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INDUSTRIAL WASTE OF CHEMICAL - METALLURGICAL INDUSTRIES CONTAINING RARE AND RARE EARTH METALS: METHODS FOR OBTAINING PRIMARY CONCENTRATES

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The monograph presents methods of processing technogenic waste to extract rare and rare-earth metals from them, forms of processing vanadium catalysts, procedures for obtaining concentrates of rare and rare-earth metals from various environ. Although the technology of securing metal concentrates makes it possible to increase the extraction of industrially important metals into primary productive materials, topical issues on the disposal of industrial waste are also partially considered.

The monograph is intended for engineering workers, technical and scientific workers engaged in the theory and practice of metallurgy and geoecology processes, processing of technogenic waste, and can also be used by students, master's students, and doctoral students of technical universities in the specialties: geoecology, metallurgy and chemical technology.

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DEFINITIONS, DESIGNATIONS AND ABBREVIATIONS

Leaching is a complex heterogeneous process of interaction of liquid reagents with a solid substance-ore.

Underground leaching is a technology based on the forced injection of aqueous solutions of inorganic compounds (sulfuric acid, etc.) into underground horizons, followed by pumping out a solution containing valuable elements for further processing.

Pulp is a heterogeneous mixture of water and solid mineral or technogenic particles.

The degree of conversion is the ratio of the amount of converted raw materials to the amount of introduced raw materials.

The product yield is the ratio of the amount of the product obtained to the amount calculated by stoichiometry.

REE – rare-earth elements
TPS – thermal power stations
AMD – analytical methods of determination
SLF – Shymkent lead factory
MPW – mining and preparatory work of a productive solution
ICPMSM – Inductively coupled plasma mass separation method
UL – underground leaching
DRS– dynamic reaction system
ETA – electrothermal atomization
LA – laser ablation
PS– productive solutions
RS – returnable solutions
HLP – hydraulic laboratory press
CP – chemically pure
SPE – solid-phase extraction
SPME – solid-phase matrix extraction
PFA –Perfluoroalkoxy Polymer
CIS – Commonwealth of Independent States
FDEC – full dynamic exchange capacity

INTRODUCTION

The mineral resource base for the production of rare refractory metals and rare-earth elements in Kazakhstan is large enough to create on its basis a mining and processing industry capable of meeting the domestic and export needs of new branches of technology.

The share of rare metal products in the global production of modern equipment is increasing. For example, a large proportion of rare, scattered, rare-earth, refractory metals are used as magnets, contacts, catalysts for complete fuel combustion, etc. For example, in the automotive industry, electrical engineering, and other modern high-tech industries.

The rare-metal chemical industry uses metals that are the basis of structural materials (radio electronics, europium for highly efficient absorbing elements, gadolinium, and erbium for the production of uranium-gadolinium uranium-erbium fuels). In addition, some elements accompany uranium and thorium in the processing of ores (rhenium, scandium) and are included in the technological chain of processing raw materials and obtaining nuclear-clean materials. The industry's demand for nonferrous, rare, and rare earth metals is constantly increasing since their use largely determines the development of Kazakhstan's strategic, scientific, and technical base. However, the use of known methods for obtaining these metals from traditional sources of raw materials does not fully meet the ever-increasing volumes of their use. Therefore, the task of developing new effective methods for extracting rare and rare-earth metals from unconventional sources of raw materials and technogenic low-concentration waste from metallurgical and chemical industries is urgent.

The chemical industry's complex (multicomponent) ores and technogenic wastes containing rare and rare-earth metals are characterized by complex material composition. The possibility of industrial development of such ores depends not only on the quantitative content of valuable components in the ores but also on the technological methods of extracting valuable components during mining, processing, and metallurgical processing of ore raw materials. The material composition of ores and the possibility of their industrial development are found in testing and laboratory research.

At the current level and scale of consumption of natural raw materials, the importance of full use and involvement of secondary material resources in social production is of paramount importance. The role of this factor is especially great when assessing the economic efficiency of the national economy in its various sectors, including industrial waste, agriculture, and substandard natural minerals.

Technogenic waste from chemical and metallurgical industries is a valuable raw material for extracting rare and dispersed metals. Although rare metals are becoming popular today, they are contained in various ores, where their share is very small, in tenths, hundredths, sometimes in thousandths of a percent. Therefore, their extraction can be profitable only in combination with base metals. This is now also an important area for researchers. Japan is the leader among importers of rare-earth and rare metals. But in China, where 95% of rare earth metals are supplied to world markets, its industry for consuming such products has begun to develop intensively, which is why exports are declining. Therefore, importing countries are showing interest in other producers, including Kazakhstan, to meet their needs. The Program of industrial-innovative development of the country notes the development and increase in the complexity of the use of raw materials. The task is set to extract all associated metals in the processing process. Therefore, the complexity of using raw materials and increasing the level of extraction becomes highly important.

The problem of waste disposal is acute all over the world. The protection of the environment from industrial waste pollution is the most urgent problem of our time, the solution of which is being paid more and more attention every year, not only in our country but also abroad. These problems are particularly acute at phosphorus production enterprises and in the nuclear industry.

A large amount of technogenic waste creates technical and environmental problems of their disposal and neutralization, leading to significant environmental loads due to the emission of pollutants.

The management of technogenic waste includes the following stages of movement: formation, collection, temporary storage, transportation, processing, neutralization, and burial of non-recyclable residues. Each stage of waste management has a positive or negative impact on the entire waste management system, depending on the effectiveness of the decisions taken. The management of technogenic waste is mainly reduced to the organization of their collection, transportation, and disposal. The resulting technogenic waste is stored in landfills, many of which do not meet the requirements of environmental and sanitary safety. This waste disposal practice leads to long-term environmental pollution, comparable in the degree of danger to radiation pollution. Since waste is a potential secondary material resource, the current system of technogenic waste disposal leads to the irretrievable loss of valuable secondary material resources, energy, and land resources. It should be taken into account that the probability of violations in the engineering protection system increases over time, which is not designed for operation for ten years, and, therefore, cannot guarantee the environmental safety of such facilities in the long-term aspect.

Therefore, a promising method of environmental protection is the processing of technogenic waste with their further use in various industries.

To extract rare and rare-earth metals, it is necessary to develop technologies for converting these metals into primary productive materials containing such concentrations of these elements for their industrial and economically profitable production to increase the percentage of direct extraction into finished products. For this purpose, research has always been aimed at finding inexpensive, affordable, and sufficiently effective oxidizing agents that can significantly increase the extraction of metals. One of these oxidizing agents that meet the specified requirements is a manganese dioxide concentrate or a rich manganese ore. Earlier, we developed and implemented at the Shymkent Lead Factory the technology of hydrometallurgical processing of lead production dust (waste of the main processing) using manganese ore from the Zhairem deposit, which allowed increasing the extraction of such rare and dispersed metals contained in them as rhenium, cadmium, and thallium. cadmium up to 95%, rhenium up to 97%, thallium up to 94%.

Thus, research in the field of the use of manganese ore as an oxidizer in the processing of technogenic waste from chemical and metallurgical industries for the extraction of rare and rare-earth metals from them, allowing the use of environmentally safe and effective technologies, is relevant and requires further research.

For future engineer specialists in the rare and rare metal industry, a certain minimum of knowledge in the methods of obtaining these elements is necessary. This monograph presents the number of works on the selective extraction of rare and rare-earth metals from various raw materials, the content of the works is divided into three stages: physical and chemical preparation of raw materials, opening and extraction of rare metals into a technological solution, extraction of rare and rare earth metals from their technological solutions into primary mischmetals.

The content of the monograph presents laboratory methods for studying the material composition of complex ores and technogenic wastes that are a source of rare and rare-earth metals. The monograph describes the main industrial and genetic types of the metallurgical industry's most characteristic complex ores and technogenic waste. The manual describes the basic principles of ore testing and describes laboratory research methods that determine the chemical and mineralogical composition of ores and their technological qualities. The main methods of research of rare metal and polymetallic materials are described. The study of the material composition of ores allows to determine the technological qualities of the ore and give an industrial assessment of complex ores.

During the laboratory research work, they were guided by the developed technologies for extracting rare and rare-earth metals, novice employees of the engineering and technical profile and students of technical specialties will get acquainted with the modern level of technology in solving specific problems. For example, when studying the chemical composition of raw materials of rare and rare-earth metals, it is proposed to study the principles of operation and hardware design of modern devices such as mass spectrometer with inductively coupled plasma VARIAN-820MS, scanning electron microscope JSM-6490LV, bi-beam scanning spectrophotometer Cary-50 Scan. The implementation of the work will allow novice employees of the engineering and technical profile and students of technical specialties to get acquainted with the technical problems and tasks of hydrometallurgy at the current stage of the development of the chemical industry.

1 THE CURRENT STATE OF THE RARE-METAL AND RARE-EARTH INDUSTRY, TYPES OF PROCESSED RAW MATERIALS IN KAZAKHSTAN

The economic well-being of the Republic of Kazakhstan is determined by the level of development of the mining industry. The development of scientific, technical, and technological developments in the field of rare-metal and rare-earth products will allow the country to take a leading position in the world market of rare metal products. Such an advantage can be preserved only in the conditions of a state monopoly on production, processing of raw materials into products of increased added value according to special state programs, expansion and increase in the production of rare-metals of high purity will allow organizing the production of high-availability industrial and technical products based on them.

There are a number of enterprises capable of processing rare-metal and rare-earth raw materials on the territory of Kazakhstan (Table 1).

Table 1 – Enterprises producing rare and rare earth metals and their compounds

Enterprise name	Main and by-products
LLP «Irtyshskaya redkozemel’naya company» (former IHMZ), Pervomaika village, East Kazakhstan region	REM of light and medium groups and products based on them. Concentrates of REM oxides, ligatures, mischmetal
Ulbinsky metallurgical factory (UMF) Ust-Kamenogorsk	Uranium products, metal beryllium, powder, beryllium-based alloys, metal tantalum, rods, sheets, and discs. Beryllium oxide products
Stepnogorsk Mining and Chemical Combine, Stepnogorsk	Uranium products, molybdenum products
Ust-Kamenogorsk titanium-magnesium combine	Titanium spongy (99.74%), magnesium (99.9%). Crystalline scandium (99.65-99.85%), scandium oxide (99-99.9%), vanadium oxide (98.6-99.95%)
LLP «Firma Balausa»	Ammonium metavanadate (73.5-75.0%)

From the beginning of the 20th century, rare metals began to acquire ever-increasing importance. Now it isn't easy to name a field of new technology that would not use rare metals, their alloys, or compounds to one degree or another. Electronics, nuclear energy, electrical engineering, space and rocket technology, superconductors, fiber-optic communications, special steels, mechanical engineering, instrument making, chemical, medical and food industries are continuously expanding the range of used rare-metals and increasing requirements for their purity. Moreover, there is an increase in the consumption of rare and rare-earth metals of high purity and quality all over the world. Tables 2 and 3 show the production and consumption volumes of rare earth products in Russia and the USA, and some imported rare earth products from the USA.

Table 2 - Volumes of production and consumption of rare and rare earth metals in Russia and the USA

Metals	Russia		USA
	Production, ton.	Consumption, ton.	Consumption, ton.
Zirconium	4000	5000-6000	55000
Niobium	800	500-600	3800
Tantalum	80	35	500
Beryllium	30	40	350
Lithium	300	300	1600
Germanium	0.5	0.5	25
Genius	<0,5	1,3	25
Cerium	-	1300	4000
Lanthanum	-	100	2000
Neodymium	-	120	800
Samaria	10	1	100
Europium	2	3	10-15
Mischmetal	2000	500	20000

Table 3-Imported rare-earth products of the USA *(ton)*

Product Name	Year				
	1999	2000	2001	2002	2003
Rare-earth metals, alloys	1780	2470	1420	1450	1130
Cerium	3990	4310	3850	2540	2630
Mixed rare earths products	5980	2190	2040	1040	2150
Rare earth, chlorides	1530	1330	2590	1800	1890
Rare earth oxides	7760	11200	9150	7260	10900
Ferrocerium, alloys	120	118	118	89	111

Many developments for the production of rare and rare-earth metals are represented by the subdivisions of the RSE "NC CPMS RK" and its subsidiaries. VNIItsvetmet, for example, proposed technology for using wastes from mining, metallurgical, and energy production as a mortgage material in mine workings. The stowing complexes built according to the technology of the institute have shown high efficiency. There are proven technologies for the production of lead salts from oxidized industrial middlings containing lead. Today it is possible to recycle waste of titanium-magnesium output successfully. Technology for polymer compositions and the manufacture of products from them with improved properties that are stable in an aggressive environment has been developed and tested at a pilot plant at the Karaganda factory "Stroyplastica". In this case, microspheres released from the thermal power plant ash are used as a reinforcing filler. A pilot batch of pipes with a diameter of 110 mm has already been produced from this material and successfully tested in zinc production.

When coal is mined, a large amount of fine mass is formed, the so-called rubble. It is especially abundant (25-30 percent) in the extraction of brown coal. This screening is carried by the wind, polluting the atmosphere and the earth's surface. Concerning the Kiyaly brown coal deposit, there are several technologies for using such waste. One of them is briquetting. The production of briquettes is widely used all over the world. This fuel is superior to coal in calorific value, mechanical and thermal strength. And the fine coal of the Kiyaly deposit can also be subjected to hydro generation to produce motor fuel and biological growth stimulants from it.

Until a particular time, we used the ores of the Lisakovskoye deposit in blast-furnace production. The cast iron produced from them contained phosphorus, and when it was split along with steel, a phosphate slag was obtained. And this is a valuable fertilizer for agriculture. Millions of tons of such slag have accumulated in the dumps of the Karmetkombinat. Fertilizers can be obtained from it, which are cheaper and more effective than superphosphate.

The «Kazzhol» research laboratory has developed a hydrosilicate marking paint, the filler of which is granular phosphorus slag. This paint is indispensable for marking the road surface, painting bridges, overpasses, roadside office buildings, and structures. Compared to paints based on polyester resins, it lasts 2-3 times longer and is 7-8 times cheaper. In the same laboratory, they have the secret of improving asphalt concrete's physical and mechanical properties. It's very simple. It is necessary to add polymer waste during its production, which is obtained during the sorting of solid household waste.

Analysis of the state of storage facilities for mining waste for their utilization and further reclamation made it possible to establish the following main factors that determine the choice of technical solutions and methods of technical and biological restoration of disturbed areas: mining-geological, mining - technical and environmental.

Mining and geological factors (or signs) of accumulated mining waste determine, first of all, the age of the dumps, their capacity, physical and mechanical properties of the constituent rocks, and the chemical composition.

The age factor of accumulated waste determines the degree of compaction of the deposited material and significantly affects the choice of the reclamation method. In relatively young (up to 15 years old) dumps, the compaction and sedimentation processes have not yet been completed, and this circumstance should be taken into account when choosing equipment. In dumps and storage facilities of older age (from 15 to 30 years), the compaction of soil and sediment has already been completed, and, in addition, the destruction of the composting material has largely occurred, which is also important when choosing methods and means of reclamation work.

The material composition of waste accumulators characterizes, firstly, the degree of its usefulness from the point of view of further development for the extraction of useful components available there, and, secondly, it establishes the physicomechanical properties of rocks, such as hardness, porosity, strength, stability, and others. The latter is necessary to calculate the operating modes and productivity of mining equipment, to determine the condition and behavior of rocks in various production processes.

The capacity of dumps varies vary widely and depends on the volume of extracted reserves and the stripping coefficient of the corresponding natural deposits. In the ferrous metallurgy, the most common dumps with a capacity of 1 million to 10 million tons (39.5% of the total number of dumps), dumps with a capacity of up to 1 million tons make up 23.3% and with a capacity of 10 million tons and above (up to 200 million tons) - 36.2%.

The volumetric weight of rocks in the accumulated waste also varies in a very wide range: from 1.4 to 2.0 t/m in loose rocks; from 2.4 to 2.7 t/m in semi-rock; from 2.7 to 3.2 t/m^3 in rocks. Internal friction angle ranges from 15° to 35°.

In the analysis, the mining technical factors included:

- conditions for the formation of dumps (dumping technologies);
- the size and shape of objects;
- granulometric composition of accumulated technogenic raw materials.

Waste from mining and metallurgical production (dumps, tailing dumps, etc.) is generated using a plow, bulldozer, excavator, conveyor dumping, as well as using hydraulic flooding. In the land allotment of mining enterprises of Kazakhstan, the share of dumps accounts for 20-25%, the share of tailings - from 30 to 35%.

In terms of height, bulk (dry) dumps are subdivided into low (up to 20 m), medium (20-50 m) and high (over 50 m). The number of dumps with a height of up to 20 m is 60% in ferrous metallurgy (78.7% in nonferrous metallurgy) relative to the total amount; with a height of dumps from 20 to 50 m in ferrous metallurgy - 24.1% (in nonferrous - 20.1%) and with a height> 50 m - 15.9% in ferrous metallurgy (1.2% - in nonferrous metallurgy). There are both single-deck and multi-deck dumps.

Forms of taps for dumps - rectangular, square, round, ellipse.

The fractional composition of rocks varies widely. So, on dumps of overburden and off-balance ores, it ranges from 0.1 to 2000 mm. At tailing dumps from 0.01 to 70 mm, at slag dumps - from 2-5 mm to 2000 mm.

The parameters of the dumps - the volume, height, shape of the base - have an impact on the intensity of soil disturbance, the timing of reclamation, technical and economic indicators of reclamation work, etc.

The height of the dump affects not only the efficiency of stripping and the intensity of disturbance of the natural environment, but also the cost and labor intensity of the processes of technical mining reclamation: with an increase in the height of the dump, the costs of utilizing black earth decrease, but at the same time, the costs of flattening the slopes increase.

There is a strict relationship between the height of the dump, its volume, and the area of alienated land. Based on these relationships, according to the developed formulas, the parameters and shapes of dumps were calculated and recommended when they were located on highly efficient agricultural lands [1]. In the case of dumps on lands unsuitable for agricultural use, the choice of their parameters is carried out according to other criteria - a minimum of costs for transport and dumping work.

The group of environmental factors includes:

- the area of land seized for accumulated waste;
- the level of dust formation and effluents from technogenic objects;
- economic damage from environmental pollution, disturbance, and seizure of land.

The impact of accumulated waste on the natural environment (OPS) is expressed in the violation of the natural landscape of the territory, pollution and a decrease in the productivity of nearby lands (soils), withdrawal from the economical turnover of lands.

The land area for accumulators of the type of overburden volumes in nonferrous and ferrous metallurgy is 13184 hectares, for the type of tailing dumps - 8880 hectares, and for the type of sludge storage - 1000 hectares.

The specific land capacity (the size of the area in hectares per 1 million tons of waste reserves) varies within a very wide range from 0.001 to 10 hectares / thousand m.

One of the main factors of the harmful effect of waste accumulators on OPS is dust emissions from the surface of dumps and tailing dumps. Therefore, based on the determination of the values of dust emissions from the surface of waste and waste storage ponds, it is possible to distinguish the zones of distribution of air pollution and groundwater flows and determine the economic damage caused by the OPS.

Air currents carry Dust-like pollution from various sources from one layer of the atmosphere to another (from the troposphere to the stratosphere). The average duration of non-settling dust (light) stays about 2 years in the stratosphere, 1-4 months in the upper troposphere, and 6-10 days in the lower troposphere.

1.1 Analysis of the state of technogenic formations and their impact on the environment

On the territory of the Republic of Kazakhstan, a huge number of technogenic mineral formations of mining enterprises have been accumulated, represented by all the characterized types of primary natural rocks. Their intensification development has acquired paramount economic and economic importance, since the stock; a number of existing mines are approaching depletion, and newly explored deposits, especially in the copper industry, are either very far from the processing enterprises, or are represented by poor ores, for the profitable development of which it is necessary to construct powerful mining and processing complexes with very large capital investments with long payback periods.

A significant part of the industrial raw materials accounted for by geological exploration falls into the dumps of mining rocks, which is inevitable in large-scale opencast mining and high-performance underground mining systems using massive explosions and powerful mining equipment. The projects of mining enterprises envisage such technological losses, they are planned, accounted for, and amount to from 10-15% of proven reserves in deposits of a simple geological structure to 30-50% in deposits (areas) of a complex structure.

