}\text{Al}_{1.91}\text{O}_4$, Mg-bearing chromite $(\text{Fe}_{0.65}\text{Mg}_{0.35})\text{Cr}_2\text{O}_4$. In Figure 1, a microparticle of gold in phosphate-(Fe) (analysis 6) is in association with nano-sized grains of REE-bearing phosphate Silicate-Fe and quartz.

In addition to rounded loose macroaggregates, there are homogeneous and zonal globular micro formations in the VRRC sample, cracked under conditions of high vacuum and temperature effect of the electron beam. In slices, the globular formations are homogeneous or zonal (Figure 3 a). In zonal ones, the outer rim consists of a heavy REE-bearing phase of sulfo-phosphate Ca and F, while the composition of the inner part is the same only with lower REEs content. In the detailed figure of the central part of globular formations, their heterogeneity is clearly visible. Like loose micro-aggregates, these formations are composed of nano-sized phases (Figure 3 b).



a



b

Figure 3 - Spherical formations of VRRC sample. *BEI*. The zoning of globular formations - a, heterogeneous structure of the inner part of the globular formation - b.

Table 4 - Chemical composition (wt.%) of heterogeneous grains in the finishing concentrate sample

Analysis	1	2	3	4	5	6
Components	Finishing concentrate sample (sample REE-2 Fc of TMF concentrates)					
F	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.00	0.00	0.00	0.00	0.00	1.70
MgO	0.00	2.24	3.77	2.26	2.27	0.73
Al ₂ O ₃	0.00	6.15	8.22	5.85	5.47	1.43
SiO ₂	0.00	0.00	0.00	0.00	0.00	0.00
P ₂ O ₅	38.39	51.45	50.25	46.36	44.95	40.83
SO ₃	0.00	0.00	0.00	0.00	0.00	0.00
CaO	2.73	4.55	3.14	5.09	4.46	3.21
TiO ₂	0.00	0.56	0.00	0.33	0.65	0.25
Cr ₂ O ₃	0.00	0.00	0.85	0.58	0.60	1.89
FeO	1.95	25.66	21.59	21.90	20.97	47.15
NiO	0.00	0.00	0.00	0.00	0.00	0.82
Y ₂ O ₃	23.31	2.72	1.85	3.39	2.19	0.00
La ₂ O ₃	3.46	1.65	1.39	1.19	1.85	0.00
Ce ₂ O ₃	6.33	2.28	2.45	1.70	2.23	0.00
Pr ₂ O ₃	1.07	0.05	0.46	0.19	0.03	0.00
Nd ₂ O ₃	3.77	0.94	1.61	1.07	1.29	0.00
Sm ₂ O ₃	1.45	0.14	0.27	0.35	0.73	0.00
Eu ₂ O ₃	0.67	0.21	0.30	0.16	0.50	0.00
Gd ₂ O ₃	2.92	0.35	0.64	0.13	0.60	0.00
Tb ₂ O ₃	0.62	0.00	0.00	0.00	0.00	0.00
Dy ₂ O ₃	3.11	0.00	0.00	0.00	0.00	0.00
Ho ₂ O ₃	0.46	0.00	0.00	0.00	0.00	0.00
Er ₂ O ₃	2.13	0.00	0.00	0.00	0.00	0.00
Σ	92.37	93.51	93.08	83.78	84.42	98.01

The enriched products studied by X-ray phase analysis are represented by poorly crystallised phases, which (considering the results of electron probe microanalysis) may presumably be of the following composition (Table 3): whitlockite $\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$, iron hydroxide phosphate $\text{Fe}_4(\text{PO}_4)_3(\text{OH})_3$, iron and aluminium phosphate $\text{Al}_{0.67}\text{Fe}_{0.33}(\text{PO}_4)$, lipscombite $\text{Fe}_{2.95}(\text{PO}_4)_2(\text{OH})_2$, pyroaurite $(\text{Mg}_6\text{Fe}_2(\text{OH})_{16}(\text{CO}_3)(\text{H}_2\text{O})_{4.5})_{0.25}$, phosphocyclite-(Fe) $\text{Fe}_2(\text{P}_4\text{O}_{12})$, rhodolicoite $\text{Fe}(\text{PO}_4)$, hydroxyapatite $\text{Ca}_5(\text{PO}_4)_{2.928}\text{O}_{1.3}\text{H}_{1.44}$, F-bearing hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3((\text{OH})_{0.8}\text{F}_{0.2})$, aluminium phosphohydroxide $\text{Al}_4(\text{PO}_3\text{H})_6$, $\text{Al}(\text{H}_2\text{P}_3\text{O}_{10})(\text{H}_2\text{O})_2$, $\text{Al}_2(\text{P}_2\text{O}_{11})\text{FH}_7$, iron phosphate $\text{Fe}_2(\text{P}_4\text{O}_{12})$, where REEs are apparently present in fluorine and fluorine-free phosphates (in apatite, by substitution of calcium, and in xenotime, monazite).