When enriching ores into concentrates 75-85% of the main and 50-80% of the accompanying metals are recovered, included in the supplied ores, the rest of them is lost and stored in tailings. During metallurgical redistribution, the extraction of base metals from concentrates B rough products is 80-95%, the rest are lost and stored in dumps. Accompanying metals, close in physicochemical properties and mineralogically related to the base metals (gold, silver, bismuth), are extracted into their crude products by subsequent release in electrorefining sludge, rare metals (scandium, tellurium, cadmium, germanium and others) are sublimated with waste gases and are captured in dusts and cakes of sulfuric acid production. The recovery and losses in the slags of the first of them are close to the recovery and losses of base metals, the recovery of the second is 30-60%, the rest evaporates with the exhaust gases. As a result of the listed losses in the technogenic mineral formations of the activities of mining and processing enterprises - dumps of mining rocks, tailings, metallurgical processing slags - so many under-extracted valuable components accumulate that their amount is commensurate with the reserves of natural mineral deposits.

In many cases, they can be of great interest for processing. They must be considered in the balance of mineral raw materials and are estimated by geological exploration as technogenic deposits of minerals. An important reserve for increasing the efficiency of the sale of natural mineral resources is the intensification of the use of technogenic mineral formations in mining. In connection with the reorientation of the investment policy (a sharp reduction in funds for the construction of new mining enterprises), the problem of processing technogenic mineral resources becomes especially urgent. It should also be taken into account that at a number of nonferrous metallurgy enterprises in Kazakhstan, reserves of high-quality ores are decreasing, mining and geological conditions for developing deposits are deteriorating, capacities at concentrating plants and metallurgical plants are partially vacated. Under these conditions, the involvement in the processing of stored technogenic mineral formations of 30-50 years ago with a high content of useful components will allow, with moderate capital investments, to significantly increase production efficiency.

The mining enterprises of the Republic of Kazakhstan as of 01.01.2004 accumulated over 17572704.7 thousand tons of technogenic mineral formations, of which: -

- 14783656.7 thousand tons - dumps of overburden, preparatory and mining operations;
- 39584.5 thousand tons - off-balance ore dumps;
- 218553.7 thousand tons - tailings of concentration plants;
- 234 692 thousand tons - metallurgical processing slags.

The areas occupied by storages and storage facilities of technogenic mineral resources amount to 2,435.43 hectares, of which:

- mining dumps occupy 12933 hectares of area;
- dumps of off-balance ores - 681 hectares;
- dressing tailings - 7820.10 ha;
- slag dumps of metallurgical processing - 1000 hectares.

A large specific weight distinguished the quantitative indicators of technogenic mineral formations in nonferrous metallurgy of Kazakhstan, and in them, the rocks of overburden and mining operations amounted to 71.2%, tailings - 22.6%, and metallurgical redistribution slags - 6.2%.

In the full cycle of mining production, dumps of mining operations make up 72.5%, ore dressing tailings - 25.7% and metallurgical redistribution slags - 1.8%.

Technogenic mineral sources of raw materials differ in a wide range of characteristics: in terms of density, size of pieces, strength, physical and mechanical properties, mineralogical, petrographic and chemical composition, content. A wide range of qualitative composition of technogenic mineral formations determines various directions of their use, and their large volume is a real source of raw materials for additional extraction of valuable associated components - nonferrous and noble metals, rare and trace elements, sulfur and barite. The nonmetallic part of technogenic mineral formations (feldspar, mica, kaolin, sericite, quartz, dolomite and tuff) can be used in the glass and ceramic industries production of building materials (bricks, slag blocks, cement and lime). Waste rocks are partially used for filling gaps, cavities in mine workings, preparing backfill mixtures, sand and crushed stone, are used in road construction and can be used much more fully. In the future, using modern computing technology and computers, it is necessary to purposefully manage the formation of dumps of off-balance ores, metal-containing overburden and enclosing rocks and plan the effective use of dump formations in industry and, first of all, additional extraction of valuable accompanying components by geotechnical methods.

The content of useful components in the tailings of concentration plants is characterized only by their volumes without the spatial distribution of metals in the tailings. Therefore, the least reliable information is about the quality of dumps of mining operations. Due to the joint storage of rocks of different composition and physical and mechanical properties, their mixing with clay material during long-term storage, oxidation and leaching by atmospheric agents, their initial qualities undergo significant changes.

At the gold mining enterprises of Kazakhstan, out of the total amount of accumulated techno-genic mineral formations, 86.1% were dumps of rocks from mining and overburden works, tailings of concentration production - 13.9%. The areas occupied by the dumps of technogenic mineral formations for the production of noble metals amounted to 1170.61 hectares. The dumps of mining rocks occupy 664.06 hectares of area, the tailings of enrichment factories - 506.55 hectares.

In the gold and rare metal industries, the volumes of technogenic mineral formations are many times lower than the volumes of formed manufactured resources in nonferrous and ferrous metallurgy enterprises but differ in relatively higher contents under-extracted basic and accompanying valuable components.

At the largest mining enterprises of rare metals, 86.2% of the accumulated man-made mineral formations were rocks of overburden, preparatory and mining operations; ore dressing tailings amounted to 13.8% (JSC Belogorsk Mining and Processing Plant - 8.06%, JSC Akshatau Ken Bayytu Combines "- 4.1%, Kairaktinsky Mining and Metallurgical Combine - 0.67%). Dumps of technogenic mineral formations of rare metal enterprises occupy 662.3 hectares of area, of which 541.15 hectares are allotted to heaps of overburden and ore-bearing rocks, tailing dumps of tailings of processing plants occupy 121.15 hectares.

The features of man-made deposits are: 1) location in industrially developed areas; 2) the deposits are on the surface, and the material in them is mainly fragmented; 3) the number of artificial mineral forms that are formed in technogenic deposits exceeds 30,000, which significantly exceeds the number of currently known natural minerals, which is about 3300.

Like natural mineral deposits, technogenic deposits have a certain distribution structure of useful components, zones of secondary enrichment, oxidation, but unlike them, they are usually characterized by low contents of useful components.

More than 20 billion tons of solid industrial wastes have been accumulated in Kazakhstan, which are annually replenished at dumps by another 1 billion tons. Most of this waste (58%) is waste from ferrous and nonferrous metallurgy.

Ferrous metallurgy is represented by iron ore, chromium ore and manganese ore industries, which are represented by 5 mining and processing and 3 metallurgical enterprises. The total amount of accumulated solid waste is more than 6 billion tons. At the same time, mining waste - 92.8%, enrichment - 6%, metallurgical processing - 1.2%. The area occupied by waste is more than 15 thousand hectares. The distribution of waste by subsector is as follows: iron ore - 84.3%, chrome ore - 11.2%, manganese ore - 4.5%.

Thus, in terms of the annual output of mining waste, the "leading" place is occupied by iron ore enterprises. They account for 53.8 million m of rocks per year, or 79.9% of the total annual output of mining waste.

At nonferrous metallurgy enterprises, the total amount of solid waste from mining, enrichment, and metallurgical processing is about 5 billion tons, and they occupy land areas of more than 13 thousand hectares. The largest amount of waste is represented by rocks of associated mining and overburden - 72%, enrichment waste is 26.4% and metallurgical waste is 1.6%.

In many ore regions, technogenic deposits are quite widespread, represented by crushed rocks and poor ores. Dump masses are used for construction purposes, laying of worked-out space in underground workings, reclamation. However, quite often, such dumps also end up with useful components that were not of industrial interest during the development, such as barite during the processing of polymetallic ores at Salair. In many cases, processing technogenic raw materials requires other technologies than natural ores, most often new methods based on the latest achievements of science and technology.

The waste of the concentration of ferrous and nonferrous metals is more promising in terms of the content and reserves of useful components compared to the dump deposits of mining enterprises. Tailings are waste of mineral processing, in which the content of the valuable component is naturally lower than in the feedstock, since waste rock particles dominate them. The solid phase of the tail slurry is represented by a mixture of mineral particles of different sizes - from 3 mm to fractions of a micron. The composition of the particles and their density depend on the mineral composition of the rocks containing the mineral. In the production of copper, zinc and pyrite concentrate, 5-7 million tons of tailings are generated annually, which contain 0.3-0.4% zinc, 0.2-0.3% copper, 20-35% sulfur, more than 35% iron. A significant area (260 hectares) is occupied, for example, by the Cheremshanskoye sludge storage facility of the Vysokogorsky GOK, which contains about 40 million tons of iron ore dressing wastes.

Waste enrichment is more convenient for disposal than dumps, because, firstly, they are more homogeneous, and secondly, they are already crushed, sometimes fractionated material. The most promising use in construction was the waste generated by dry enrichment methods - tailings of dry magnetic separation and dry gravity.

Dry magnetic separation tailings are characterized by increased coarseness (20-70 mm) and reduced metal content. After preliminary preparation (sieving), they are completely used as crushed stone. Wet magnetic separation tailings are fine waste. They contain many valuable metals, including scandium, gallium, strontium, titanium. At the same time, the amount of scandium in waste exceeds 100,000 tons - this is more than 60% of the world's metal reserves.

They are in no way inferior in terms of the set and quantity of valuable components of the tailing dumps of concentrating factories processing nonferrous metal ores.

Their involvement in development is facilitated by the fact that stripping and drilling and blasting operations are not required. Instead, the crushed material is prepared for the extraction of metals by modern methods, in particular by acid leaching.

The reserves of metals in the waste of metallurgical production, mainly in slags, are also significant. Slag is a solidified metallurgical melt that covers the surface of the liquid metal. Slag is formed when waste rock, fluxes, etc. are melted. It is a valuable secondary raw material and is widely used in construction. For example, granular slags are used to obtain slag Portland cement, as aggregate for concrete, in road construction; from slag melts produce mineral wool, slag pumice, slag casting.

The development of technogenic deposits, represented by dumps of metallurgical production, is associated with certain difficulties due to the complexity of the composition of the slags and often significant heterogeneity of the dumps, especially those that accumulate during the electrometallurgical production of ferroalloys.

The second group of technogenic deposits accumulates nonferrous metallurgy slags, which enter the dumps after preliminary granulation or in a hot state. Converter copper smelting slag contains up to 70% FeO with relatively small amounts of silica. Its mineral base is fayalite (2FeO * SiO2). In contrast, minor minerals are zinc-bearing magnetite, cuprite (Cu2O), tenorite (CuO), copper, and iron sulfides. Glass and metallic copper are also present in small amounts in the slags.

Ash dumps of thermal power plants occupy a special place. Ash - a solid residue formed during fuel combustion (coal, oil shale, peat), consists of a fine powder, the so-called fly ash, and slag-fused lump material.

Slag is used in construction, fly ash is mainly stored in wet ash dumps and is only partially used in the cement industry as raw materials and additives, in the production of building ceramics, asphalt concrete, roasted and non-fired gravel.

Kazakhstan is just beginning to develop technologies for the industrial development of technogenic deposits.

1.2 A brief analytical review on technologies for the extraction of rare and rare-earth metals from technogenic wastes of the chemical and metallurgical industries

The country has accumulated over 20 billion tons of solid dumps of nonferrous and ferrous metallurgy, heat power engineering, phosphorus and other industries. They need to be used. This is dictated not only by considerations of environmental safety. There are fewer and fewer rich and easy-dressing ores. We have to involve the poor and hard-to-mine in production, to climb after them into deep quarries and mines at a time when huge deposits of artificial origin are located near the enterprises on the surface of the earth, many of which contain a valuable component more than natural ore, and have a positive market value.

Mining production leaves behind heaps of crushed rocks containing ores, poor ores that are economically unprofitable to process, as well as the products of processing industrial ores - enrichment wastes.

This group of technogenic deposits includes waste heaps of coal mines and open-pit mines; dumps of mines and open pits of sulphide ores of nonferrous metals; dumps of mines and open pits of oxide and silicate ores of ferrous and alloying metals; sludge and tailing dumps of ore-dressing factories (experts call ore dressing waste tailings).

Technogenic deposits have a complex structure, represented by dumps of energy and metallurgical production, which consist of slags, sludge, dust, ash, metals and their alloys used in the metallurgy of refractory materials.

Technological methods used in the rare metals industry have a number of features associated with the nature of the starting material and the requirements for the quality of the finished product. These features include a low concentration of rare metals in industrial waste, the complexity of their composition, the chemical resistance of most rare metal minerals and very high requirements for the purity of the final product. Therefore, the technology for the production of pure and high-purity rare metals from technogenic raw materials always has a multistage nature and usually consists of the following main stages:

1) waste enrichment;
2) decomposition (opening) of concentrates;
3) obtaining pure chemical compounds of the mono element;
4) their restoration to metal;
5) metal refining;
6) obtaining compact ingots of metals and alloys and products from them.

Usually, when obtaining pure compounds of one metal, the greatest difficulties are caused by purification from analogous metals, for example, zirconium-hafnium, niobium-tantalum, rare earth metals. For the separation of these metals and their effective reduction, physicochemical methods are used, including fractional crystallization and sedimentation, distillation and sublimation, ion transfer, chromatographic method, liquid extraction, and zone recrystallization. In ion exchange technology concerning the separation of rare earth elements, the greatest success has been achieved.

The profitability of the production of rare-metal and rare-earth metals, like many others, its competitiveness with other manufacturers determine the feasibility of creating an enterprise in real conditions.

Rare earth metals

The known methods of waste disposal containing rare and rare-earth metals are mostly insufficiently effective. Therefore, the development of effective methods for the disposal of such wastes, taking into account the specificity of the processed material and possible ways to intensify the processes, remains an urgent task.

Low concentrations of rare earth metals in productive solutions and tailwaters, as well as infractions after separation of coexisting forms, necessitate their preliminary concentration. For this purpose, methods of both absolute (evaporation, freezing) and relative (sedimentation, extraction, ion exchange, sorption) concentration can be used. The choice of one method or another is determined, first of all, by the properties of individual forms of metals and the method of their subsequent detection. The optimal case is when the concentration of individual forms of metals is combined with their separation. One of the most important conditions for using a particular method for concentration is the minimum impact on the equilibrium established in the system between coexisting forms.

The distribution of rare earth metals in the products of phosphorite processing by the dihydrate and hemihydrate methods are different. Most of all, lanthanides are concentrated in the extraction phosphoric acid (REM) of the hemihydrate process and in the extraction phosphoric acids of the dihydrate process. Although the solubility of rare earth metals increases with an increase in the concentration of REM, the temperature and other conditions of decomposition have a great influence on the decrease in the content of lanthanides in the REM of the hemihydrate process.

The complex sulfuric acid method provides for the separation of REM phosphates from EPA. There is information in the literature on the extraction of rare-earth metals from EPA [24]. Various methods have been proposed for the extraction of lanthanides. But all methods are mainly reduced to extraction [25-27], sorption [28] and sedimentation methods [29]. There is also a known method of ionic flotation, which makes it possible to extract rare earth metals from highly dilute solutions [30].

When extracting lanthanides from phosphogypsum (apatite), basically two methods are assumed - acid leaching [31–35] and conversion of phosphogypsum to carbonate or hydroxides, followed by acid leaching.

At present, there is also a known method for extracting rare-earth metals from phosphogypsum by elutriation and the separation of phosphates of rare-earth metals by the gravitational method. Isolation by the gravity method is carried out at S: L = 1: 300, which makes it unsuitable for industrial implementation.

Based on the analysis of possible ways of separating rare earth metals from phosphogypsum (conversion to carbonates, leaching, gravity concentration), the author of [36] proposes leaching phosphogypsum with 0.5–1% sulfuric acid solution. In this case, 20 - 40% Ln_2O_3, 40 - 60% Y_2O_3 and 30 - 50% Eu_2O_3 pass into the solution. In this work, a method was developed for the isolation of REM by leaching phosphogypsum with circulating solutions after the isolation of the REM concentrate by neutralizing the leaching solution or with magnesium oxide. Magnesium oxide has advantages in that the resulting hydrated sediment is less hydrated, better settled, and filtered. The use of recycled solutions of magnesium sulfate does not reduce the extraction of rare earth metals.

Another area for the extraction of rare earth metals is uranium waste solutions from the metallurgical industry. The extraction of associated components from the uranium industry uranium waste solutions enriched with rare and rare earth elements is methodologically and practically a rather difficult task. This is due to the lack (for the subsoil user - the complete absence) of information on the technical and economic indicators of the extraction of associated useful components and the variety of their possible marketable forms (collective product, oxides, salts, metals of varying degrees of purification, characterized by different yield, price and other technical and economic indicators). Physicochemical analyzes of technological solutions of uranium production were determined on a device in the laboratory of the engineering profile of the university. The results are shown in Table 4.

For further research on the extraction of rare earth metals from solutions, technological solutions of underground leaching of the Uvanas deposit were selected since the content of lanthanides is average over the contents of all the deposits under consideration. A full report on the work done on the extraction of rare earth metals from primary liquid solutions is expected at the 2nd stage of this project.

Table 4 - Average contents of rhenium and total contents of rare-earth metals in technological solutions sampled at different mines of «NAC «KAZATOMPROM» JSC

Deposit (mine)	Process solution type (productive solution - ps; discharge solution – ds)	REM amount, µg / l	Rhenium content, µg / l
Akdala	PS	31780	444
	DS	30352	427
Appak	PS	14136	63.9
	DS	14086	51.2
Irkol	PS	9301	2.6
	DS	9369	1.9
Kendall	PS	31772	263
	DS	29710	261
North Karamurun	PS	6501	52.6
	DS	6886	50.7
Southern Inkai	PS	8145	78.0
	DS	7697	72.2
Uvanas	PS	25712	256
	DS	26127	231
Kharasan-1	PS	5643	17.3
	DS	4144	16.7
PV-19	PS	30070	251
	DS	27483	229
Kanjugan	PS	13237	80.2
	DS	13384	78.7

Rhenium

It is known that productive solutions obtained by underground leaching during the development of uranium deposits in Kazakhstan contain rhenium in concentrations from 0.01 to 0.5 mg/l. A progressive method of mining uranium ore deposits is the method of underground leaching. Reservoir-infiltration exogenous epigenetic deposits developed by underground leaching on the territory of the former USSR are concentrated within several ore-bearing provinces: Central Kyzylkum, Syr-Darya, Chu-Sarysu, Ili, which form the world's largest uranium-ore province – Prityanshan [37]. At the multi-well site of sulfuric acid leaching of ores of the Southern Karamurun deposit with a rhenium content of < 0.5 g / t, its stable concentrations in productive solutions for more than a year were established-0.05-0.3 mg/l (the predominant content is 0.1-0.15 mg/l). In pumping sulfuric acid solutions of underground leaching of ores of the Zarechnoye deposit, where the initial rhenium content also did not exceed 0.5 g/t, for 1 year of operation with oxygen supply, the rhenium concentration varied from 0.1 to 0.25 mg/l. In sulfuric acid productive solutions of underground leaching of the Kanzhugan, Uvanas and Moinkum deposits, rhenium was recorded in concentrations from 0.08 to 0.4 mg/l.

Thus, during the leaching of rhenium from the ores of reservoir-infiltration deposits in the presence of an oxidizer, stable concentrations of rhenium in productive solutions amounting to 0.1-0.3 mg/l were established.

Rhenium is extracted from PV solutions by sorption method [38,39]. From productive sulfuric acid solutions, rhenium together with uranium is sorbed by a strongly basic anionite of the AM-p type or their analogues. Rhenium's selective desorption is carried out with acidic solutions containing nitrate ions (80-90 g/l of NO_3 -, 4-4.5% HNO_3). Rhenium is extracted from eluates containing 10-15 mg / l of rhenium with a solution of trialkyl amine of the C7 – C9 fraction in kerosene with the addition of decanol as a modifier. The rhenium content in the extract reaches 12-15 g / l, which allows its re-extraction with a solution of ammonia in the solid-phase version.

Rhenium is also sorbed together with uranium with AMP-type anionites from bicarbonate solutions of underground leaching. The AMP capacity for rhenium is 7.2-8.0 kg/t, and for uranium 153-159 kg/t. At the same time, the sorption of uranium with anionite is completed much earlier than rhenium [40].

Along with uranium and rhenium, molybdenum, vanadium, selenium, yttrium, REE, and scandium can be extracted from multicomponent solutions. Sorption and extraction options for processing complex solutions have been developed [41-45].

The sorption method includes the collective sorption of uranium, rhenium and molybdenum with anionites of the type AMP, AM-p, etc. Residual solutions can be directed to the additional extraction of vanadium, scandium, selenium and other elements from them. After selective desorption of molybdenum with solutions of a mixture of ammonia and ammonium sulfate, the elution of uranium and rhenium can be carried out in two variants.

Rhenium is recovered from the mother liquors of uranium concentrate sedimentation by the sorption method on anion exchangers such as AMP, AM-p or others, with elution of it with solutions of ammonium thiocyanate; ammonium perrhenate is isolated from the commercial desorbate by evaporation (at pH ~ 9).

The degree of extraction of useful components in underground leaching of polymetallic ores is different: uranium 70-80%, rhenium 50-80%, molybdenum 50-80%, selenium 60-80%, scandium, yttrium and lanthanides are rarely higher than 5-30% [46].

Integrated processing of in situ leaching solutions can help to increase the profitability of developing low-grade ore deposits. Despite the low value of the share of the cost of rhenium in the product, the processing of significant volumes of productive solutions makes it possible to obtain tons of rhenium [47].

The study showed that all known technologies for opening chemical and metallurgical wastes containing rare and scattered metals require high-temperature, environmentally unsafe methods, expensive electrochemical methods, or ineffective hydrometallurgical processes.

For the extraction of rare and rare-earth metals, it is necessary to develop technologies for converting these metals into primary productive materials containing such concentrations of these elements for their industrial and economically profitable production to increase the percentage of direct extraction in finished products. For this research has always been aimed at finding inexpensive, affordable and sufficiently effective oxidants that can significantly increase the recovery of metals. We offer a technology for opening waste and transferring rare and trace metals into solutions using an affordable, inexpensive and effective oxidizer - natural manganese-containing materials that allow you to extract into productive solutions up to 95-97% of nonferrous, rare and trace metals, which include manganese dioxide concentrate or rich manganese ore. Previously, we developed and introduced at the Shymkent Lead Plant a technology for hydrometallurgical processing of lead production dust (waste of the main processing) using manganese ore from the Zhairemsky deposit, which made it possible to increase the extraction of such rare and trace metals contained in them as rhenium, cadmium, thallium, cadmium up to 95%, rhenium up to 97%, thallium up to 94%.

The use in leaching (opening) of various materials containing nonferrous and rare metals of such oxidants as nitric acid, hydrogen peroxide, potassium permanganate, Bertholletia salt, copper sulfate leads either to a significant increase in the cost of technology, or due to additionally introduced impurities, complicates further processing .

The development of the use of manganese ore as an oxidizer from technogenic wastes of the chemical and metallurgical industries requires a number of studies:

- to investigate the chemical and material composition of industrial waste from the chemical and metallurgical industry;
- to study the kinetics of leaching of industrial wastes of the chemical and

metallurgical industry with solutions of mineral acids in the presence of manganese ore;

- to study the mechanism of redox reactions in systems rare, scattered metals - manganese dioxide - mineral acid;
- to study the influence of the nature of manganese-containing ions on the subsequent extraction of rare and scattered metals.

The proposed technology will increase the extraction of rare and trace metals into primary productive materials by 20-25%.
The following materials and equipment were selected for research (Table 5).

Table 5 - List of used equipment

Equipment name	Characteristics
Hydraulic laboratory press (manual)	Type of PGP Maximum force, kN 39.2 Plunger diameter, mm 58.0
Hydraulic press with electric drive Armavir	Type P-10 GOST 5905-73 Maximum force 10000 kgf The price of dividing the scale is 20 kgf
Planetary-centrifugal activator AGO-2	Number of drums 2; Drum capacity, 160 ml The mass of the crushed material in one drum, g (not more than) 100; The mass of the ball loading in one drum, g (maximum) 250; Centrifugal acceleration 20g, 40g, 60g Diameter of balls, mm 2-8; Operation mode is discrete
Electric resistance furnace chamber laboratory VTP 12/15	Temperature profile control software Installed power, kW 8; Supply voltage, 220 V; 178; Number of phases 1; AC frequency, Hz 50; Maximum temperature, °C 1550; Nominal temperature, °C 1500; Working environment air Automatic temperature control range, °C 200÷1550
Electric resistance furnace shaft vacuum	Type SSHB3–1-2.5/25- I2 Maximum vacuum, Pa 6.65·10-3; Supply voltage, V 380/220; Number of phases 1; AC frequency, Hz 50; Working environment vacuum, Ar, Ar/H2 The material of the heaters is Tungsten
Analytical scales	Type VLR-200g-M GOST 24104-88 Accuracy class II; Maximum weight, 200 g Division price, g 0.00005
- magnetic stirrer; - technical scales; - chemical dishes	

The list of equipment required for the leaching process design is selected according to the following parameters.

1. Technology and equipment for the leaching process.
2. Mode of supply of solid products for leaching.
3. Regime of supply of reagents and solutions for leaching, consumption coefficients for reagents.
4. Leaching mode - temperature, time, heat effects, chemical reactions,

particle size distribution of the solid phase.

5. Recommendations for the selection of leaching devices and devices for dosing reagents.
6. Controlled process factors and methods of control.
7. Chemical composition of solutions and pulps, the degree of extraction of valuable components.
8. Data on the corrosive and abrasive activity of slurries and mixtures.
9. Gas evolution during leaching, rate of gas and vapor evolution, quantity and composition of waste gases.
10. Radioactivity of initial products and activity distribution by phases (solution, solid residue, gas).
11. Characterization of liquid, solid and gaseous leaching products (toxic properties, explosive concentrations, density, solubility, etc.).

1.3 Physico-chemical analysis of technogenic waste from the chemical and metallurgical industry for the content of rare and rare-earth metals, their phase composition

In developed and developing countries, rare metals are classified as factors that ensure the progress of science and technology. They are used in almost all branches of modern industry - nuclear, thermonuclear, space, aircraft construction, instrument making, etc. The largest producers and consumers of rare metals are the USA, Japan, Great Britain, and Germany, where research works on the 4th and 5th redistribution production.

Kazakhstan is one of the largest regions in the world with significant reserves and prospects for expanding the mineral resource base of rare and rare earth metals. It ranks first in the world in terms of proven tungsten ores reserves, second in chromium reserves, and fourth in manganese, copper, lead, molybdenum, and phosphorite ores. Among Asian countries, Kazakhstan ranks first in terms of production of chromite, copper, polymetallic, molybdenum and tantalum ores, second - iron, manganese, bauxite, nickel and coal. All these raw materials contain increased elements such as rhenium, indium, thallium, tellurium, gallium, germanium, yttrium, lanthanum, and platinum group metals.

Currently, Kazakhstan's industry extracts and processes tungsten, molybdenum, tantalum, and beryllium. However, the entire range of rare and rare earth elements is not extracted from these ores.

Scientific and technological progress in various spheres of material production is associated with the widespread use of rare and rare-earth metals, which necessitate the intensive exploitation of natural resources and thus have a significant impact on the state of the environment. The dynamics of the extraction of rare earth metals in some countries for 1999-2006 in tons is shown in Table 6.

Table 6 - Production of rare earth metals in the countries of the world, tons

Countries	1999	2000	2001	2002	2003	2004	2005	2006	2014
USA	5000	5000	5000	5000	5000	-	-	-	7000
China	70000	70000	73000	75000	90000	96000	98000	120000	95000
CIS	2000	2000	2000	2000	2000	2000	2000	2000	2500
Brazil	1400	1400	200	200	-	-	-	-	330
India	2700	2700	2700	2700	2700	2700	2700	2700	3000

As can be seen from Table 6, at present, China, on whose territory about a third of the world's proven reserves of rare earth metals are located, produces more than 90% of the total volume of this strategic raw material consumed by the global market. Considering the rate of extraction, it can be assumed that already in the foreseeable future, the known reserves of ores of some metals, for example, molybdenum, tungsten, gold, antimony, etc., will be completely depleted.

In addition to developing new deposits and increasing production by the main producers of rare-earth metals, the search for new ways of more efficient use of rare earth metals also affected the prices of their products. Specifically, the following steps for corporate buyers:

First, Hitachi found a way to use less dysprosium to make magnets in electronics.

- Panasonic has developed a method for recycling neodymium from old electrical appliances;
- the use of LED technologies has grown, which replace fluorescent lighting and require less rare earth metals;
- Toyota has developed engines for hybrid and electric vehicles, the production of engines does not need rare earth metals;
- oil refiners have managed to exclude rare earth elements from the catalysts used in oil refining.

As a result of an increase in production in other countries and the introduction of new technologies that do not require the use of rare-earth metals, according to the Council on Foreign Relations, the share of China in the total production of rare earth metals has currently decreased from 97 to 70%

The replenishment of the raw material base is possible both through the discovery and development of new deposits and through the broader use of various secondary raw materials and waste generated in the process of human production. Waste can be divided into the following groups by sources of generation:

1. Waste from the coal mining industry and thermal energy (burnt mine rocks, waste from coal mining factories, ash and slag from thermal power plants).
2. Waste from the forestry and woodworking industry (sawing waste and woodworking).

3. Waste from the biochemical industry (hydrolysis lignin).
4. Waste from ore processing (flotation waste).
5. Waste from the chemical industry.
6. Waste from the building materials industry (waste from crushing and sorting enterprises, waste from the ceramic industry, etc.)
7. Waste from the metallurgical industry (waste from the steel industry, waste from the phosphorus, lead industry).

The expediency of using waste is dictated by two main factors: the need to improve the environmental situation, development of resource and energy-saving technologies, reduction of production costs.

At present, with significant volumes of technogenic accumulations, the level of their useful utilization is low. The development of material production at a modern scale is accompanied by an increase in the volume of various waste. Removing them requires costs, sometimes reaching 8-10% of the cost of the main production. In modern conditions of particular importance for the effective development of the national economy is the problem of wider involvement in the production of the resulting waste, which makes it possible to expand the raw material base and reduce environmental pollution.

The use of secondary raw materials allows:

- preservation of irreplaceable natural resources;
- improvement of the ecological situation;
- reduction of capital and energy costs;
- increasing the degree of extraction of valuable components and increasing the range of products;
- creation of low-waste industries.

The production of a finished product usually consists of numerous sequential operations, from processing raw materials to the receipt of the finished product. In this case, physical, chemical and physical-mechanical processes are used. At each stage of obtaining a particular product, as a rule, waste or residues are formed in the form of dust, sludge, and often in the form of particles of raw materials. When grinding ore, for example, the resulting dust can be recovered and returned to the process.

Chemical and metallurgical waste is generated in the process of manufacturing products and loses completely or partially the consumer properties (chemical or physical) of the original material. The yield of the target product when processing, for example, phosphate ores is no more than 30-40%, the rest of the materials and substances goes to waste and sludge collectors [1].

Involvement of technogenic mineral formations in processing is one of the priority directions of developing the mineral resource base of Kazakhstan's mining and metallurgical complex. According to the Law of the Republic of Kazakhstan, "On Subsoil and Subsoil Use", technogenic mineral formations include accumulations of mineral formations, rock masses, liquids and mixtures containing useful components that are wastes from mining and processing, metallurgical and other types of industries. Today the volume of technogenic mineral formations in the Republic of Kazakhstan is up to 34.5 billion tons [2]. Of these: overburden and enclosing rocks - 25.8 billion tons (70%); metallurgical slags, waste of metallurgical processing, tailings of concentration plants - 5.5 billion tons (15%); off-balance and substandard ores - 3.2 billion tons (9%,); clinker - 2.4 million tons (6%).

Raw materials sources of scattered rare metals (indium, thallium, selenium, tellurium, germanium, gallium, rhenium) are by-products from the processing of lead-zinc, copper, aluminum-containing ores, ash and tar water from coal combustion, dust from the processing of iron ore raw materials, solutions and sludges of sulfuric acid production [3]. For example, the dust of agglomerating roasting of lead charge is a collector of rare metals - cadmium, thallium, rhenium, indium. Since 1962, on the basis of these dusts, the production of cadmium and thallium, later rhenium, was organized at ShSZ. These dusts are processed together with the dusts of mine sinter smelting according to the technology developed by the teams of the institutes: VNIItsvetmet, Gintsvetmet, IMO HAH RK and IHN HAH RK. The composition of dusts obtained at the enterprises of the lead industry of the republic is complex and characterized by chemical and phase diversity, but the main component is lead (40-70%). In the dust of ShSZ, in contrast to other enterprises processing lead-containing raw materials, rhenium is present in significant quantities (0.05-0.1%). Therefore, the choice of a rational ¬go method of opening the dust causes great difficulties.

The widespread use of technogenic mineral formations in the country will increase resource conservation on a huge scale by saving operating and capital costs for the exploration and production of mineral raw materials and partially solving the environmental problem. When choosing a method for processing secondary raw materials, it should be borne in mind that its composition in most cases differs significantly from primary raw materials. So, for example, the presence of various synthetic materials absent in nature, pollution with toxic and explosive substances during operation, etc., do not automatically allow the use of technological processes and devices designed to implement the main production processes for their processing. In this regard, it becomes necessary to solve the following tasks:

- analysis of the sources of formation of secondary raw materials;
- classification of secondary raw materials supplied for processing;
- selection of technological schemes for enrichment and processing for a specific type of secondary raw materials.

In particular, man-made wastes from mining, metallurgical and chemical complexes are distinguished by a high content of undercovered main and accompanying valuable components. The content of technogenic waste, according to some experts, of rare-earth metals in them reaches 0.6%, which is comparable to some ore deposits. Therefore they can be considered as an independent raw material base of metallurgy in Kazakhstan. However, the lack of information on the exact volumes of accumulated technogenic waste indicates the urgent need to create an inventory and assessment with recommendations for effective processing.

Currently, no more than 2% of all such accumulated waste is recycled in the country [4].

Reanimation of rare metal plants is not the only way to provide the country with rare metals. You can quickly, easily, and cheaply get them from all kinds of technogenic sources and various incidentally extracted products. For example, from the ash obtained from the combustion of bituminous and brown coal, from the products of processing and refining of oil and gas; from mine and mine waters, as well as from volcanic waters and gases. Our hydrocarbon feedstock contains commercially valuable quantities of yttrium, lanthanides, vanadium and other metals, the price of which is commensurate with the cost of oil itself.

The industrial technology for processing ore raw materials and industrial waste in Kazakhstan is based on sequential processes for the extraction of rare and rare earth metals by hydrometallurgical methods. Potential sources of rare and rare earth compounds and metals are uranium tailing dumps, solutions of underground leaching of uranium ores and mineral deposits of rare earth metals.

The constantly increasing volumes of stored waste form new technogenic intensively dusting landscapes. Waste processing by enterprises is carried out practically haphazardly. Waste recycling is constrained by the lack of low-waste resource-saving technologies for the integrated extraction of minerals from secondary facilities. Since waste is a potential secondary material resource, the current system for managing technogenic waste leads to an irreversible loss of valuable secondary material resources, energy, and land resources. The environment has been negatively affected by stored waste for decades. Over the years, the intensity of this impact does not always decrease, but can have sharp periodic increases as a result of changes in geological, hydrological and hydrogeological conditions.

The integrated use of raw materials and waste is also important because it is associated with solving the problem of creating waste-free and environmentally friendly industrial technologies. The development and implementation of waste-free technologies are of great importance for enterprises of chemical, mining and chemical, microbiological, metallurgical, coal and other resource-intensive industries in Kazakhstan. As an example of the identity of the use of raw materials and wastes of different properties, one can cite the fact that overburden rocks formed during the extraction of mining and chemical raw materials, coal, brown coal and a number of ferrous metal ores can be widely used for the production of various building and binding materials. And also, the issues of handling the accumulated wastes of the uranium industry are becoming especially relevant - their relocation, disposal, control over the state of tailing dumps and maintaining them in a satisfactory engineering-geological state.

Serious attention should be paid to studying the physical properties of waste, their chemical and mineralogical composition, to determine the possible area of their application. Such major problems as the use of sand sludge from phosphorus plants and phosphogypsum in Kazakhstan, overburden of coal basins (Shubarkolskoye, Yubileinoye, Lengerskoye), waste from the uranium industry, etc. should be resolved on the basis of comprehensive coordination plans with the involvement of a number of research and design organizations.

Phosphogypsum

Among the technogenic waste, rich in rare earth elements, it should be noted phosphogypsum - a product of apatite processing for mineral fertilizers, dump cakes of tungsten production, as well as intermediate products of uranium ore processing. The content of rare earth elements in these industrial waste is 0.5-0.6%, corresponding to some ore raw materials. The presence of rare-earth metals in natural phosphate ores drew the attention of researchers to the possibility of developing methods for the extraction of concentrates of rare-earth metals during the process of obtaining phosphorus fertilizers. As well as apatites, phosphorites can be processed into phosphoric fertilizers by the extraction method, i.e. By decomposition of sulfuric, hydrochloric, nitric and phosphoric acids with phosphoric acid, then at the Taraz plant of mineral fertilizers, sulfuric acid opening became widespread. Technogenic raw materials, in contrast to mineral raw materials, are opened more easily due to the altered phase composition. Therefore, the technology for concentrating REE from industrial waste does not require large capital expenditures and is relatively simple to implement.

A significant number of scientific works have shown the effectiveness of using preliminary washing with solutions of mineral acids (primarily sulfuric acid) for processing phosphogypsum, followed by the extraction of RZK from the washing solution.

It was found in [24] that when phosphogypsum is washed with a sulfuric acid solution with a concentration of 80–100 g / l, up to 50% of REE passes into the washing solution. Washing phosphogypsum in a countercurrent mode made it possible to increase REE extraction and obtain solutions with a REE content of up to 1.5 g / L. Further concentration of REE was carried out by neutralizing the wash water with ammonia to obtain phosphates. The technical phosphate concentrate contained about 20% REO. Its processing by extraction with 70% hexaran made it possible to obtain a 96% concentrate of REE oxides in one stage. The technology for extracting REE from phosphogypsum by washing with sulfuric acid in a counterflow model was tested in a pilot plant, extraction of REEs - in a laboratory setup in a full counterflow mode. Through the extraction of REE into the group concentrate was about 35-40%.

However, a comparatively effective sulfuric acid leaching of REE from phosphogypsum is possible only after it has been kept for at least 1-2 months in an open landfill. This is explained by the transition of a significant part of low-hydrated REE phosphates into fluorides, which are characterized by a higher solubility in sulfuric acid solutions with the formation of complexes (REE) SO4F, as a result of hydrolysis reactions of silicofluorides contained in phosphogypsum:

$$Na_2SiF_6 + 2H_2O = SiO_2 + 2NaF + 4HF,$$

$$(REE)PO_4 \cdot nH_2O + 3HF = (REE)F_3 + H_3PO_4 + nH_2O.$$

The technology of extracting REE from phosphogypsum using sulfuric acid for washing has been developed in a number of studies [25, 26]. REEs were extracted from the washing solution by sedimentation of double sulfates. However, the separation of REE from phosphogypsum by the aforementioned methods requires significant energy and labor costs associated with filtration and washing double sulfate sediments. In addition, at the crystallization stage of sulfates, a loss of REE occurs due to their co-crystallization with gypsum.

According to [27-31], to increase the degree of extraction, REE from the washing solution was separated by sorption on a cation exchanger. It should be noted that the use of a cation exchanger containing sulfuric acid functional groups leads to a decrease in the selectivity of the extraction of rare earth elements due to the competitive sorption of ions of concomitant impurities of calcium, magnesium, iron, aluminum, and some others [32]. To increase the selectivity, in [33], the sorption of REEs was carried out on the CMDF sorbent, which made it possible to increase the degree of extraction from the solution to 71%. However, the introduction of sorption processing increases the cost of the obtained REEs due to the high cost of the sorbent and the complication of the instrumental circuit.

The known method [34], according to which the extraction of REE was carried out by treating phosphogypsum with nitric acid with the addition of calcium nitrate. This method obtained nitric acid solutions with a REE content of 1-1.3 g / l. However, they were sent to the extraction process to concentrate REE and purify them from impurities, which requires additional time, reagents, equipment, and energy resources. In addition, the use of organic reagents in technology requires further deep purification of aqueous solutions from them.