Initial samples, tailings and concentrates after thermal treatment in thermal activator [10] were again divided into light, magnetic, electromagnetic and non-magnetic fractions and studied by a complex of methods. Minerals of the light fraction are represented by quartz, feldspar, mica, graphite and fragments of grayish-black phosphorus-bearing minerals. The magnetic fraction contains brown and dark-brown iron ochres (technogenic) in the form of crusts; the electromagnetic fraction consists of iron hydroxides, hematite, less frequently epidote-zoisite, light pink garnet, dark green pyroxene, ilmenite, titanite, and ash-grey lumpy phosphorus-bearing aggregates; non-magnetic fraction, mainly light grey, ash-grey phosphate, rarely apatite and columnar white phosphate, zircon, pyrite.

According to semi-quantitative spectral analysis, content of all thermal products (thermal tails,

thermal concentrate, thermal initial) increased (g/t) as follows: yttrium up to 5000; REE: lanthanum up to 1500, cerium up to 5000, praseodymium <10,000, neodymium <10,000, samarium up to 1000, gadolinium up to 2000, dysprosium up to 1500, erbium up to 500, lutetium up to 300.

According to electron probe microanalysis, the bulk elemental composition of three thermo samples contain significant amounts of light REEs compared to heavy ones (%): cerium up to 1.76; lanthanum up to 1.10; neodymium up to 0.98; samarium up to 0.42; gadolinium up to 0.62; europium up to 0.62. For exact determination of REEs occurrence, polished sections with selected grains of non-magnetic fraction of thermal products were prepared. The secondary electron images (SEI) show thermal samples as aggregates of rounded, sometimes hollow, microparticles (Figure 4).

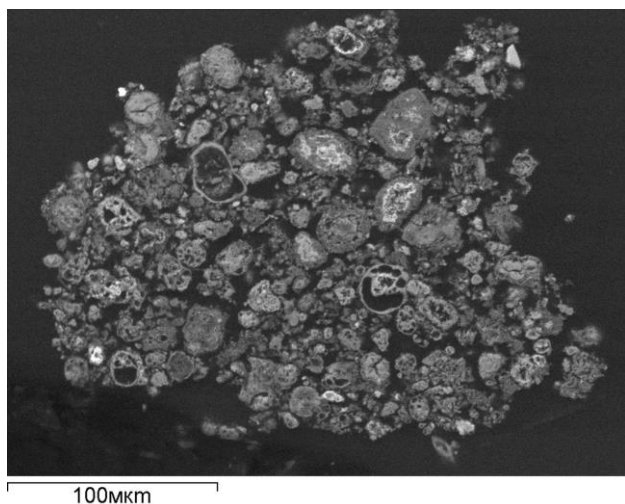


Figure 4 - Porous aggregates of thermo-products (thermo-tails) consisting of round particles. *SEI*

The rounded aggregates are heterogeneous, often zonal (Figure 5) and consist of nano-sized phases. The heavy phases are phosphates of REEs and Fe. The dense phases of the rims do not contain REEs and are close in composition to iron phosphates. There are frequent phases closer to the florensite composition, with significant contents of light REEs. In zonal rounded aggregates (Figure 5), the central part consists of nano-sized REE-bearing heavy phases: REE and iron phosphates, the outer shell is lighter due to the lower content of REE phosphate.

In thermal products, according to X-ray phase analysis, REEs are included in phosphates: florensite and phases $\text{Ce}(\text{P}_5\text{O}_{14})$, $\text{Ca}_8\text{MgSm}(\text{PO}_4)_7$. In Figure 6,

heavy rounded inhomogeneous microinclusions of REE phosphate (florensite) and iron phosphate are located in a porous matrix of lazulite composition $\text{MgAl}_2[\text{PO}_4]_2(\text{OH})_2$.