A known method of extracting REE from phosphogypsum previously washed from phosphorus [35]. Phosphogypsum containing 0.52% of rare-earth oxides and 0.23% of P2O5 was treated with a sulfuric acid solution with a concentration of 15-250 g / l by heap leaching. Leaching was carried out with a sulfuric acid solution in a closed cycle, including the transfer of REE from phosphogypsum into solution, then their concentration on a cation exchanger and returning the sulfuric acid solution to the leaching cycle. The process was carried out until 80% of rare earth metals from their original content were washed out of phosphogypsum. Then, the production solution was fed to the stage of sorption concentration, and the REE with the REE content of at least 60% was obtained. The disadvantage of this method is the long duration of heap leaching and the use of sorption processes, the disadvantages of which were mentioned earlier.

One of the most effective and least labor-intensive methods is in which REE in the form of oxalates was sedimented from the solution after washing the phosphogypsum with 100 g / L with a sulfuric acid solution. The sedimentation of oxalates was carried out with oxalic acid (or its soluble salts) with preliminary neutralization of the sulfuric acid solution to pH = 1-2.5. The pulp was stirred for 0.5-1.5 hours, then the sediment was separated from the mother liquor, washed, dried at 120 ° C and calcined at 850 ° C. The principal technological block diagram of the considered method is presented in the literature [16].

This technology has a number of advantages, including: it provides a decrease in energy and labor costs for filtration due to high filterability and thickening rates of the obtained crystalline sedimentates of rare-earth oxalates, is waste-free and complex, since it allows producing a wide range of building materials in addition to rare-earth metals.

The technology [16] was tested at a pilot plant in Pavlovsky Posad. In accordance with the test regulations, 10 tons of dump phosphogypsum of OJSC Voskresensk Mineral Fertilizers were processed, from which a pilot batch of RZK in the amount of 22.5 kg was obtained, as well as pilot batches of gypsum binder α- and β-modifications, which can be used for the manufacture of building materials destination.

RZK obtained by the technology [16] contains over 98% ΣRZO, including about 46% of cerium oxides (of which about 32% are oxidized to (+4) form) and 17% of neodymium oxide, which makes it possible to use it in as a raw material for their production.

However, radioactive impurities also pass into the concentrate [36, 37]. Therefore, in accordance with [38], it will be necessary to introduce a stage of purification from radioactive impurities (deactivation) into the technology of its processing.

Ashes and slags of metallurgical industries

The specificity of the mineral part of the waste is determined by the material composition of the rocks in which the coals are deposited, and the composition of the mineral part of the interlayers inside them. Most of the coals of Kazakhstan contain the following minerals: silicates, carbonates, sulfates, sulfides, halides, phosphates. According to this material composition, coal preparation waste is a multicomponent mixture of various mineral inclusions and coal residues. Recently, there has been an increase in interest in extracting rare metals from dust and fumes of various industries, particularly power engineering. Fly ash from coal combustion can be considered a technogenic raw material for producing many valuable metals, especially since it has zero cost so far. Therefore, the extraction of rare metals and the main components (aluminum, iron) can make fly ash processing profitable in the near future.

The utilization of ash and slag waste from the CHPP will expand the mineral resource base and reduce land areas for ash dumps and improve the environmental situation in the ash dump area.

Depending on the type of processed raw materials, the output of slags in nonferrous metallurgy is 10 - 200 tons per ton of the produced metal. In this regard, the volume of slag formation in nonferrous metallurgy, despite the much lower production volume of nonferrous metals, is comparable to the output of slags in ferrous metallurgy. Solid waste from thermal power plants - ash and slag is close to metallurgical slag in composition. Their output is currently about 60 million tons/year, and half of this waste is ash from coal combustion. The degree of utilization of ash and slag waste does not exceed 1.5 - 2%. In terms of chemical composition, these wastes are 80 - 90% composed of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, with significant fluctuations in their content. Also, the composition of this waste includes the remains of unburned fuel particles (up to 20%) compounds of titanium, vanadium, germanium, gallium, sulfur, uranium.

Ash and slag of a CHP plant is a residue from the combustion of solid fuels. They are products of thermal processing of the mineral, non-combustible part of the coal. At the same time, two types of waste are obtained in chamber furnaces: fly ash and slag. Mine rocks of the Lengerskoye deposit are valuable raw materials for obtaining fertilizers containing many trace elements necessary for plant nutrition (Mo, Zn, Mn, Ag, Cu, etc.). When treating mine rocks with chemical reagents, effective complex fertilizers (fertilizers such as "Donbass") can be obtained, which are necessary for the mineral nutrition of soils, the imbalance of which occurs as a result of the intensification and chemicalization of agriculture.

To increase the volume of waste use, it is necessary to increase the efficiency of research and development work, to create such conditions that the problems of involving secondary raw materials and waste bother industrial enterprises as well as issues related to the development of the main production.

Dust of lead production

Despite a significant number of works [5] devoted to the processing of dusts in order to extract rare and nonferrous metals from them, there is no information about rhenium in them. This is because the presence of this metal in the dust of the ShSZ was established in 1972. The first publications on the extraction of rhenium from the dusts of lead production date back to 1977. A hydrometallurgical method for the non-oxidative opening of the dust was proposed. Leaching was carried out with water, sodium sulfate and sodium chloride solutions, and sulfuric acid. Studies have shown that in water leaching, the degree of transition of rhenium into solution is 40-60, cadmium - 50-55, zinc - 5-7%; when leaching dusts with sulfuric acid solutions, the extraction of rhenium into the solution was 55-60%. Unfortunately, there are no data on the extraction of cadmium and zinc during sulfuric acid leaching.

When using as leaching reagents aqueous solutions of sodium salts (L: S = 5: 1, temperature - 80 ° C, concentration of Na_2SO_4 and NaCl - 300 g / dm3), 70-75% of rhenium, cadmium ~ 40 are extracted into the solution. It should be noted that the nature of the salt does not affect the transition to solution of rhenium and cadmium, but it does affect the extraction of zinc. So, when leaching with sodium sulfate solutions, 53% of zinc is extracted into the solution, and in the case of sodium chloride - 75%. The authors do not provide any explanation for the different extraction of zinc into solution.

The low performance of this method for the conversion of rhenium, cadmium, zinc into solution led to the use of various oxidants in the leaching process. In addition, the process of leaching of lead dust with solutions of nitric acid, hydrogen peroxide and a mixture of nitric and sulfuric acids was also investigated.

Nitric acid leaching of lead dust under optimally selected process conditions (L: S = 3: 1, temperature - 70 ° C, leaching time - 1 hour, nitric acid consumption - 200 kg / t) allows to extract up to 80% rhenium into solution; data on cadmium, zinc, thallium are absent.

The use of hydrogen peroxide as an oxidizing agent (L: S = 3: 1, sulfuric acid concentration - 30 g / dm3, hydrogen peroxide consumption - 1.9 t / t of dust) increases the extraction of rhenium into solution up to 90-92%.

In order to more efficiently use nitric acid and reduce its consumption, the authors of [6] suggested using this reagent in the process of dust granulation with subsequent leaching of granules. The granules are then leached with water. In this case, there is a more complete oxidation of the compounds of rhenium, cadmium, thallium, zinc, as well as the destruction of organic compounds present in the dust, which negatively affect the subsequent release of rhenium from solutions. The extraction of rhenium into the solution reaches 97%. There is no information about other elements.

The method of granulation of rhenium-containing dust with solutions of various sulphate salts was used by the authors of [7]. Dust granulation was carried out with aqueous solutions of sulfate salts of zinc, cadmium, copper, iron (II), potassium and sodium. The resulting granules were fired at a temperature of 400 ° C for two hours after which they were leached with a solution of sulfuric acid (acid concentration - 70 g / dm^3, L: S = 3: 1, temperature - 80 ° C, leaching time - 2 hours). Laboratory research data showed that rhenium mainly remains in the fired product (85-90%) and, regardless of the nature of the granulating agents, about 69-74% of its content in the dust is extracted into the solution. There are no data on the extraction of cadmium, zinc, thallium. Using zinc sulfate as an example, it is shown that its concentration in solutions used for dust granulation affects the behavior of rhenium during firing.

So, when dust is granulated with solutions with a zinc sulfate concentration of 25 g / dm^3 and the subsequent firing of granules, up to 20% rhenium passes into the gas phase. As the content of zinc sulfate in the granules increases, the degree of stripping decreases. When the content of zinc sulfate in solutions is 300 g / dm^3, the firing of granules proceeds without distillation of rhenium into the gas phase; rhenium almost completely remains in the cinder. When leaching fired granules, the amount of zinc sulfate contained in them does not affect the extraction of rhenium into the solution, which remains at the level of 62-69%.

The authors of the work [8] proposed and investigated the method of direct hydrometallurgy. The dust is opened with solutions of sulfuric acid in the presence of copper sulfate. Copper sulfate acts as an oxidizer of sulfide sulfur. The optimal parameters of the direct hydrometallurgy process were determined experimentally. dust: concentration of sulfuric acid-60 g / dm^3, copper (II) - 5 g/dm^3, temperature-90 °C, L: S=3:1, leaching time-2 hours. Under the selected conditions, % is extracted into the solution: rhenium 78, cadmium 80, thallium 84. However, despite the high rates of extraction of rare metals into the solution, this technique was not implemented in production in the conditions of operation of the hydrometallurgical shop of the SHSZ. In this workshop, along with the dust of oxidative agglomerating firing of the charge, the dust of melting the agglomerate is also processed. The latter are raw materials of indium and zinc and are processed according to the sulfurization-leaching scheme. Independent processing of agglomerating charge firing dust would increase the volume of productive solutions and additional capital costs for installing the necessary equipment (leaching tanks, filtering equipment, collection tanks of productive solutions). Therefore, the same authors proposed to process by direct hydrometallurgy, not the entire agglomeration charge firing dust entering the hydrometallurgical shop, but only a part (1-3 tons per day). Moreover, solutions from the leaching of dust are directed to the leaching of the sulfate product and not to the extraction of metals from them. According to this scheme, the total extraction of metals from dust was %: rhenium 28, cadmium 78, thallium 56; there is no data on zinc.

The results of industrial testing of the schemes presented in previous works showed that both of these schemes have certain disadvantages: they increase the water circulation in the shop, require the installation of additional equipment and increase the production area; the number of filtration operations increases, which leads to losses of valuable components during additional pumping of solutions and washing of cakes from leaching of dust from agglomerating firing of the charge.

To eliminate these disadvantages and intensify the process, joint leaching of a part of the agglomerates and the sulfate product is proposed [9]. The process parameters were refined under laboratory conditions: the ratio of dust and sulfate product is 1: (3-5), the concentration of sulfuric acid is 70 g/dm^3, the amount of copper sulfate is 10% of the dust weight, the process temperature is 80 °C, the leaching time is 3 hours. The degree of extraction of rare metals into the solution when using a combination of hydrometallurgy and sulfating firing methods for opening dust was,%: rhenium 40, cadmium 73-33, thallium 61-73. The introduction of this scheme into production at the SHSZ increased rhenium extraction into commercial products by 18 %.

A number of systematic studies are devoted to the electrochemical opening of lead production dust in an electrolyzer with the separation of the anode and cathode spaces by ion-exchange membranes [10, 11].

The method's essence consists of combining acid leaching of dust with anodic oxidation of the obtained products of the reaction of dissolution of sulfide compounds and impurities in the anode chamber at pH=0.5-1.5.

The anode space of the electrolyzer is separated from the cathode part by a membrane MA-40, which provides the separation of anions and cations. The method and some components of the electrolyzer are protected by copyright certificates of the USSR [12]. Based on the analysis of the results of laboratory studies devoted to the influence of various factors (temperature, sulfuric acid concentration, W: T, anode current density) on the indicators of the process of electro-leaching of lead production dust, the optimal model was determined [10]. At a current density of 50-60 A / m^2, a voltage of 4.76 V, a pH in the anode space equal to 0.5-1.5, L: S=3:1, a process temperature of 40 °C, % is extracted into the solution: rhenium 93-93. 1, cadmium 85.3-87, zinc 78.5-79.6, thallium 70.1-70.5, arsenic 91.9-92.5, indium 81.2-81.3.

In order to reduce the electricity consumption and the duration of the leaching process, it was proposed to use iron disulfide [13] as an insoluble electrically conductive material at its ratio to the sulfide ion in the initial dust (1-3):1. This made it possible to reduce %: electricity consumption by 15-20, the duration of the process by 20-30, increase the extraction of valuable components by 2-3. At the same time, 95% rhenium, 89 cadmium, 74 thallium and 92 arsenic are extracted into the solution. In the future, the same authors improved the electrochemical method of opening dust, which made it possible to transfer rhenium, indium, cadmium, thallium, zinc, arsenic to a solution as completely as possible and to obtain practically pure lead sulfate suitable for the production of lead oxides [14]. In all the previously described technical solutions, the cake was returned to the" head " of the process of processing lead-containing materials to agglomeration. The essence of the improvement is a combination of hydrometallurgical and electrochemical methods of dust extraction. The dust is subjected to leaching with solutions obtained from the anodic oxidation of the cake from the previous dust batch. The process is carried out at a temperature of 70 °C until the redox potential of the pulp is 0.45-0.47 V. Then, the solution and cake (I) are separated by filtration. The solution is directed to the extraction of metals, and the cake (I) is subjected to electro-leaching in the anode space of the electrolyzer with the transfer of the remaining valuable components into the solution. The filtered and washed cake (II) (practically pure lead sulfate) is directed to the production of lead oxides, and the solution is used to leach a fresh batch of dust. The method has been tested on an enlarged laboratory scale. High indicators for the conversion of rare and nonferrous metals into a solution were obtained. In the solution, depending on the content in the dust, % is extracted: 93.57-98.52 rhenium, 98.08-98.19 cadmium, 97.5-97.8 thallium, 94.4-94.58 indium, 97 zinc. The positive results of the electrochemical method of dust opening served as the basis for the creation of a pilot plant in the hydrometallurgical workshop of the SHSZ and conducting tests. The obtained results confirmed the data of the laboratory tests and revealed the structural shortcomings of the device, because of which the method was not introduced into production.

Methods of the pyrometallurgical opening of rhenium-containing lead dust are also investigated. In [15], the behavior of rare metals during the independent agglomeration of rhenium-containing dust of the SHSZ was studied. With independent agglomeration of dust, rhenium, cadmium, thallium pass into secondary sublimations, making it possible to obtain dust richer in these metals. The influence of various parameters (the composition of the charge, its humidity, the amount of air, the temperature of the process) on the conversion of rhenium, cadmium, thallium and the quality of the agglomerate was studied in the laboratory. Under the optimal conditions found (temperature-800-1000 °C, blast pressure-0.2-0.6 kg / cm^2, air flow-50-200 l / min, charge humidity-25 wt. %) during the agglomeration process of the charge, an average of 81% rhenium, 75 cadmium and 98 thallium passes into the sublimates. The average yield of the suitable agglomerate was 75 %.

In order to obtain a high-quality agglomerate, the same authors studied the effect of the amount of reducing agent [16]. Coke was used as a reducing agent.

The introduction of 5-10% of the reducing agent from its weight into the charge makes it possible to obtain a well-melted durable agglomerate. At the same time, high degrees of desulfurization and extraction of rhenium (77 %) and cadmium (92%) are ensured. There are no data on thallium and zinc.

The paper [17] presents the results of studies on the firing of lead production dust at low pressures. Only the behavior of rhenium as a function of temperature, residual pressure, firing duration, the amount of sulfide and oxidizer (CMG1O4), a mixture of potassium permanganate and sodium chloride, was studied. The analysis of the obtained dependencies allowed the authors to choose the optimal mode of conducting the dust-firing process: temperature-700 °C, residual pressure-2-3 mm Hg, time-2 hours, the ratio of dust to sulfur is 2:1, the mixture is 10 % $KMnO_4$ and 15 NaCl. At these operating parameters, the degree of rhenium distillation was – 90 %.

Based on the analysis of the literature data, it can be stated that pyro-, hydrometallurgical and electrochemical methods have been proposed for the opening of rhenium-containing dust of lead production.

Samples with an estimated content of rare and rare earth metals were selected as the starting material for the research:
m aqueous solutions.

- Phosphorus PPO "Phosphorus" (Shymkent);
- Phosphogypsum PO "Kazphosphate" (Taraz);
- outbreaks of the Lenger coalfield;
- coal strips with gold bars TPP-1 and TPP-2 (Shymkent);
- landfills of JSC "PC" Yuzhpolymetall "(Shymkent);
- landfills of ChSZ with terricon (Shymkent);
- sawdust production (SHSZ, Shymkent);
- solutions of uranium industry PV-19;
- waste pulp tailings of JSC "Achpolymetall" (Kentau).

Technological samples for testing, taking into account the variety of types of technogenic raw materials containing rare and rare earth metals, and the lack of a unified classification, variants of its classification by physical and Physico-chemical characteristics and by branches of material formation, given in Table 7, can be recommended.

Solid materials, both of natural origin and technical products, can be bulk (phosphogypsum, charge, fluxing materials, ferroalloys, slags, coke) regardless of the size of the pieces (from very large to powdery). Large and small pieces of many bulk materials may have a different compositions. Therefore, when sampling, it is necessary to select both large pieces and small items in quantities proportional to their actual content in the material. The greatest difficulties arise when sampling lumpy materials (ores, limestones, etc. P.) at the storage site from the storage of stacks or piles, since due to delamination, the composition of one piece may differ sharply from the composition of another. When taking a sample, it is necessary to keep the ratio between large pieces and small things the same as in the source material. When selecting a representative sample of liquids, significant errors are unlikely since liquids are more homogeneous than solids. Therefore, liquid sampling is easier. If the liquid is homogeneous, it is enough to scoop a small amount of it anywhere to get an average sample. Semi-liquid materials include ointments, resins, slurries, pulp, etc. The selection of average samples of these materials is difficult due to the heterogeneity caused by the delamination of the mass. The semi-liquid mass can be at rest in a vessel of large or small capacity (cans, cans, barrels, boxes) or in motion (pulp). In the first case, samples are taken from a number of places. The standards determine the number of samples. Sampling is carried out manually using samplers of various designs.

Table 7 - General classification of technological samples of rare and rare earth metals

Source of raw materials	Character	By branches of formation of material	By physical and chemical characteristics
Technogenic waste	Solid technogenic raw materials	Non-ferrous metallurgy waste: substandard metals, alloys, salts, slags, sludge, cakes, dust, a scrap of metallurgical equipment	Rich, poor
		Waste from the mining industry: overburden, waste of mining and chemical raw materials, burnt mine rocks, waste of coal visiting factories, ash and slag from CHP	Rich, poor
		Chemical industry: catalysts, slurries, cakes, dust, solutions, a scrap of chemical reactors and other equipment	Rich, poor
	Liquid technogenic raw materials	Chemical industry: solutions of the uranium industry, cottrel milk, rich pickling solutions, solutions of waste electrolytes, washing and wastewater, mother solutions of the chemical industry.	Acidic, alkaline or neutral
	Gaseous technogenic raw materials	-	-

As shown in Table 7, technogenic waste is divided according to the aggregate state into solid, liquid, gaseous.

The process of taking a representative sample is difficult because there is no universal rule for selecting such a sample that is equally suitable for different materials. Sampling methods are very diverse and depend on the material's aggregate state, the material's nature (bulk or lumpy), the degree of its uniformity, and whether the material comes without packaging or in containers (boxes, bags, barrels, tanks, etc.). Preparation of the lump material is carried out initially by ore picking with subsequent radiometric enrichment for some of the samples presented containing scattered or radioactive metals. For the selected sample to correspond in its composition to the actual composition of the material under study, a large number of samples should be taken from the batch and take into account the size of the pieces, segregation and liquation (for alloys), as well as changes under the influence of external conditions during long-term storage of the material in heaps and stacks.