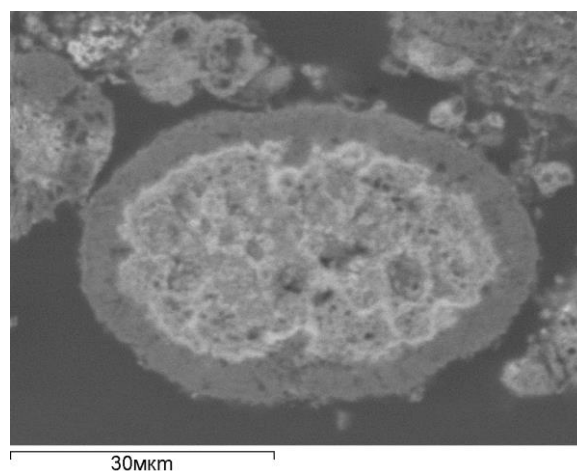


Figure 5 - Rounded formations of a thermal sample. *BEI*. The central part of rounded heavy formations (white) with a high content of REE, the shell with a lower content of REE is a lighter phase (gray)

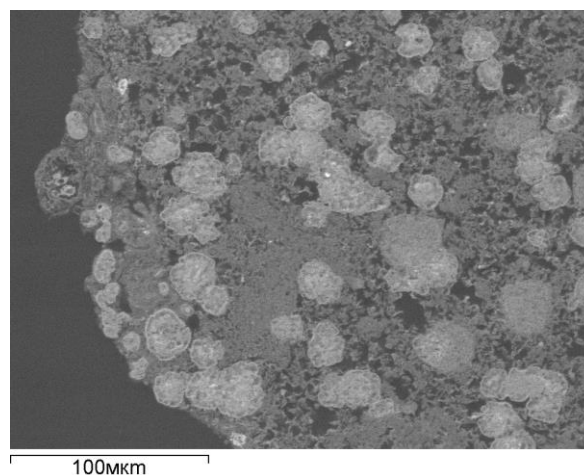


Figure 6 - Rounded inhomogeneous grains of REE-bearing inclusions (florensite) in a porous matrix of lazulite composition. Pores (black). *BEI*

The diffraction patterns of the three thermal products, as well as the bulk elemental composition, almost do not differ from each other (Table 5). According to X-ray phase analysis, the main phases in the heavy fraction of thermal products, considering the bulk elemental composition presumably can be: iron phosphates $\text{Fe}_2\text{Fe}(\text{P}_2\text{O}_7)_2$, rodolicoite $\text{Fe}(\text{PO}_4)$, phosphocyclite-(Fe) $\text{Fe}_2(\text{P}_4\text{O}_{12})$; REE-bearing phosphates $\text{Ce}(\text{P}_5\text{O}_{14})$, florensite-(Ce) $\text{Al}_3(\text{Ce}_{0.54}\text{La}_{0.27}\text{Nd}_{0.11}\text{Sm}_{0.04}\text{Ca}_{0.04})(\text{PO}_4)_2(\text{OH})_6$ and $\text{Ca}_8\text{MgSm}(\text{PO}_4)_7$, and iron oxides.

Table 5 – X-ray powder diffraction pattern for thermal products

Thermal tails		Thermal concentrate		Thermal initial		Phase
<i>l</i>	<i>d</i> _{изм.} , Å	<i>l</i>	<i>d</i> _{изм.} , Å	<i>l</i>	<i>d</i> _{изм.} , Å	
-	-	-	-	17.8	4.32	Fe ₂ Fe(P ₂ O ₇) ₂ , Rodolicoite Fe(PO ₄), phosphocyclite -(Fe) Fe ₂ (P ₄ O ₁₂), Ca ₈ MgSm(PO ₄)
53.2	4.14	45.9	4.14	53.9	4.13	Al(PO ₄), Ca ₈ MgSm(PO ₄), Al(PO ₄), Ca _{19.1} Mg _{1.56} Fe _{0.44} (PO ₄) ₁₄
-	-	15.1	3.69	-	-	Al(PO ₄)
17.0	3.46	28.6	3.45	15.3	3.45	Fe ₂ Fe(P ₂ O ₇) ₂ , Rodolicoite Fe(PO ₄), florencite -(Ce) Al ₃ (Ce,La,Nd,Sm,Ca)(PO ₄) ₂ (OH) ₆ , Ca ₈ MgSm(PO ₄),
-	-	28.4	3.35	-	-	Fe ₂ Fe(P ₂ O ₇) ₂ , florencite-(Ce) Al ₃ (Ce,La,Nd,Sm,Ca)(PO ₄) ₂ (OH) ₆ , Ca ₈ MgSm(PO ₄)
100.0	3.03	100.0	3.03	100.0	3.03	Fe ₂ Fe(P ₂ O ₇) ₂ , phosphocyclite-(Fe) Fe ₂ (P ₄ O ₁₂), calcite Ca(CO ₃), Ca ₈ MgSm(PO ₄), Ca _{19.1} Mg _{1.56} Fe _{0.44} (PO ₄) ₁₄
36.5	2.93	40.7	2.93	39.1	2.93	Fe ₂ Fe(P ₂ O ₇) ₂ , florencite-(Ce) Al ₃ (Ce,La,Nd,Sm,Ca)(PO ₄) ₂ (OH) ₆
34.8	2.86	40.6	2.86	28.2	2.85	Fe ₂ Fe(P ₂ O ₇) ₂ , Ca ₈ MgSm(PO ₄),
-	-	10.3	2.70	-	-	Fe ₂ Fe(P ₂ O ₇) ₂ , florencite-(Ce) Al ₃ (Ce,La,Nd,Sm,Ca)(PO ₄) ₂ (OH) ₆ , phosphocyclite-(Fe) Fe ₂ (P ₄ O ₁₂), Ca ₈ MgSm(PO ₄), hematite Fe _{1.987} O ₃
16.8	2.54	20.3	2.55	18.8	2.55	Fe ₂ Fe(P ₂ O ₇) ₂ , Al(PO ₄), Ca ₈ MgSm(PO ₄), hematite Fe _{1.987} O ₃ , Al(PO ₄), Ca _{19.1} Mg _{1.56} Fe _{0.44} (PO ₄) ₁₄
-	-	10.5	2.13	-	-	florencite-(Ce) Al ₃ (Ce,La,Nd,Sm,Ca)(PO ₄) ₂ (OH) ₆ , phosphocyclite-(Fe) Fe ₂ (P ₄ O ₁₂)

Research Discussions

The enrichment products from technogenic wastes are difficult objects for research, because are represented by heterogeneous micro-sized aggregates with nano-sized grains of various minerals and phases (Figure 2 b, 4). X-ray analysis in the case of nano-sized grains is uninformative, since such samples are X-ray amorphous. In an electron probe, even under a focused beam on nano-sized inhomogeneity, the bulk elemental composition of several nano-sized dispersed phases is obtained. The composition varies not only from grain to grain, but also from site to site in one grain. The identification of phases is hindered by a diverse set of elements, and the construction of correlations is hindered by their different number. So, it may turn out in practice that complex REE-bearing sulfo-phosphates and phosphate silicates are mixtures of nano-sized grains of sulfate (gypsum) with apatite and apatite with silicate, respectively, therefore, it is necessary

to return to the study of technogenic wastes every time to clarify the technology of their enrichment.

The authors of this study revealed fine gold and increased REE content in technogenic deposits of uranium-phosphate processing of CMMP deposits for the first time. According to earlier studies, gold and other noble metals are present in phosphate deposits in different regions of the world (Alaska, North Africa, East European platform, oth.) [[12], [13], [14], [15], [16]]. A tendency was established for selective concentration of gold in phosphorites, the genesis of which is associated with organic matter of bottom sediments, extracting these elements from sea or silt water [15]. Chinese colleagues noted the presence of platinum, silver and, less frequently, gold in phosphorites [12], with platinum being extracted for many years from phosphorite enrichment tailings. In this regard, of scientific interest is the obtainment of a formation of phosphorus-rare-earth with nanoscale gold from the coastal-marine and shelf zones of ancient Cretaceous-Paleogene deposits of Kazakhstan, as a new very promising source of gold and rare earths.