Table 8-Chemical composition of lead production dust

samples	Content, mass.%												
	Pb	Zn	Cd	Re	Se	Te	Tl	Jn	Fe	Cu	S	CI	As
№1	66,7	1,0	4,80	0,06	0,11	0,05	0,24	0,0015	0,2	0,6	9,17	5,0	0,88
№2	66,5	0,9	5,09	0,10	0,12	0,07	0,40	0,0010	0,4	1,0	9,31	5,5	1,36
№3	67,0	0,7	5,20	0,07	0,08	0,06	0,24	0,0040	0,5	1,1	8,41	5,3	1,20
№4	63,8	0,9	5,03	0,12	0,10	0,08	0,27	0,0010	0,9	0,9	8,00	5,1	0,80
№5	64,5	1,5	4,90	0,08	0,08	0,06	0,40	0,0020	0,6	0,3	8,90	5,0	1,20

As can be seen from Table 8, the basis of dust is lead and sulfur. The lead content varies in the range of 63-67 %, sulfur from 8 to 9 %. The content of other components in dust, kg / t: rhenium 0,6-1,2, zinc 7-15, thallium 2,4-4 and 48-52 cadmium. Fluctuations in the contents of rhenium, thallium and other metals are explained by the different compositions of the incoming raw materials and the conduct of the agglomeration process. It should be noted that the dust due to the developed surface contains a significant amount of adsorbed sulfur oxide (IV).

The phase elemental composition of the dust was determined in the Central Analytical Laboratory of the SHSZ. Lead is present in the form of oxides and sulfates for 80% of the total amount of this element; rhenium is present in the form of oxides of various degrees of oxidation (IV, VI) and perrenates, 12-in the form of rhenium (VII) sulfide; zinc-in the form of sulfate and oxide for 87; cadmium-in sulfate and oxide forms 39 and 60 in the form of sulfide (table 9).

The generalization of the research results showed that the largest amount of rhenium is found in the dust of the agglomeration of lead production, significantly ahead of all other materials studied; the content of rare earth metals in phosphogypsum is not of interest due to its low content. Methods of the utilization of phosphogypsum with the production of commercial products in the form of building material and an alternative version of the drug "Majef." Since the phosphogypsum obtained during processing contains soluble phosphates, phosphoric acid can be obtained by mixing manganese ore and iron-containing materials. The drug "Majef" is used for ferrous metals, which includes manganese salts $Mn(H_2PO_4)$ and $Fe (H_2PO_4)_2$. These compounds form an inseparable whole with the metal, changing the nature of the surface and making it passive in terms of corrosion. According to their physical properties, these solutions are very stable. The production technology is very easy, allowing you to obtain a high-quality phosphate film of anti-corrosion action. The concentration of the drug "Majef" is 30-35 g/l, the solution temperature is maintained at 96-98 °C.

Table 9 - Phase elemental composition of lead production dusts

Connection forms	Relative content, %	Connection forms	Relative content, %
PbO	18,00	TlO_2	10,50
$PbSO_4$	63,50	Tl_2O_3	59,50
Pb	0,880	Tl_2SO_4	29,20
PbTe	0,100	Tl_2S	0,800
$Pb_3(AsO_4)_2$	17,32	As	8,000
$ZnSO_4$	64,60	$As_2O_3+As_2O_5$	2,200
ZnS	12,80	$Pb_3(AsO_4)_2$	57,60
ZnO	22,60	As_2S_2	20,10
$CdSO_4$	21,90	ReO_4^-	50,00
CdO	17,30	ReS_2	12,00
CdS	60,70	$ReO_2+Re_2O_3$	40,00
Hg	83,30	HgSe	6,600
HgS	10,10	and other difficult-to-dissolve compounds	0,500

Thus, the metals of interest to us in agglomerates are in sulfate, oxide and sulfide forms.

More than 30 samples of phosphogypsum were selected and examined from the storage unit of Kazphosphate LLP. According to the calcium sulfate content, phosphogypsum from dumps belongs to grade 1 gypsum raw materials according to GOST 4013. Fluctuations in the content of calcium sulfate for phosphogypsum - from 74 to 77 %. The total content of impurities does not exceed 23-27 %. These include non-bound phosphoric and sulfuric acids, potassium, sodium and calcium phosphates, potassium and sodium silicofluorides, and others. To prevent the ingress of acidic water into the environment, a screen of plastic film and a special moat with a dam around the sludge accumulator are arranged in the storage tank.

The technical conditions for EFC production allow the content of orthophosphoric acid and phosphates to be dissolved in water (according to P_2O_5) up to 0.5-0.7% and fluorides up to 0.15-0.20 % (according to F -) in phosphogypsum. A significant excess of this level in some samples indicates the instability of the process parameters. Acid phosphogypsum is a corrosion-active material, and special equipment made of alloy steel is required for its processing.

In the production of Portland cement, the phosphates and fluorides contained in it, which are soluble in water, have a negative impact on the quality of the clinker and cement obtained.

Foreign technologies for the utilization of phosphogypsum provide for removing part of the soluble phosphates, fluorides and other impurities by washing. At the same time, 2 to 5 m^3 of water is consumed per 1 ton of phosphogypsum, wastewater is subject to neutralization or evaporation, increasing production costs.

The CaO-P_2O_5-H_2O system has a number of features that need to be taken into account. At molar ratios of CaO/P_2O_5 from ∞ 1, regardless of the initial stoichiometry of the reacting substances, the initial reaction product is always metastable X-ray amorphous calcium phosphate, characterized by a CaO/P_2O_5 ratio above 3.5 and having a high shielding ability. The formation of the latter is characteristic of most processes of neutralization of phosphogypsum and is undesirable since its further transition to a three-substituted form is very slow (tens of hours), which is unacceptable from the point of view of technological processing).

The duration of the existence of this intermediate phase is reduced with a decrease in the CaO/P_2O_5 ratio and an increase in the intensity of mixing of the suspension. The liquid phase of activated phosphogypsum is a complex solution containing more than twenty impurities, calcium sulfate and neutralization reaction products. The processes of ion-molecular interaction occurring in liquid layers lead to the formation of film gels. During diffusion, liquid shells play the role of a matrix for strengthening coagulation contacts, i.e., they perform the functions of an adhesive component-an adhesive.

When optimizing the activation parameters of phosphogypsum, the influence of its humidity was determined.

When assessing the optimal moisture interval of phosphogypsum, we proceeded from the criteria adopted in soil mechanics for determining the plasticity of heterogeneous systems consisting of three phases − granular material, water, air – the limits of plasticity, sometimes called the Atterberg limits in the literature.

They are characterized by the water content at the critical points that define the boundaries between the system's liquid, visco-plastic and bulk states. The upper limit corresponds to a humidity value at which the water layer between the particles is large enough that, with a weak mechanical action, the molecular bonding forces cease to hold them close to each other while the system turns into a suspension. The lower limit characterizes the state of the system, in which the sorbed water is contained in sufficient quantity to move under mechanical action on the surface with the formation of a mirror. This limit determines the minimum moisture content at which all the free space between the particles is filled with water, and the system turns from a three-component system into a two-component one. The interval between the lines characterizes the visco-plastic state of the system.

Based on the Atterberg limits, the optimal humidity of phosphogypsum was assumed in the range from 15 to 20 %.

The chemical composition of waste from overburdened rocks of ore materials of Bolshoy Karatau was determined in an inductively coupled plasma mass spectrometer VARIAN-820MS. The composition is presented in Table 10 and Figures 1.

Table 10-Composition of overburden rocks of Bolshoy Karatau

Name of indicators	Spectrum							
	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8
O	41,93	44,16	44,36	34,83	47,85	36,24	29,50	54,73
Al				0,18		0,21		1,06
Si	0,47	0,14	0,10	2,78	0,38	11,03	3,83	39,61
P				11,08		0,63	11,86	
S		12,79	12,68		12,80	0,43	0,15	0,97
K		7,38	7,16		7,37	0,15		0,66
Ca				0,26		0,71	0,25	1,31
Ti	57,29				0,13			
V	0,41	0,12	0,20		0,11	0,63		
Cr						0,55		0,77
Fe		31,29	31,53		31,20	52,14		
Cu						0,52		
Ba		0,47	0,51					
La				16,51			14,95	
Ce				24,30			21,90	
Pr				2,94			2,44	
Nd				10,57			9,22	
Sm				0,82			0, 94	
Th				0,62			0,46	
Total	100,10	96,34	96,53	104,89	99,84	104,09	95,51	99,09

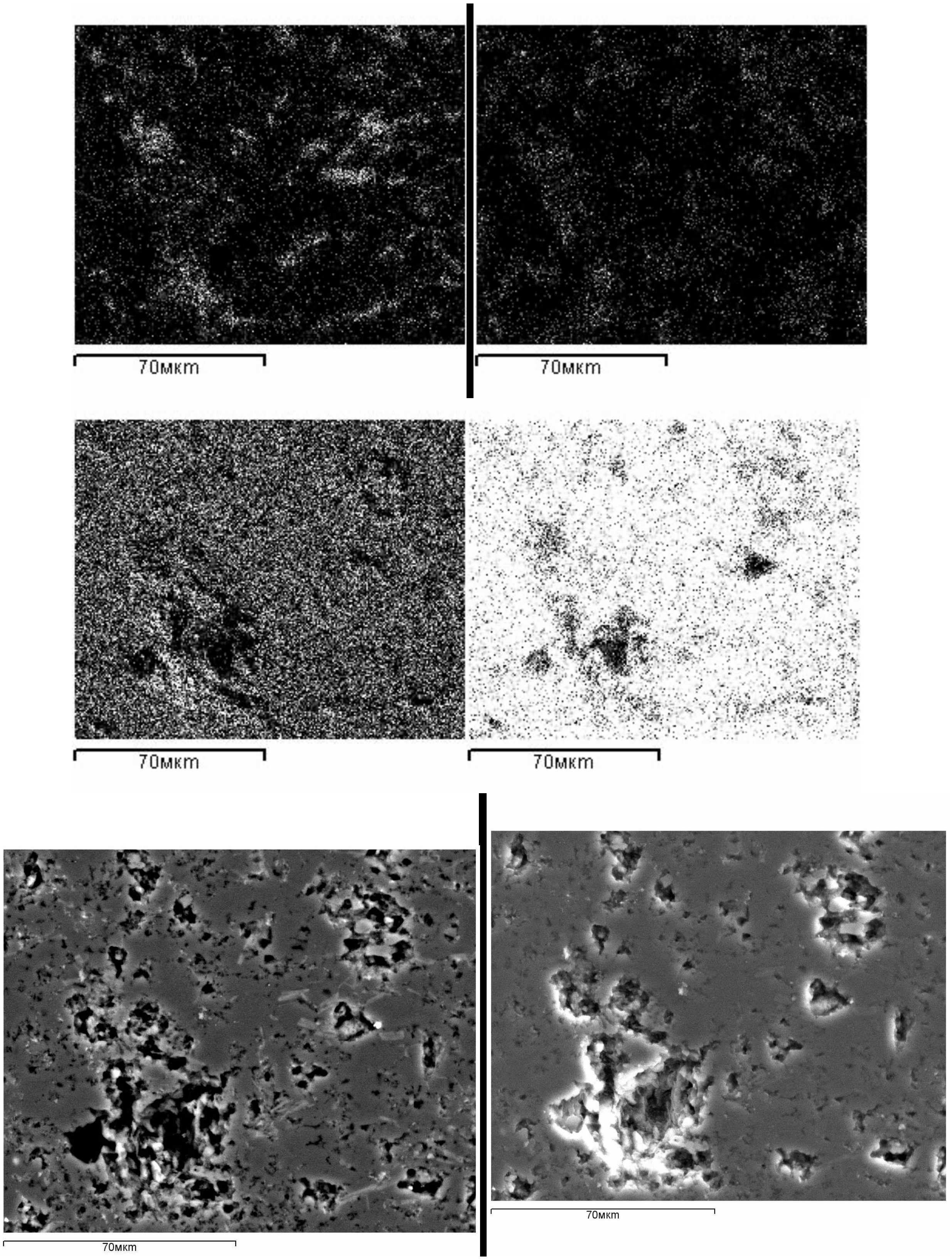


Figure 1 - Micrograph of overburden rocks of Karatau

It is necessary to expand the work on the study of other technogenic waste, primarily waste from the uranium industry. A feature of the uranium deposits of Kazakhstan is a wide variety of types according to mineralogical and physicochemical compositions. Many types of uranium ores are complex in composition and contain such valuable components as molybdenum, vanadium, tungsten, zirconium, rhenium, rare earth elements, etc. The separation of rare earth elements into a collective concentrate will allow:

- expand the range of products;
- to enrich the domestic and world market with valuable products.

The relevance and practical significance of the research work carried out are due to the need for the integrated use of uranium-containing raw materials and the increased global demand for rare and rare earth metals, which is not provided by the sources of rare earth raw materials currently being developed in the CIS and Kazakhstan.

Extraction of associated components from productive solutions of the uranium industry, enriched with rare and rare earth elements, is methodologically and practically quite a difficult task. This is due to the lack (for a subsurface user – a complete lack) of information on the technical and economic indicators of the extraction of associated useful components and the variety of their possible commodity forms (collective product, oxides, salts, metals of various degrees of purification, characterized by different yield, price and other technical and economic indicators).

Until now, manufacturers have not faced the direct task of extracting rare and rare metals as commercial products of hydrometallurgical production. At the processing stages of productive solutions, classical schemes for the extraction of metal ions and their complex anions are mainly used, such as sedimentation, extraction and ion exchange sorption or their combinations. However, there are progressive methods for concentrating rare and rare earth metals from waste solutions and ash and slag waste using membrane separation processes and electrical influences.

When performing analyses of samples of productive and leaching solutions for the content of REM and rhenium, the methods described in section 2 of the current report were used. The results of chemical analyses of uranium-containing ores are presented in Table 11.

Table 11-The content of REM and rhenium in uranium solutions of the PV-19 mine

Element	Sampling month						Average ± standard. Off.
	march	April	may	June	July	august	
La, mcg/l	4489	5000	5246	5189	5969	4879	5047 ± 429
Ce, mcg/l	11479	11793	14376	12382	15243	14053	13155 ± 1349
Pr, mcg/l	1296	1143	1448	1601	1610	1395	1378 ± 156
Nd, mcg/l	4783	4812	5587	5326	6623	4988	5415 ± 581
Sm, mcg/l	989	964	1123	1489	1521	1302	1198 ± 199
Eu, mcg/l	224	225	291	315	340	235	255 ± 52

Gd, mcg/l	2285	1296	1863	1491	1958	1659	1590 ± 356
Tb, mcg/l	150	162	131	162	237	202	167 ± 32
Dy, mcg/l	783	746	1023	901	1157	1020	908 ± 124
Ho, mcg/l	135	150	181	143	203	187	163 ± 21
Er, mcg/l	331	362	482	364	520	418	416 ± 60
Tm, mcg/l	43.8	42.9	51.3	59.1	64.1	55.6	51.2 ± 6,8
Yb, mcg/l	263	298	301	352	366	286	286 ± 60
Lu, mcg/l	34.1	36.8	42.4	39.2	49	45.3	41.6 ± 4.9
Re, mcg/l	253	220	234	289	276	261	251 ± 21

As shown from Table 11, the content of rhenium and rare earth metals in solutions of the uranium industry varies between 0.25 and 25 mg/l. The ISP MS method analysis was carried out in the regional testing laboratory of the engineering profile "Structural and biochemical Materials."

The general characteristics of the methods of analysis of ores, rocks and enrichment products are presented in Table 12.

Table 12-General characteristics of methods of analysis of rocks, minerals of ores and products of enrichment

Type of analysis	Method	Analyzed elements	The interval of the determined content
Chemical, Physico-chemical	Gravimetric	Be, Ni, Mo, Ba, W, Th, ΣРЗМ	$n10^{-2}$ - n10
	Titrimetric	B, Co, As, Zr, Ag, Sn, Sb, TR, U	$n10^{-2}$- n10
	Photometric	Ga, Ge, In, Be, Te, Re, U Zr, Ru, Rh, Pd, Ta, Os, Ir, Pt, Th Ti, V, Mo, Sn, Sb B, ΣРЗМ, Ti	$n10^{-5}$ - $n10^{-2}$ $n10^{-4}$ - $n10^{-1}$ $n10^{-3}$ - $n10^{-1}$ $n10^{-2}$ - n10
	Electrochemical	Mo Tl, Po Ge, Sn, Re, Bi	$n10^{-6}$ - $n10^{-1}$ $n10^{-5}$ - $n10^{-1}$ $n10^{-4}$ - n
	Kinetic	Ru, Re, Os	$n10^{-7}$ - $n10^{-4}$
Optical spectral	Emissive	Mo, Rh, Pd, Pt, Au Yb, W, Ir, Bi Be, Ge, Y, In, Cs, La, Ce, Pr, Nd, Sm, Er, Hf, Ta, Tl, Th Ti, V, Ga, Zr, Cs, Cd, Ly, W Sr, U	$n10^{-6}$ - $n10^{-1}$ $n10^{-5}$ - $n10^{-1}$ $n10^{-4}$ - $n10^{-1}$ $n10^{-3}$ - $n10^{-1}$ $n10^{-2}$ - n1
	Atomic absorption	Pd, Te, Au Cd, Ag,Pt	$n10^{-6}$ - $n10^{-3}$ $n10^{-4}$ - n

		Sr, Mo, Sb, Cs, Bi V, Cr, Sn Ti, W	$n10^{-3}$ - n,n10 $n10^{-2}$ - n,n10 $n10^{-1}$ - n,n10
X - ray spectral	Fluorescent	Rb, Y, Th, U Ti, As, Se, Zr, Nb Cs, Ta	$n10^{-4}$ - n $n10^{-3}$ - n10 $n10^{-2}$ - n10
Nuclear-physical, elemental	X - ray radiometric	Ti, V, Zr, Nb, Mo, Ta, W, Sr, Sn	$n10^{-2}$ - n10
	Activation	Sc, As, Se, Mo, Ru, Ag, Sb, Te, Cs, La, Ce, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Au, Th, U	$n10^{-7}$ - $n10^{-1}$
	Photoneutronic	Be	$n10^{-3}$ - n10
	Neutron absorption	Li, B, Cd	$n10^{-2}$ - n
	Radiometric	Ra, Th, U	$n10^{-4}$ - n10
Isotopic	Mass spectrometric	Изотопы элементов: Li, B, Ar, Sr, Mo, Rb, Ra, U, Th	$n10^{-7}$ - $n10^{-8}$
	Isotope-spectral	Cu, Zn, Pb	$n10^{-3}$ - $n10^{-1}$

It should be noted that there is some conditionality of dividing methods into chemical, physicochemical and physical. There are also other classifications. In recent years, the so-called combined methods of analysis have been developed, including chemical-spectral, extraction-atomic-absorption, and extraction-photometric methods. These methods combine the preliminary chemical preparation of the sample (separation, concentration) with the subsequent determination of the content of elements by physical or physicochemical methods.

Currently, the need to be guided by the norms of European Standards entails a change in the requirements for testing methods of manufactured products. The European standards often change the range of concentrations of detectable impurities or introduce elements that were not normalized by the regulatory documents in force in Kazakhstan. The production of new types of commercial products of rare metals (alloys for various purposes, fine powders, etc.) forces us to improve the old or create new analytical control methods to produce comparison samples of the appropriate composition. The production of standard samples of the MSO, GSO, SOP grades is a long and expensive process. It can be avoided by applying the method of inductively coupled plasma atomic emission spectrometry (ICP) for the analysis of metals. Modern mass spectrometry is one of the most subtle and sensitive methods of substance analysis. It is characterized by the lowest limits for detecting traces of elements during their simultaneous registration [18]. The mass spectrometric method determines the elemental and molecular composition of various natural and synthesized substances [19], studies the kinetics of chemical reactions and measures the binding energy between atoms and between molecules [20], identifies chemical compounds and deciphers the structure of molecules [21], measures the presence of micro-impurities at a level of less than 10-8 % in semiconductor materials and metals.

The South Kazakhstan State University, named after M. Auyezov, has modern devices on its material and technical base in the regional testing laboratory of the engineering profile "Structural and biochemical materials", such as:

-VARIAN-820MS inductively coupled plasma mass spectrometer (measurement of elements from beryllium to uranium with an accuracy of 1*10-9 in technical solutions and solid products),

- scanning electron microscope JSM-6490LV (study of the microstructure and texture of polycrystalline materials);

- two-beam scanning spectrophotometer Cary-50 Scan (measurement of the concentration and kinetics of chemical processes in research products).

Such advantages of the presented devices as high stability of discharge radiation, rapid measurement, ease of calibration, the possibility of simultaneous multi-element determination of macro - and micro-components, poorly developed matrix interference led to the rapid introduction of these analysis methods into the practice of many research and industrial laboratories. The number of publications on the study of the characteristics of the ICP method and its application to the analysis of various objects is constantly increasing. For example, the analysis of minerals and ores containing niobium and tantalum belongs to analytical chemistry's most complex and difficult sections. First of all, the difficulties are explained by the complexity of the chemical composition of niobium and tantalum minerals. The analysis of this type of minerals by chemical methods requires a large number of separation operations, which can lead to errors due to losses of the analyzing element, not to mention errors due to the proximity of the chemical properties of niobium, tantalum and related elements (especially transition elements of groups IV and VI of the periodic table). Most of the analysis methods used (chemical, spectral, chemical-spectral, electrochemical, spectrophotometric, X-ray spectral, etc.) are labor-intensive, require preliminary concentration, separation of interfering components, separate determination of each of the analyzed elements, and at the same time do not always give reliable results, since a large number of operations can lead to errors caused by losses. To eliminate these effects of analytical control of samples of rare metals using mass spectroscopy methods, it is possible to use the method of autoclave decomposition of the sample. The method of autoclave mineralization of samples using analytical autoclaves for the subsequent determination of the content of rare metals and rare earth elements by atomic spectrometry (atomic absorption spectrometry with atomization in a flame, in a graphite furnace and using the technique of generating hydrides, atomic emission spectrometry with inductively coupled plasma) and inversion-voltammetric method and are intended for laboratory studies of the chemical composition of the raw materials under study.

Preparation of samples according to the classical scheme, which provides for drying and decomposition (dissolution in acids, evaporation, and sometimes salting), takes 2-11 hours (the time of the analysis itself is 2-3 minutes). Moreover, the longest stage is the dissolution of samples in acids (from 30 minutes to 8 hours). In addition, being the longest stage of the sample analysis process (up to

61% of the total time), sample preparation introduces the largest error in the final results. Analytical autoclave of the MKP-05 type (Ankon-AT, Russia), placed in a resistive furnace (there are from two to six) in the installation. The autoclave itself – the reaction chamber-is a fluoroplastic vessel with a sealing cap, in which the sample is located together with the acid. The chamber is placed in a metal case, and sealing is carried out by compressing the spring when the pin is twisted into the upper lid of the autoclave. Due to good sealing, the acid vapor pressure that occurs in the autoclave leads to an increase in its boiling point and accelerates the decomposition of the sample into elements. In such an installation, the time of dissolution of any organic and inorganic material with the help of an appropriate acid mixture is only 15-30 minutes. According to Milestone specialists, this design allows the decomposition process to be carried out at a pressure of up to 200 bars and above and bring the temperature of the acid mixture to 270 of [22].

The calcium content in phosphogypsum of intermediate and final products (solutions) was determined by flame photometry and trigonometric titration in the presence of an indicator of eriochrome black T. The sum of rare earth elements, impurities of silicon, iron, titanium, magnesium, aluminum and manganese was determined by the spectral method. The paper presents the results of the extraction of rare earth elements from fosmel obtained by converting phosphogypsum with ammonium carbonate to produce ammonium sulfate. The degree of extraction was 99.5 % of their content in phosphogypsum. There is a known method of leaching rare earth elements from phosphogypsum with sulfuric acid, extraction of rare earth elements in order to obtain a commercial concentrate of rare earth elements.

Wastes of the chemical and metallurgical industry (cake, dust, waste solutions) contain a number of rare metals, in particular such an element as rhenium. For its industrial production, it is necessary first of all to extract into productive primary materials, which primarily include the so-called technological solutions. Depending on the rhenium content in the initial products, the rhenium concentration ranges from 0.006-0.03 g/dm^3. One of the most effective methods for determining the rhenium content in such solutions is the method of spectrophotometry – a physicochemical method for studying solutions and solids based on the study of absorption spectra in the ultraviolet (200-400 nm), visible (400-760 nm) and infrared (>760 nm) spectral regions, i.e., in the nano-range.

In the course of the work, the main metrological characteristics of the developed methods were determined, such as reproducibility, repeatability and accuracy of the analysis. Based on these data, relative measurement errors were calculated for several ranges of elements' concentrations. When determining metrological characteristics, standard samples were used' entered into the State Register of the Republic of Kazakhstan IAEA SL-1, IAEA SL-3 и IAEA Soil-7, containing certified values of rare earth metals and renia.

The method based on the analysis of samples using neutron activation analysis is focused on the determination of the contents of rare earth metals and rhenium in solid samples in the concentration range from 0.00001% to 10% with a relative error of 3.5% to 28% and can be used for the analysis of liquid samples in the case of their preliminary drying. In this case, the samples are irradiated at the research reactor with a stream of thermal neutrons. The contents of the elements of interest are determined based on the measured gamma activity of the corresponding radionuclides. The analysis time of the batch of samples under study ranges from several days to several weeks, depending on the elements being determined and the required sensitivity.

The technique 'based on the analysis of samples using X-ray fluorescence analysis is focused on determining the contents of rare earth metals and rhenium in solid samples in the concentration range from 0.0001 % to 10 % with a relative error of 2.5 % to 22 % and can be used for express analysis of liquid samples in the case of their preliminary drying. When calculating the contents of the elements of interest, the characteristic spectrum of secondary X-ray radiation results from X-ray quanta's interaction with an energy of 22.1 keV (Cd109 isotopic source) and 59.5 keV (Am241 isotopic source) with the atoms of the sample is analyzed. The analysis time of one sample can vary from 20 minutes to 1 hour, depending on the required sensitivity.

The method 'based on the analysis of samples using the method of inductively coupled plasma with mass separation' is focused on the determination of the contents of rare earth metals and rhenium in liquid samples in the concentration range from 0.0000001 % to 0.01 % with a relative error of 5 % to 15 % and can be used for the analysis of solid samples in the case of their preliminary decomposition. In the case of high concentrations of detectable elements' or highly mineralized samples' study, preliminary dilution of the sample is required. The analysis time of a single sample can range from 5 to 30 minutes, depending on the range of elements to be determined.

The technique 'based on spectrophotometric analysis' is designed to determine the total content of rare earth elements and yttrium in the concentration range from 0.0003 to 5%, with permissible discrepancies between repeated definitions from 5% to 80 %.

Sampling, storage and preparation of samples

The customer carries out sampling in accordance with the regulatory documents for sampling' valid at the customer's enterprise' or the regulatory documents' valid on the territory of the Republic of Kazakhstan and approved by the competent authorities.

The samples are stored at a temperature of 15 ° C to 25 ° C and humidity exceeding 80 %.

Solid samples. Open decomposition.

On the analytical scales, a sample weight of 0.01 – 0.10 g is taken. The sample weight is placed in a fluoroplastic cylinder (PTFE, Viton, Teflon, PFA), 0.2 – 1.0 ml of concentrated nitric acid is poured, covered with a protective laboratory film and placed in a thermoblock heated to 115 ° C, kept for 0.5 – 1.0 h until the sample is completely dissolved. The dissolved sample is quantitatively transferred to a measuring polypropylene tube, washed three times from the walls of the cylinder, and brought to 10 ml with deionized water. It is hermetically sealed with a protective laboratory film, mixed and passed for analysis.

Liquid samples. Open decomposition.

The weight of the analyzed object 0.1-0.5 g (0.1 – 0.5 ml) is taken on analytical scales in fluoroplastic cylinders (PTFE, Viton, Teflon, PFA), determining the weight of the sample by the difference in the mass of the test tube before and after taking the sample. 0.3 – 1.0 ml of concentrated nitric acid is poured into the cylinder, covered with a laboratory film and placed in a thermoblock heated to 115 ° C. They are kept in a thermal block for 0.5-1.0 h until the sample is homogenized and then act as described above for the decomposition of solid samples

When working with homogeneous aqueous media, it is allowed to simply dilute the sample with 2-3% nitric acid immediately before analysis. To do this, 5-7 ml of deionized water is added to the sample in a measuring tube, then 0.3-0.5 ml of concentrated nitric acid and the sample is brought to 10-15 ml of deionized water. In this case, it is not recommended to reduce the dilution factor of the sample below 1:100.

Microwave sample preparation.

A weighed sample is placed in a fluoroplastic insert, and 5 ml of nitric acid is added. The autoclave with the sample in the insert is placed in a microwave oven, and the sample is decomposed using the decomposition program recommended by the oven manufacturer. In general, the following heating mode is used: raising the temperature to 200 ºC within 5 minutes, holding for 5 minutes, at 200 ºC, cooling up to 45 ºC. The cooled autoclave is shaken to mix the contents, and the lid is opened slightly to equalize the pressure. A qualitatively decomposed sample after distilling off nitrogen oxides should be a colorless or yellowish transparent solution without undissolved particles on the bottom and on the walls of the insert. The dissolved sample is quantitatively transferred into a 15 ml test tube by shaking the insert with a lid with 1 ml of deionized water three times and transferring each wash to a test tube; adjust the volume to 10 ml with deionized water, close and mix. An aliquot of 1 ml is taken with an automatic dispenser with a replaceable tip and adjusted to 10 ml with 0.5% nitric acid, covered with a protective laboratory film, and transferred for analysis. The data on the volume of the aliquot part and the volume of the dilution are entered into the software of the spectrometer along with the name and weight of the sample. Direct sampling of 0.1 - 0.5 ml aliquots from a decomposed sample in an autoclave is allowed. To compensate for the dilution error, an internal standard solution (In or Rh) must be added to the sample before digestion so that the standard internal concentration in the final solution sent for analysis is approximately 10 mkg / l (for example, add 100 mkl of the solution to the sample, containing 10 mg / l Rh, then take an aliquot of 0.5 ml from 5 ml of the decomposed sample and makeup to 10 ml). The internal standard solution must be added to all blanks and calibration solutions. The target concentration of the internal standard (10 mkg / l) in blanks and standard solutions must be strictly observed. A blank sample solution is prepared with the performance of all the above operations, except for the operation of taking a sample.

One of the modern devices in the field of spectrophotometry is the VARIAN Cary-50 spectrophotometer, which allows you to determine the concentration of rhenium in a large number of samples and in a short time.

In solutions, rhenium is usually found in the form of heptavalent oxide Re_2O_7. To detect it, it is necessary first of all to convert it into a complex compound, which allows it to be stained in a certain color for further comparison with a standard solution and subsequent calibration of the obtained data using a spectrophotometer. Based on the readings of the standard solution, a calibration graph is built, with which the data of the analyzed solution is compared. The measurement technique applies to productive (technological) solutions obtained in the process of leaching waste from the metallurgical and chemical industries and establishes a photocolorimetric method for determining the mass fraction of rhenium in the concentration range of 0.006 - 0.03 g / dm^3.

The technique is intended for the quantitative analysis of rare earth elements (La, Ce, Nd, Pr, Sm, Eu, Gd ,Tb, Dy, Ho, Er, Tm, Yb, Lu) and rhenium in samples of rocks, ores, minerals and technological products of uranium production and establishes the procedure for determining the mass content of the analyzed elements.

The methods described above were used when analyzing samples of productive and leaching solutions for the content of rare earth metals and rhenium in them. In addition, analyzes using the ICP MS method were carried out at the M. Auezov South Kazakhstan State University on its own material and technical base in the regional engineering testing laboratory "Structural and biochemical materials". In this case, no special sample preparation was required except for the necessary dilution of the sample with bidistilled water.

2 VANADIUM-CONTAINING TECHNOGENIC WASTE

The revolutionary changes in the chemistry and technology of vanadium are closely related to the change in fundamental ideas about the Spatio-temporal evolution of the formation of its compounds. Unfortunately, the history of the development of scientific concepts in the chemistry and technology of vanadium is full of amazing delusions and errors that have catastrophic environmental consequences. Misconceptions include the use of:

- the methodology of equilibrium thermodynamics, the Baikov principle of the sequence of transformations and jump-like structural transformations in vanadium salt systems;
- systems of principles of vanadium oxidation in spinels and converter slags;
- the theory of electrolytic dissociation to explain the various ionized forms of vanadium (+ V) in aqueous solutions, for example, potentiometric studies of the formation of decavanadic acid and the numerous family of poly vanadium acids;
- the theory of hydrolytic sedimentation of vanadium from aqueous solutions.

Vanadium is one of the important metals widely used in various fields.

2.1 Developed vanadium catalysts

Vanadium is a component of high-speed steel, its substitutes, low-alloy tool steels and some structural steels. Vanadium introduced into steel is both a deoxidizing and carbide-forming element. Alloys based on niobium, chromium and tantalum-containing vanadium additives are used in aviation, rocket and other fields of technology. Various heat-resistant and corrosion-resistant vanadium-based alloys with the addition of other metals are being developed for use in aviation, rocket and nuclear engineering. Pure vanadium metal is used in the nuclear power industry (cladding for fuel elements, pipes) and in the manufacture of electronic devices. Compounds of vanadium are used in the chemical industry as catalysts, in agriculture and medicine, in textile, paint and varnish, rubber, ceramic, glass, photo and movie industries.

For direct extraction of vanadium from vanadium-bearing material, the raw material must have a special property that would allow the maximum amount of ore to be treated with a minimum amount of acid. Acid leaching and acid pressure leaching will be effective when H_2SO_4 is used as a reagent. Sulfuric acid destroys the structure of many materials, resulting in a byproduct that has the property of preventing metal leaching from vanadium-bearing feedstock, affecting the degree of vanadium recovery while having no effect on the cost of production.

Vanadium is insoluble in water, non-oxidizing acids and liquid alkali, but is converted to trivalent vanadium, which as an isomorphic substance is replaced (acid+metal) by the crystal lattice Al, and when interacting with acid creates a very strong structure, which is not easy to destroy and release vanadium ions.

The chemical formula for the process is as follows: $(V_2O_3)\cdot X+2H_2SO_4\cdot 1/2O_2=V_2O_2(SO_4)+2H_2O+XO$

$V_2O_2(OH)_4+2H_2SO_4=V_2O_2(SO_4)_2+4H_2O$

For vanadium leaching from various industrial technogenic wastes a standard system of low-temperature vanadium extraction about a standard hydrometallurgical scheme is used: "leaching - separation - enhancement (enrichment) of mother liquor - filter press - ion exchange - ammonium sedimentation (ammonia) - ammonium methavanadate - ammonium pyrolysis - V_2O_5".

The great advantage of using this technology, as compared to conventional methods, is that no combustion products are released with exhaust gases. Wastewater is purified and the tailings go for secondary treatment (secondary production). The vanadium recovery factor is high, this technology is promising.

2.2 Sorption technology for the production of ammonium metavanadate from used vanadium catalysts leaching solutions

Spent vanadium catalysts provided from the production of vanadium in Kyzylorda region (Balausa LLP) were selected as feedstock on the basis of an agreed memorandum of cooperation.

Vanadium was leached with sulfuric acid solutions, followed by sorption mother solutions. The first run of the leaching solution in the volume of 7,500 cm^3 is carried out with sulfuric acid solutions (H_2SO_4 in – 1.5-2.0%) for 3 days by percolation in laboratory conditions. Sorption mother solutions with a density of 1.067 g/cm^3 containing 0.1-0.3g/l V_2O_5 with a pH of 1.0-1.5 were fed to the second and subsequent runs, the total content of sulfates did not exceed 100g/l. The total number of runs is 9, the total volume of V-solutions will be 67,500 cm^3. Sorption mother solutions, due to their high acidity, are diluted to an H_2SO_4 content of 1.5%.

The obtained vanadium-containing solutions are pre-filtered on a vacuum installation (Figure 2), the degree of oxidation of vanadium due to the content of restorative substances in the solutions is E_H +3. In such production solutions, vanadium has the form of vanadyl ($VOSO_4$). For solutions with a salt content of 120-140 g/l, it is necessary to choose the optimal variant of the types of oxidants for the oxidation of vanadium into a 5–valence form. This is due to the refining of 5-valent vanadium by anionite ion exchange resins. We have carried out work on the selection of the optimal oxidizer for the oxidation of vanadium into a pentavalent form (table 13).

Initial data: Initial vanadium solution: pH =1.37; V_{tot}=4.83g/l; Fe^{2+} = n/o; R_{tot} = 1.6g/l, salt residue – 120 g/l.

Table 13 – Selection of the optimal oxidizer for vanadyl ion oxidation

Type of oxidizer		Volume of the initial solution, ml	Oxidizer		Oxidized solution					Filtration rate, sec	Sediment		Note
			Method of submission	Oxidizer consumption, kg/m^3; ml/l	pH	V^{5+} g/l	V^{4+} g/l	Oxidation degree, %	P_2O_5, g/l		Weight, gr	V_{tot}, %	
Oxygen oxidizers	1. MnO_2 pyrolusite	200,0	1. fully	2,5	1,37	0,53	0,3	64,0	1,8	500	2,7	0,18	Takes a long time to filter
			2. partially	0,625 0,625 0,625 0,625	1,35	0,48	0,35	58,0	2,35	387	2,9	0,13	Takes a long time to filter
	2. $(NH_4)_2S_2O_8$ ammonium persulfate	200,0	1. fully	8,85	1,31	0,38	0,45	46,0	2,25	-	-	-	Lowers the pH
			2. partially	2,2 2,2 2,2 2,2	1,31	0,25	0,58	30,0	2,55	-	-	-	Lowers the pH
	3. CaO_2 CO_3 Calcium bicarbonate	200,0	1. fully	2,5	1,41	0,45	0,38	55,0	2,6	660	0,73	0,07	Rapid boiling
			2. partially	0,625 0,625 0,625 0,625	1,43	0,45	0,38	55,0	2,0	250	0,52	0,12	Rapid boiling
	4. H_2O_2 hydrogen peroxide	200,0	1. fully	2,5	1,33	0,8	0,03	98,0	2,6	-	-	-	A day later, the color of the solution was restored
			2. partially	0,625 0625 0,625 0,625	1,31	0,78	0,05	96,0	1,9	-	-	-	After a day, the color of the solution has not changed
	5. $H_4(O_2)SO_4$ Peroxymonosulfu	200,0	1. fully	2,5	1,28	0,5	0,33	63,0	2,6	-	-	-	Slow brown coloring
			2. partially	0,625 0625 0,625 0,625	1,29	0,52	0,31	64,0	2,6	-	-	-	Slow brown coloring

	ric acid												
	6. $Ca(OCl)_2$ Calcium hypochlorite	200,0	1. fully	10,0	1,56	0,45	0,3	55,0	2,6	150	3,3	0,1	Sediments do not dissolve, mixed with flakes, blurred
			2. partially	2,5 2,5 2,5 2,5	1,52	0,43	0,32	52,0	2,1	97	3,1		Sediments do not dissolve, mixed with flakes, blurred
	7. $NaOCl_2$ Sodium hypochlorite	200,0	1. fully	10,0	1,44	0,48	0,35	58,0	2,6	-	-	-	Abundant release of gas (chlorine)
			2. partially	2,5 2,5 2,5 2,5	1,41	0,43	0,4	52,0	2,6	-	-	-	Abundant release of gas (chlorine)
	8. $HClO_4$ perchloric acid	200,0	1. fully	1,0	1,34	н/о	0,83	0,0	2,6	-	-	-	Abundant release of gas (chlorine)
			2. partially	0,25 0,25 0,25 0,25	1,34	н/о	0,83	0,0	2,6	-	-	-	Abundant release of gas (chlorine)

*** Oxidation time - 30 minutes**

Figure 2 - Vanadium-containing solution, after leaching

Vanadium oxidation

Oxidation of vanadium-containing solution from the heap is carried out in two ponds operating alternately. Vanadium-containing solution at a rate of 12.5m^3/hour is sent for oxidation to the first pond, where it passes through a battery of manganese concentrate of Zhairemskoye deposit (the content of manganese dioxide 43-47%) in the amount of 36 tons. The battery represents 20-25 nets with manganese concentrate, which is packed in 1,5-2,0 tons in each grid. After a month, the vanadium-containing solution from the pile is switched to the second pond, also filled with a battery of manganese concentrate in the amount of 36t. The spent manganese concentrate from the first pond is extracted by a truck crane, sent for oxidizing roasting and returned to the technological cycle. An oxidized productive solution is sent for sorption.