In the Mangistau region, the known uranium-phosphorite deposits Melovoye, Tomak, Taibor, and Tasmuryn, where technogenic deposits we have already studied, are the objects of the Mangistau scandium-rare-earth-phosphorus-uranium Oligocene mineral complex of the Caspian uranium-ore province. They are found in sedimentary deposits, organogenic clays saturated with fragments of bone and plant detritus, and sulphides. In addition to uranium, they contain rare earth, phosphorous, rhenium, and other elements. As the researchers note, all of them are unique, syndiagenetic, complex scandium-rare-earth-phosphorus-uranium, sorbobiogenic, associated with dark grey clay horizons, saturated with bone, mainly fish, detritus [[17], [18], [19], [20], [21]].

In view of the above, other areas in Kazakhstan, where similar marine phosphorite-bearing deposits of Cretaceous-Paleogene age are also developed, are of interest.

There are phosphorite deposits in the Aktobe Urals region and in the Mangyshlak Island, which belong to the Cretaceous Mangystau-Aktobe phosphorus terrigenous mineragenic complex (Shilisai, Alga, etc.) [[18], [19]]. The Cretaceous phosphorite-bearing sediments include sandy, calcareous clays, glauconitic-quartz sandstones, carbonaceous clays, siltstones, marls, chalks, partially cemented nodular-sandy phosphorites, quartz-glaucanitic sands, polymictic crossbedded sands impregnated with iron oxides with small iron peas, boulder-like sandy-limey concretions.

Phosphorite-bearing objects of Eocene age are common in East Aral, and are associated with the glauconite-terrigenous formation. The rocks contain isolated fragments of ostracod shells and sponge spicules. In thin sections, scraps of minute diatoms replaced by brown carbonaceous matter and phosphate are observed in the phosphate cement matter. In the Syr Darya region, Central Kyzylkum [19], the phosphorite-bearing sediments are represented by terrigenous carbonate formation. The granular phosphorites and phosphorite-bearing rocks are mainly composed of phosphatized organogenic material (phosphate biomorphoses, bones) and chemogenic formations, oolites.

The phosphorus-rich brown-iron objects of the Ayat iron-ore basin are of interest [22]. At the Ayat deposit, depressions of the Paleozoic basement contain Lower Cretaceous lake-marsh-type sediments: clays, sands, and sandstones with commercial deposits of bauxite and refractory clays, and above are Cretaceous and Tertiary marine

deposits represented by basal conglomerates, siderite sandstones, quartz and quartz-glaucanite sands, clays and loams with phosphorites and marine fauna.

During geological surveys in the eastern side of the Turgai Trough, geologists found [19] significant areas of Upper Cretaceous and Paleogene phosphoritic nodules close to the surface.

In Northern Kazakhstan, glauconite and phosphorite occurrences of the Cretaceous age are widespread in the Selety district [[19], [23], [24], [25]] (phosphorite and glauconite deposit of Selety, glauconite of Izobilnenskoye).

In the Upper Jurassic-Lower Cretaceous age soil-infiltration deposit of Semizbai the maximum uranium content is noted in clay horizons with a significant admixture of carbonized plant detritus [17].

Conclusions

The enrichment products from technogenic wastes of the Caspian Mining and Metallurgical Plant are difficult objects for research because are represented by heterogeneous micro-sized aggregates with nano-sized grains of various minerals and phases. With nanosized inhomogeneity, the result of electron probe microanalysis will be the bulk elemental composition of several nano-sized dispersed phases, which complicates their identification.

A technological sampling of enrichment products shows that "invisible" dispersed gold predominates in technogenic wastes. Native gold is revealed as single, micron-sized grains. The gold content in the initial material is 2.93 g/t, which increases to 6.37 g/t after sample thermal activation.

According to the data of electron probe microanalysis, REEs are mainly found in nano-sized fluorine and fluorine-free phosphates (in apatite, by substitution of calcium), and in REE phosphates (in xenotime and monazite). In thermal products, REEs are included in phosphates: florensite and phases $Ce(P_5O_{14})$, $Ca_8MgSm(PO_4)_7$.

Total sampling is proposed for gold of the Cretaceous-Paleogene phosphorus-bearing coastal-marine quartz-glaucanite and overlapping black Paleogene clays in Selety-Teniz area of Akmola region, Aktobe and Kostanay regions; of infiltration uranium deposits (Semizbai and others), etc. Besides REE, attention should be paid to scandium and rhenium. Sample processing should be carried out with mechanical and subsequent thermal activation

of sample material according to the flow chart developed by the authors of this study.