Vanadium sorption

Productive vanadium solution after oxidation is fed for sorption to SNK-1.5 columns loaded with Ambercep sorbent and operating in a periodic wandering mode. Productive vanadium solution is pumped through five sorption columns at a rate of 12.5m^3/hour. The sorption mother solution is sent to the solution preparation pond for pumping to the heap. After saturation of the sorbent in the first two columns (SNK-1,5) with vanadium compounds to V_2O_5 content of 250 kg/t and 200 kg/t, the first column is switched to the double-column sorption mode, and the second column continues to saturate with vanadium to V_2O_5 content of 250 kg/t.

Technical mode:

- pH of the solution entering the 1st sorption column 2.0-2.2 V_2O_5 content 1.75- 2.25 g/l;
- V_2O_5 content on the sorbent in the 1st column 250 kg/t;
- V_2O_5 content on the sorbent in the 2nd column 200-250 kg/t;

- The pH of the solution entering the 2nd sorption column is maintained at 2.0-2.2;
- the pH of the mother solution coming out of the 2nd column of sorption is 1.8-2.0, the content of V_2O_5 is not more than 0.2 g / l.

Preparation of vanadic acid solution.

A solution of vanadium acid with a variable polynuclear complex is prepared from the current ammonium metavanadate at the rate of 15-30g / l V_2O_5 pH 3.5-4.0. Ammonium metavanadate (MVA) – 1.5-2.0 tons is loaded into a reactor with a stirrer and 10-12 m^3 of water is poured, which is heated to t-60-70^0C. The mixing time is 1.5-2 hours. It is diluted with water to a concentration of 15-20 g / l according to V_2O_5 and neutralized with sulfuric acid to pH 3-,-4.0 and is fed to two-circuit sorption without filtration.

Two-circuit sorption

A concentrated vanadium solution of 15-20 g/l V_2O_5 and pH 3.5-4.0 is fed to the bottom SNK-1,5 containing V_2O_5 250 kg/t resin at a rate of 4-5 m^3/h. After about 2 hours, the mother solution begins to flow from the drain holes, which in the volume of 10-15 m^3 is sent to the sorption cycle.

Solid-phase desorption

In the SNK-1.5, a desorbing solution of 150-200 g / l NH_4NO_3 and ammonia water is fed through the lower part of the column at a speed of 3 m^3 / hour and air mixing. In the process of solid-phase desorption, the pH in the column is maintained at 8.5. The supply of am. water is fractional. The outgoing MVA pulp is drained through drainage cups onto filters to separate the mother liquor. The mother solution is collected in a separate container and used to prepare a desorbing agent for the next desorption cycle.

Resin separation.

The final separation of ammonium metavanadate pulp from resin is performed on the trommel. Solid-phase desorption mother solution is used as washing solution. The slurry with the fallen ammonium metavanadate crystals is drained into a two-phase settler, where the crystals accumulate in a cone and are periodically pumped through the sump into the trough of the drum vacuum - filter. In the sump, ammonium metavanadate crystals are washed from sulfates and phosphates with water to minimize the content of sulfur and phosphorus in the finished product. The content of sulaate and phosphate ions in washing solutions is not less than 1.5 g/l and 0.5 g/l, respectively.

Recharging - resin denitration

Recharging resin from NO_3^- to SO_4^{-2} form is carried out with a solution of ammonium sulfate - 150 g/l acidified to pH 1.0 with sulfuric acid. For one volume of resin three volumes of the solution are passed for 1.5-2 hours.

Through SNK with 5 tons of Ambersep $5m^3$ is passed to V_2O_5 content on the resin 8 kg/t, NO_3^- 60 g/t, SO_4^{-2} 200g/t. Washing liquor with NO_3^- concentration of 10g/l and SO_4 of 110g/l is discharged into a pond for natural evaporation. After 50% of the packed pond, ammonium sulfate $(NH_4)_2SO_4$ crystallizes and is used to prepare the regeneration solution and the mother liquor for the desorption solution.

Chemistry and physico-chemical basis of the main stages geosorption scheme of vanadium oxide production from shale Big Karatau

The leaching

The V^{4+}- Ba variety of Karatau fengite is characterized by the constancy of the chemical composition of hydroxides of elements of different oxidation states (+II, +III, +IV). The chemical reaction equation of fengite with sulfuric acid can be represented schematically.

$MeO{\cdot}Me_2O_3{\cdot}MeO_2(OH)_x + H_2SO_4 \rightarrow \downarrow CaSO_4 + \downarrow BaSO_4 + Al_2(SO_4)_3 + Fe_2(SO_4)_3$

$+ VOSO_4 + H_3PO_4 + H_2SiO_3$ (1)

The main consumption of sulfuric acid is for the formation of poorly soluble calcium and barium sulfates. To reduce the consumption of H2SO4 the process of salt conversion by the reaction

$BaO{\cdot} VO(OH)_2 + Al_2(SO_4)_3 \rightarrow \downarrow BaSO_4 + VOSO_{4ag} + 2Al(OH)SO_{4ag}$

Oxidation of vanadium (+IV) in solution

Oxidation of vanadium (+IV) in sulfuric acid medium by pyrolusite (MnO_2) occurs at pH 2.0-2.5 according to the reaction:

$2VOSO_4 + 3MnO_2 + H_2SO_4 \rightarrow H_4V_2O_7 + 3\ MnSO_4$ (2)

with the formation of vanadium acid capable of polymerization. The process of vanadium oxidation on manganese ore and dissolution of its carbonate component eventually leads to an increase in the pH of the productive solution to 2.5. The stability of the vanadium solution decreases, so the process is carried out in a dynamic mode with continuous transfer to sorption.

Vanadium (+V) sorption on Ambersep resin.

Vanadium concentration in productive solution in terms of V2O5 varies in the range of 1.75-2.25 g/l. The exchange of anionic groups of vanadium acid is carried out for sulfate-ion resin at pH 2.0-2.5 by the reaction

$R_3NHSO_4 + H_4V_2O_7 \rightarrow R_3NH_3V_2O_7 + H_2SO_4$ (3)

with an increase in acidity.

In the case of two-circuit sorption, the process is described by the equation

$R_3NH_3V_2O_7 + 4H_4V_2O_7 \rightarrow R_3NH_5V_{10}O_{28} + 7H_2O$ (4)

Solid-phase desorption.

Solid-phase desorption is carried out only from the resin saturated with vanadium in terms of V_2O_5 at least 450 kg / t. The process of solid-phase desorption is described by the equation

$R_3NH_5V_{10}O_{28} + NH_4NO_3 + 9NH_4OH \rightarrow R_3NHNO_3 + 10\ NH_4VO_3$ (5)

From equation 5 we can calculate the cost of 1.7 kg of ammonia or 3.5 kg of ammonia for one kilogram of V_2O_5. Solid-phase desorption is carried out at pH

8.0-8.5, providing coagulation of silicic acid and removal of silica from the resin. This is one of the conditions of stable operation of the sorption process and elimination of resin gelling.

Resin recharge

The conversion of the nitrate form of the resin to the sulfate one is carried out with mother solutions of ammonium sulfate at a pH below 2. In the field, it is supposed to use the resin in nitrate form without recharging for vanadium sorption. Nitrate ions will accumulate in the sorption mother liquor, the effect of which on the heap has not been studied. It is assumed that part of it will play the role of an oxidizer, and part of a barium solvent.

Thermal decomposition of ammonium metavanadate. The material balance of the technology is presented in the table 14. Thermal decomposition of NH_4VO_3 is carried out at 550^0C by the reaction

$$2\ NH_4VO_3 \rightarrow V_2O_5 + NH_3 + H_2O \qquad (8)$$

*T*able 14 - Material flow and material characteristics

No o/n	Operations and parameters	Unit of measurement	Parameter values
1	2	3	4
1.	Preparation of V-ore		
1.1	Drilling and blasting operations		
	- downhole-sized pieces	mm	250
1.2	Grinding on I/D		
	- pieces of V-ore	mm	-150
1.3	*Screening*		
	- lumps under a screen	mm	- 20(80%)
	- lumps above the screen	mm	+20 (20%)
2.	Formation of V-ore heap	t	30000
	- by sections	t	5000
2.1	Acidification of the V-ore section	m	1
	- water (H_2O)	l/t	50
	- acid H_2SO_4 conc.	kg/t	30
	- total volume by H_2O section	m^3	300
	- total consumption for section H_2SO_4 conc.	t	150
	- number (sections)	pcs	6
	- total volume by H_2O heap	m^3	1500
	- the total consumption of the heap H_2SO_4 conc.	t	900
2.2	Leaching 1		
	- sorption mother liquor	l/t	750
	- time of one run	days	75
	- volume of the V-solution from the first run	m^3	22500
	- number of runs	pcs	3
	- volume of the V-solution	m^3	67500
	- V_2O_5 content	g/l	1,85
	- the hydrogen index	pH	1,5-1,8
	- content of sulfates	g/l	100
	- total number of V_2O_5	t	124,8
	- irrigation density	$l/m^2 \cdot ch$	4,0
2.3	Leaching 2		

.	- H_2SO_4 solution	%	5
	- solution volume	l/t	300
	- solution volume	m^3	5250
	- run time	days	23
	- number of runs	pcs.	2
	- volume of V- solution-2	m^3	10500
	- V_2O_5 content	g/l	3,2
	- the hydrogen index	pH	0,8-1,0
	- content of sulfates	g/l	100
	- total number of V_2O_5	t	33,6
	- irrigation density	$l/m^2 \cdot ch$	3,0
3	Oxidation of V-solution	m^3	78000
	- volume of V-solution per day	m^3	300
	- V-solution velocity	m^3/ch	12,5
	- V_2O_5 content	g/l	2,0
	- the hydrogen index	pH	2,10
4	Vanadium sorption		
	- amount of sorbent	t	5
	- volume of productive V-solution	m^3	1200
	- the content of V_2O_5 in the prod. Solution	g/l	2,0
	- V2O5 content on the resin	kg/t	250
	- sorption time	days	2,0
	- sorption mother liquor	m^3	1200
	- V2O5 content in the mother liquor	g/l	0,2
	- the hydrogen index	pH	2,0
	- V-solution delivery rate	m^3/ch	12,5
5	Dual circuit vanadium sorption		
	- amount of sorbent	t	5
	- V2O5 content on the resin	kg/t	250
	- volume of vanadic acid	m^3	60
	- Vanadic acid content	g/l	16,5
	- the hydrogen index	pH	4,0-3,5
	- the content of V_2O_5 in the double-circuit resin	kg/t	450
	- V2O5 content in the mother liquor	g/l	0,5
	- the hydrogen index	pH	2,5
6	Solid-phase desorption		
	- volume of desorbing solution	m^3	15
	- NH4NO3 content	g/l	200
	- NH4OH content	pH conc.	8,5
	- desorption time	hour	24
	- hydrogen index of the mother liquor	pH	8,5
	- V2O5 content in the mother liquor	g/l	0,5
	- number of revolutions	quant.	15
7	Separation of MVA from resin		
	- The rate of continuous supply of desorbate with turnover through drainage screens and filters.	m^3/ch	20
	- time of the release of MVA pulp and resin to trommel.	hour	5
8	ammonium metavanadate filtering		
	- pulp volume	m^3	1040
	- MVA number	t	209

9	Thermal decomposition - temperature - amount of V2O5	 t	 550 156,6

2.3 Vanadium-containing slags

The main amount of vanadium slag in the world is produced in the countries with the largest reserves of vanadium-bearing titanium-magnetite ores. These are Russia, Republic of South Africa, People's Republic of China. Titaniferous magnetites account for more than 90% of the world's reserves of vanadium and titanium. The chemical composition of titanomagnetite ores is shown in Table 1. The mineralogical composition varies from magnetite and titanomagnetite to ilmenite [3].

There are two main methods of vanadium-bearing titanomagnetite processing: hydrometallurgical and pyro-hydrometallurgical. The technological scheme of vanadium extraction is chosen in each specific case taking into account the chemical composition and structural and mineralogical features of raw materials [5-11].

In Russia, the second method of vanadium extraction has been adopted. According to this method, titanomagnetite in a mixture with limestone and coke is agglomerated and goes to blast furnace processing. In the process of blast furnace smelting, trivalent vanadium is reduced and goes 80-86% into pig iron [8]. Then pig iron in converters is subjected to devanadiumization with obtaining a semi-product and vanadium slag, in which the mass fraction of vanadium in recalculation on V_2O_5 varies from 13 to 20% [11]. Depending on the regulations of vanadium pig iron processing, slags are obtained by one of the following methods: duplex-process, mono-process, or NICOM-process. They are a complex multicomponent material consisting of oxide compounds of vanadium, manganese, iron, titanium, chromium, silicon, calcium, and phosphorus, and have different technological properties [12-17]. The chemical composition of vanadium slag produced by different methods of vanadium pig iron processing is given in Table 2 [18].

Vanadium slag is a melt (alloy) of oxides enriched with up to 10-30% vanadium trioxide and formed during oxidative treatment of vanadium pig iron (when blowing iron with oxygen or air in the converter).

In terms of appearance, converter vanadium slag is a porous, micro-granular, strongly cemented mass containing iron dispersed and metal inclusions.

Metal inclusions are solidified iron–carbon droplets with a small content of V, Mn, Si, and Ti, trapped in the liquid phase during the devanadiumization of pig iron in the form of slag-metal splashes flying away from the reaction zone, as well as splashes and remnants of metal films captured by the oxide melt when gas bubbles break through the metal-slag interface when bubbles rise and collapse they are at the exit from the slag.

There is no consensus in the literature on the formation of dispersed iron. It is considered that dispersed iron is formed in case of mechanical abrasion of metal inclusions during milling [14], and also as a result of conservative self-organization during solid-phase interaction of wustite and Me_2O_3 (Me - Al, Cr) with the formation of iron aluminates and chromates which dissociate under reaction at high temperatures (during slag cooling):

$FeMe_2O_4 \rightarrow Fe + Me_2O_3 + \frac{1}{2} O_2$ [18] (1.1)

The mineralogical composition of converter slag has been studied in detail in [19-23]. Studies have established that industrial converter vanadium slags consist of three main phases:

solid solutions with spinelid structure of $(Fe,Mn,Ca,Mg)O\cdot(Fe,V,Cr,Ti,Al)_2O_3$ composition in which divalent Mg,Ca,Mn ions isomorphically replace a part of iron cations in MeO structure and trivalent iron cations in Me_2O_3 structure. Almost all vanadium is concentrated in spinel.

•- The silicate part of the slag consists of orthosilicate, metasilicate and glass. The content of vanadium oxides in the silicate phase does not exceed 2%.

• Metal crowns and dispersed iron.

The extraction of vanadium from slag during its subsequent processing, to a greater extent, depends on its composition and properties, which, in turn, depend on the prehistory of their receipt: the composition of pig iron and oxidizer, temperature in the converter, oxygen concentration at the time of slag formation, the slag cooling rate. For example, the latter determines the slag crystal structure [24-26]. Slow cooling of slag in the air contributes to the enlargement of its crystals, more complete separation of spinelid from silicate component, and consequently, more complete opening of slag at the subsequent processing.

The technology of obtaining vanadium slag is constantly being modernized, the raw material base is also changing, and the compositions and properties of the slag are naturally changing. These circumstances and the multi-component nature of spinelides and silicates make it difficult to study the processes occurring during firing and to solve the problem of creating an optimal technological scheme for the processing of high-manganese vanadium-containing slag to obtain vanadium oxide.

When processing the initial vanadium-containing raw materials to final products, the technology involves concentrating vanadium from one intermediate product to another with variable valence, repeatedly changing the nature of processes, including both solid-phase transformations and the interaction of vanadium-containing compounds in aqueous solutions of acids, salts and hydroxides, as well as its subsequent extraction from solutions.

Turning to the description of the basics of vanadium oxide production technology, we note that there are three main ways of processing converter slags: pyrometallurgical (chlorination in melt chlorides of alkali metals [30-32]); hydrochemical (slag treatment with hydrochloric acid [33]; pyrohydrochemical, which includes several stages: slag preparation for roasting (crushing, grinding, magnetic separation, mixing with reagent additive); oxidative roasting of the charge with various additives, usually sodium- or calcium-containing, leading to oxidation of vanadium and its conversion to soluble compounds; leaching of vanadium compounds from the cinder with water or acid and alkali solutions; separation of vanadium salts from the solution by sedimentation in the form of technical vanadium pentoxide and other compounds, which are the initial products for the production of ferrovanadium, pure vanadium pentoxide and other vanadium products and decontamination of spent solutions [34-59].

Since one of the main objectives of any technology is a high degree of vanadium extraction, we reviewed the physicochemical bases of various technology options in terms of not only the reactivity of the main vanadium-containing compounds formed during burning but also the patterns of vanadium complexation and extraction from solutions with the analysis of the compounds formed in this process.

1.1.1Oxidative burning.

The main purpose of the oxidative burning stage of converter vanadium slag is to convert trivalent vanadium to pentavalent vanadium, which is soluble in leaching.

1.2.1.1. Mechanism of kinetics of spinel oxidation.

Thermodynamic analysis of the oxidation reactions of vanadium spinels (1.1-1.8) formed in the process of pig iron conversion and the products of their interaction is given in the monograph [60]:

$$FeV_2O_4 + 1,25\,O_2 = Fe_2O_3 + V_2O_5 \qquad (1.1.)$$

$$2FeV_2O_4 + 2,5O_2 = 2FeVO_4 + V_2O_5 \qquad (1.2.)$$

$$MnV_2O_4 + O_2 = MnO + V_2O_5 \qquad (1.3.)$$

$$MnV_2O_4 + 1,25O_2 = 0,5Mn_2O_3 + V_2O_5 \qquad (1.4.)$$

$$MnV_2O_4 + 1,5O_2 = MnO_2 + V_2O_5 \qquad (1.5.)$$

$$MnV_2O_4 + O_2 = Mn(VO_3)_2 \qquad (1.6.)$$

$$MnFe_2O_4 + FeV_2O_4 + O_2 = Mn(VO_3)_2 + Fe_3O_4 \qquad (1.7.)$$

$$FeV_2O_4 + MnFe_2O_4 + 1,5O_2 = Mn_2V_2O_7 + Fe_3O_4 \qquad (1.8.)$$

According to the dependence of Gibbs energy on temperature, it follows that all reactions are possible in a wide range of temperatures. At temperatures up to 600°K the oxidation of manganese-vanadium spinel proceeds by reaction (1.5) above 600°K - by reaction (1.4). There is a high probability of formation of manganese pyrovanadate - $Mn_2V_2O_7$ - as a result of joint oxidation of iron-vanadium spinel and manganese ferrite or their solid solutions by reaction 1.8.

However, given the formality of the values of thermodynamic quantities, the advantage of certain reactions in the oxidation process can be assumed only when determining the kinetic parameters.

1.2.1.2. Oxidation of slag without additives.

Slag enters the oxidative firing, in which vanadium is present mainly in the spinelide phase. Using high-temperature microscopy, thermoanalytical and X-ray phase analyses, the mechanisms of slag oxidation were investigated [61, 62], which are formulated in the form of principles:

- ✓ Oxidation of lower vanadium oxides with oxygen proceeds in accordance with Baykov's principle of the sequence of transformations. Under conditions of continuous temperature increase up to 650o C, vanadium trioxide is oxidized to quadroxide, and then the latter is converted to vanadium pentoxide
- ✓ The formation of vanadate salts proceeds through vanadium pentoxide,
- ✓ Vanadium pentoxide is not subjected to dissociation.

Some results of the experiments of heating V_2O_3 in an air atmosphere up to 700^0C as a noticeable decrease of sample weight during melting (650^0C), a sharp decrease of solubility by 20% of the fused sample in 10-sulfuric acid, are explained, in the first case, by evaporation of sample, and, in the second, by crystals enlargement. At the same time in the insoluble residue, the lower vanadium oxides are fixed [62]. Sputtering of vanadium oxide during melting and crystallization due to the emitting oxygen has been repeatedly noted in the literature, a similar phenomenon is characteristic of oxide vanadium bronzes (OVB) [63]. In [64] it was shown that the destruction of the crystal lattice of OVB and transition of the sample into a liquid state is accompanied by complete oxidation of vanadium V^{4+} due to the absorption of the corresponding amount of oxygen from the surrounding atmosphere. The described process is reversible - crystallization of molten and oxidized bronzes is accompanied by the release of oxygen corresponding to the amount of reduced vanadium into the atmosphere. The authors performed thermodynamic calculations and found that reduced vanadium oxides can oxidize again only at temperatures no higher than 400-600°K. However, the oxidative roasting process proposed in [62] does not explain the sintering of the charge, the chemisorption of oxygen at 350°C, and the evaporation of vanadium oxide at 650°C.