Conflict of interest. On behalf of all the authors, the correspondent author declares that there is no conflict of interest.

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Каспий тау-кен металлургиялық комбинатының техногендік шөгінділерінен өңделген өнімдердегі алтын және сирек жер элементтері (Ақтау, Қазақстан)

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ТҮЙІНДЕМЕ

Техногендік шөгінділердің макро- нано-өлшемді деңгейіне дейін өңделген өнімдерін кешенді зерттеу нәтижелері берілген. Өнімдер алдын ала механикалық және термиялық активтендіру арқылы алтын мен СЖЭ үшін зерттелетін үлгі материалды өңдеу және дайындау кезінде гравитациялық байыту әдістерінің әзірлемелерін пайдалану арқылы алынды. Нәтижесінде дара, микрон өлшемді түйіршіктер түріндегі таза алтын және байыту өнімдерін технологиялық сынауға сәйкес, «көзге көрінбейтін» майда дисперсиялық алтынның басымдығы анықталды. Алтынның мөлшері бастапқы материалда 2,93 г/т болса, ал үлгі термиялық белсендірілгеннен кейін 6,37 г/т дейін артады. Спектрлік талдау және электронды зондтық микроанализ нәтижелері бойынша байытудың барлық кезеңдерінің өнімдері итрий мен СЖЭ мөлшерлері жоғарылайды. СЖЭ пайда болу формалары анықталған. СЖЭ негізінен микрон және нано өлшемді фтор және фторсыз фосфаттарда (апатитте, кальцийді алмастыру арқылы), СЖЭ-фосфаттардың өзінде (ксенотимде) және сирек, мүмкін, күрделі сульфосфаттар мен фосфатты силикаттарда кездеседі. Рентгендік дифракциялық талдауға сәйкес элементтік құрамын ескере отырып наноөлшемді фазалардың біртекті емес агрегаттарынан тұратын термиялық өнімдерде, СЖЭ фосфаттарға кіреді: олар флоренсит және $\text{Ce}(\text{P}_5\text{O}_{14})$, $\text{Ca}_8\text{MgSm}(\text{PO}_4)_7$ фазалары.

Түйін сөздер: алтын, СЖЭ, микро- және наноөлшемді түйірлер, техногендік шөгінділер, Каспий кен-металлургиялық комбинаты, Қазақстан

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Золото и редкоземельные элементы в продуктах переработки из техногенных отложений Прикаспийского Горно-Металлургического Комбината (г. Актау, Казахстан)

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<p>Поступила: 10 марта 2023 Рецензирование: 7 апреля 2023 Принята в печать: 28 апреля 2023</p>	<p>АННОТАЦИЯ</p> <p>Изложены результаты комплексного изучения от макро- до наноразмерного уровня продуктов переработки из техногенных отложений. Продукты получены благодаря использованию наработок по гравитационным методам обогащения в обработке и подготовке исследуемого материала проб на золото и РЗЭ с предварительной их механической и термической активацией. Выявлено: самородное золото в виде единичных, микронной размерности, зерен и, по данным технологического опробования продуктов обогащения, преобладание «невидимого» тонкодисперсного. Содержание золота в исходном материале составляет 2,93 г/т, которое после термоактивации пробы увеличивается до 6,37 г/т. По результатам спектрального анализа и электроннозондового микроанализа для продуктов всех стадий обогащения характерно повышенное содержание иттрия и РЗЭ. Определены формы вхождения РЗЭ. РЗЭ, в основном, находятся в микро- и наноразмерных фтористых и бесфтористых фосфатах (в апатите, путем замещения кальция), в собственно РЗЭ-фосфатах (в ксенотиме) и реже, возможно, сложных сульфософосфатах и фосфатсиликатах. В термопродуктах, состоящих из неоднородных агрегатов наноразмерных фаз, по данным рентгенофазового анализа с учетом элементного состава, РЗЭ входят в состав фосфатов: флоренсита и фаз $Ce(P_5O_{14})$, $Ca_8MgSm(PO_4)_7$.</p> <p>Ключевые слова: золото, РЗЭ, микро- и наноразмерные частицы, техногенные отложения, Прикаспийский горно-металлургический комбинат, Казахстан.</p>
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