It is known that oxidative roasting of converter slag can be carried out not only at high (600...900° C) but also at low (150...500° C) temperatures. The authors [65] developed an oxidative roasting at 400-500° C. In work [66] they propose to carry out roasting at 150-350o C after preliminary wetting the slag with a sulfuric acid solution.

1.2.1.3. Interaction of slag components with reagent additives.

As reagent additives are widely used alkali metal salts - NaCl, KCl, Na_2SO_4, Na_2CO_3, $NaNO_3$, and compounds of alkali earth metals $CaCO_3$, CaO, manganese oxides.

There is no consensus on the mechanism of interaction of reaction additives with slag components. Some researchers believe that the burning process with reactive additives proceeds in two stages: the oxidation of spinelide with the release of heavy metal orthovanadates and the interaction of the formed vanadates with the additive [62]. According to other researchers [29], the effect of the additive is not limited only to the creation of highly soluble vanadates, they also intensify the oxidation process of vanadium slags. So, in the presence of 1.0 wt.% of the alkaline additive, the oxidation temperature of V_2O_3 to V_2O_5 decreases from 640 to 595°C, the oxidation of iron oxide ends at a temperature of 900-920°C, and without the addition of alkali metal, its complete oxidation is not achieved at 1000°C.

According to [62], all three components of the slag are oxidized simultaneously during burning. It is established that starting from 350° C metallic iron is oxidized, then at 500-550° C the mineral of olivine group - fayalite (Fe_2SiO_4) is oxidized, and the latter decomposes into hematite and silicon oxide. In the region of these temperatures, the chemisorption of oxygen on the surface of spinelide begins. Active oxidation of spinelide with the formation of new phases, conditionally designated by the authors [67] as phases A, B and C begins at temperatures of 650-900°C. Phase A (solid solution of trivalent iron replacement in hematite by Ti^{+3}, V^{+3}, Al^{+3}, Mn^{3+} ions) is soluble only in a mixture of hydrochloric and sulfuric acids, phase B (solid solution of Fe^{3+} replacement in hematite by Cr^{3+}, Al^{3+}, Mn^{3+} ions) is insoluble in acids and aqua regia, phase C is represented by acid soluble vanadium compounds. Phases A and B differ mainly in the content of titanium and chromium ions.

Another group of researchers [24-26] notes the existence oxidized vanadium slag R_2O_3 and V_2O_5 phases in the composition, which between themselves can form vanadates. In [67] it is indicated that in the system V_2O5 - Fe_2O_3 hematite dissolves up to 10 wt. % V_2O_5, which is then not extracted from the slag by either acids or alkalis. In [25], a study of the interaction of vanadium with the silicate part of the slag showed that during burning above 750° C, vanadium is chemically bound in the glassy phase, rather than being captured by it mechanically and, therefore, part of the vanadium released from the spinelide is lost with the silicate part of the slag. In the study of slag burning with alkali metal salts (sodium salts) the formation of three vanadium compounds was shown: sodium metavanadate ($NaVO_3$), sodium pyrovanadate ($Na_4V_2O_7$), sodium orthovanadate (Na_3VO_4) [61]. In fact, the process of formation of vanadates of alkali metals goes through the formation of intermediate compounds called oxide vanadium bronzes (OVB) - NaV_6O_{15}, $Na_2V_5O_{13,5}$ [68-70]. These compounds are formed at temperatures of 300-600°C in the interaction of alkali metals with V_2O_5 and gradually transformed into vanadates. In case of reagent shortage or violation of the firing regime, the fired charge, along with vanadates, contains a certain amount of OVB, which are virtually insoluble in water, and NaV_6O_{15} is also insoluble in acids. Slag burning with alkaline additives, especially in their excess, is associated not only with the formation of soluble vanadates, but also soluble phosphates, chromates, and sodium silicates, which pass into the solution during leaching, polluting the product and complicating the process of pulp filtration.

Studying the CaO - V_2O_5 system A.N. Morozov [71] showed that under normal conditions the formation of three types of calcium vanadates (meta-, pyro-, ortho-) is possible, having the following sequence of transformations: $Ca(VO_3)_2 \rightarrow Ca_2V_2O_7 \rightarrow Ca_3(VO_4)_2$, intermediate phases like vanadium bronzes are not formed in this system, in the air atmosphere at temperatures to 800-900°C [72. Nevertheless, calcium was considered either as an undesirable impurity in slag because calcium vanadates are poorly soluble in water or it was noted that vanadium extraction does not depend on the mass fraction of CaO in slag if it does not exceed 1.0% [73].

The studies IMET of RAS named after Baikov [74] have established that the oxidation process of vanadium slag in the presence of CaO with vanadium transition into soluble form proceeds in stages in two optimal temperature regions at 750-800° C - low-temperature, 850-875° C - high-temperature. The first stage is characterized by high selectivity of formation of soluble vanadium compounds, in particular calcium and manganese metavanadates, with excess $CaCO_3$ practically does not participate in reactions and remains in the system in the free state.

At the high-temperature stage of the process, calcium and manganese pyrovanadates are formed as a result of the interaction of metavanadates with excess $CaCO_3$. The transition to the high-temperature region of the process, although it has a positive effect on the completeness of slag oxidation, is accompanied by the melting of metavanadates, forming a liquid-soaked mass, which leads to strong compaction of the material and sintering of particles.

During oxidative burning of vanadium-containing converter slag with pyrolusite in the high-temperature zone, manganese dioxide releases oxygen, and oxidizes spinel, forming compounds in which the degree of oxidation of vanadium and manganese is stabilized and reaches its highest value. Subsequent cooling or reheating of the charge does not affect the change in the oxidation degree of vanadium and manganese [67, 75].

1.2.2. Vanadium leaching from cinder.

During oxidative calcination of converter vanadium slags, processes occur that lead to the transition of vanadium into soluble forms, which during leaching passes into solution. The variety of pentavalent vanadium compounds indicates the importance of studying their properties in order to develop new effective methods for processing cinder.

Throughout the development of the chemistry of pentavalent vanadium, considerable attention has been paid to the elucidation of its forms in solutions.

1.2.2.1. Analysis of the pH-vanadium concentration diagram.

The diagram of the ionic state of vanadium (+V) from the concentration of vanadium and proton H^+ in aqueous solutions at room temperature was presented in several papers published in the 50s of the last century [76-84], but this issue is far from being fully resolved.

A large number of studies have shown the diversity and extreme complexity of the ionic state of vanadium in solutions, including compounds of all oxidation states. Chemical compounds of two-, three-, four-, and pentavalent vanadium are known, which have coloring - purple, green, blue, and yellow, respectively.

Lower valence compounds are not stable and are reducing agents. Tetravalent vanadium compounds are relatively stable. The peculiarity of the chemistry of pentavalent vanadium is that its state in aqueous solutions depends on the pH of the medium, concentration and potential in the system. In highly alkaline solutions, it exists as an orthovanadate ion, with a decrease in the concentration of alkali, and polynuclear anionic particles arise. In acidic solutions, vanadium pentavalent exists as a mononuclear oxocation. The variety of ionic forms of vanadium in solutions leads to the formation of a large number of compounds with inorganic and organic ligands.

Such diagrams are conditional and are used by technologists to present a general picture of the ionized forms of vanadium. At present, extensive experimental material has been accumulated on the conditions of vanadium-containing compounds in solutions, their solubility, complexation, and other aspects of vanadium chemistry. Recent advances require significant corrections to this diagram.

1.2.2.2. Leaching of cinder burned with sodium-containing additive.

The batch from the kiln with temperature 550-650ºC is supplied to the tank with water. Water leaching begins already in this tank, then the pulp with L: S = (4÷5): 1 and the 70÷80ºS temperature enters the active leaching agitator and then for filtration. The solid residue is sent for two-stage sulfuric acid leaching. In the first stage, the circulating solution is provided with a mass concentration of vanadium up to 5 g/l V_2O_5 and sulfuric acid 4÷5% at L: S = (2,5÷3): 1 and leached for 15 minutes at 20÷30ºS temperature. The second step of sulphuric acid leaching is carried out with 5÷7% sulphuric acid solution in agitators under agitation under the same conditions as the first acid leaching, then the pulp is filtered off. Vanadium-containing solutions after aqueous and the first stage of sulfuric acid leaching are sent to the stage of hydrolytic deposition of vanadium. The solid residue after the sulfuric acid leaching is the waste sludge. This technological scheme was used to process converter slag when adding sylvinite to roasting until 1978 [6] at Chelyabinsk Metallurgical Plant, the same scheme is used to process slag burned with soda. The degree of opening of water-soluble compounds is at the level of 45÷55%, and the total of soluble vanadium compounds is 85÷95% [85].

To increase the yield of water-soluble vanadium compounds in TSNIICHM, a soda-carbonate-ammonia technology was developed under the leadership of N.P.

Slotvinsky-Sidak [6, 86]. According to this technology, wet grinding of slag is carried out in bicarbonate medium, the solid residue is separated from the solution, mixed with soda (30% of the batch amount) and granulated. Burning in a tubular furnace of the obtained granules (up to 5 mm in size) makes it possible to increase the yield of water-soluble vanadium compounds to 90 ÷ 92% without sintering the batch. To extract vanadium, the granules after burning with a countercurrent are treated with water or soda solution and, after washing, sent to the dump.

For the same purpose at Perm Polytechnic Institute under the guidance of S.A. Amirova the optimum conditions for processing slags with increased vanadium content using soda technology have been determined. An increase in the yield of water-soluble vanadium compounds is achieved with the addition of soda up to 16.3 mass % [87]. The dependence of the optimum burning temperature on the consumption of soda has been established, and a decrease in temperature at the burning stage has been recommended to prevent sinter formation. Vanadium leaching consists of three-stage (one - aqueous, two - sulfuric acid).

Because processing of slags with a high content of calcium (4÷5% CaO) at OJSC ChMZ sharply reduces technological indicators (through vanadium extraction drops 10÷15%), the influence of the anulometric composition of the initial slag, as well as an increase in soda consumption, temperature and duration of burning were studied [88]. For slag with particle size $d < 0.14$ mm, the following parameters are recommended: burning temperature of 750 ° C, soda consumption of 19.5%, and burning duration of 90 minutes. At these parameters, the recovery rate in the aqueous solution is 90%. To extract vanadium more completely into the solution in [89], it was proposed to treat the aqueous solution by sorption leaching. According to the "shortened" scheme [90], one-stage weakly acid active leaching of the burnt batch with sulfuric or nitric acid [91] was provided, then filtration followed by washing on the filter with solutions of the corresponding acids.

The considered technological techniques are developed to increase the yield of water-soluble vanadium compounds and simplify the stage of hydrometallurgical processing. Almost all studies show the need to increase the consumption of soda. The latter is associated with several negative factors. This is the sinterability of the batch during burning and, as a result, an increase in vanadium losses with dump sludge; transition to hexavalent chromium solution negatively affects the environmental situation in the area of the Chusovaya River; colloidal-dissolved silicon compounds in aqueous solution worsen the pulp filtration process.

1.2.2.3. Leaching of a cinder burnt with a calcium-containing additive.

The extraction of vanadium from calcium-containing cinder can be carried out in several ways. In [92] two-stage leaching of charge with sodium carbonate solution with a mass concentration of 3-4% at boiling for 1.5-2.0 hours in an autoclave was proposed. Purifying leaching solutions is carried out by electrodialysis, in which regeneration of sodium carbonate is provided.

According to the technological scheme [93], the burnt batch is treated with sulfuric acid at pH = 1.3-1.6, with a temperature of 95ºC for 1 hour; after this treatment, manganese, iron and other impurities are present in the solution. Then the solid residue is treated with slurry of calcium oxide at 90ºC to dissolve the polyvanadates formed during the first leaching stage. The cake after the second treatment is sent to the third stage of leaching with 3% sulfuric acid.

Leaching at a lack of acid in the region of stable vanadium forms and low temperature, called pH leaching, is maintained at pH=2.5-3.2 [94]. In this pH interval, the degree of vanadium extraction into the solution in one stage reaches 80-85%. Increasing the temperature to 60-70º C positively affects the transition of vanadium in solutions. Manganese, like vanadium, is leached into the solution in the first 15 minutes. A sharp increase in the concentration of manganese in solution stops in the region of pH- 2.5-3.0. Studies have shown that the behavior of vanadium and manganese during pH leaching is identical. This is explained by the fact that manganese in the slag is a vanadate-forming element actively involved in forming vanadium-containing phases at the burning stage, so it also goes into the solution during pH leaching. In this regard, pH leaching should be considered as a technological process that provides an integrated extraction of two slag components - vanadium and manganese with simultaneous purification of solutions from impurities of phosphorus, iron, calcium and silicon.

The weak acid leaching process is one of the main stages of converter vanadium slag processing; the additional leaching stage is carried out with 3.0-3.5% sulfuric acid at L: S = 1.5-3.0. This technological scheme is implemented at OJSC "Vanadium-Tula".

Under industrial conditions, the pH leaching is organized in a continuous mode in a cascade of reactors [95]. The first stage of weakly acid leaching is carried out by a solution from acidic extraction of vanadium to pH = 3,2-4,4 with pH correction if necessary by sulfuric acid. The second stage is carried out at pH = 3.0-3.8; the third stage at pH = 2.6-3.4 and the process is completed in the fourth to seventh stages at pH = 2.1-2.5. The temperature of the leaching stages is maintained within the range of 22-58ºC.

2.4 Method for obtaining vanadium pentoxide from pulp solutions of slag leaching

Initial materials were a sample of burnt high-manganese slag, ionite type "Ambersep 920 U Cl". Scheme of the sorption column with pneumatic mixing is shown in Figure 6. This method is versatile, it is suitable for processing of pulps with solids content up to 50-60%. There are no moving parts and structures in the device, the process is easily automated and very stable. Ionite transportation is simple enough, which protects it from excessive wear and tear. This is also facilitated by the use of airlifts and a minimum number of shut-off valves.

The mixing of ionite and pulp is carried out with the help of a central airlift pulp. With another airlift, pulp with ionite is supplied to a separation device in the form of a grid.

The countercurrent pulp sorption of vanadium from highly manganese slag is shown in Figure 7. The crushed cinder is mixed with water in the ratio S: L = 1:2, treated with sulfuric acid to pH = 4.5-4.0 and supplied to the head sorption column, and ionite in sulfate form from intermediate column 1 is fed in countercurrent flow by volume at the rate of 10% per pulp volume. In the head column, the pH is maintained at 3.5, and the residence time of the pulp and resin in each stage is 1.5-2.0 hours. Removal of saturated resin from the pulp is carried out on drainage screens; resin, after being washed with 1% sulfuric acid solution goes to the desorption stage, and pulp - to intermediate column 1, where pH is constant and equal to 3.0. Ion-exchange extraction of vanadium per resin reduces the concentration of the useful component in the liquid phase and results in additional conversion of vanadium from cinder to solution.

After separation, the resin is sent to the head column, and the pulp to the intermediate column 2 with pH equal to 2.5, then to the tailing column with pH = 2.0. After separation on the drainage grid, the pulp is filtered. After separation on the drainage grid the pulp is filtered. The sorption mother liquor is used at the manganese deposition stage, and the sludge is used in the dump.

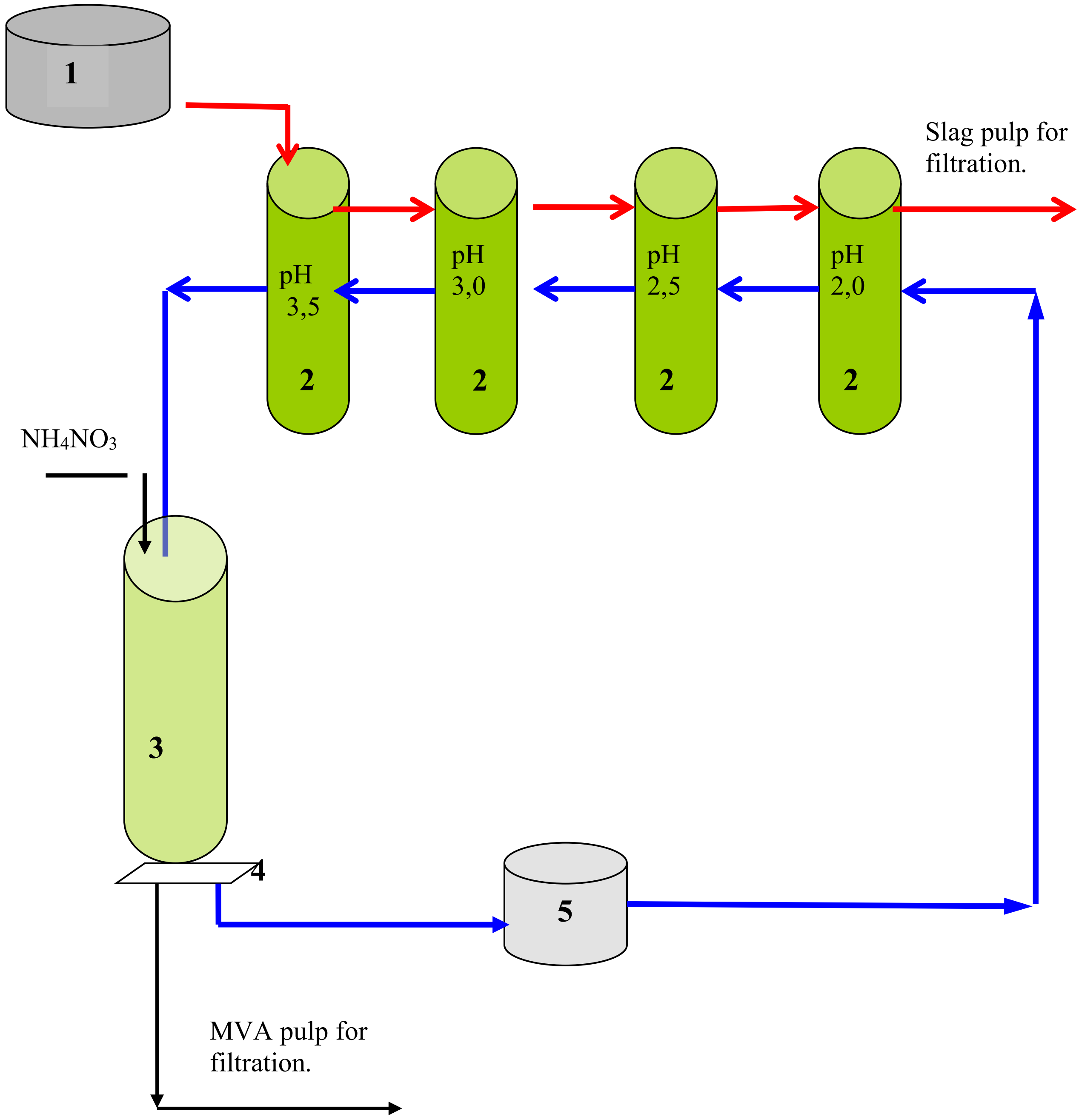
Vanadium in solutions and slurries were determined by standard methods. The resin was analyzed as follows: 10 ml of H_2SO_4 ($\rho=1.84$) was added dropwise to a sample (up to 1 g) and put on a hotplate for ashing. Then 10-15 ml of $HClO_4$ was added until the thick SO_3 vapor. After complete gas evacuation, cool down, add 100 ml of H_2O, and boil for 2-3 min, then vanadium is determined as in solutions [120].

2.2.7. The technique of desorption of vanadium from ionite.

Desorption of vanadium from ionite is carried out in devices similar to sorption columns. The resin from the head column was washed with a 1% solution of sulfuric acid with stirring for 30 minutes, separated from the washing solution on a drainage grid and sent for vanadium desorption. The desorption process was carried out in solid–phase mode with the following parameters: the mass concentration of ammonium nitrate solution 180-200 g / l, temperature - up to 50ºC, ratio S: L = 1:7.

After 3-4 hours, the resin is separated from the ammonium metavanadate pulp on the drainage grid. After recharging, the resin is sent to the sorption stage in the tail column, and the ammonium metavanadate pulp is filtered.

The analysis of the mother liquor (masterbatch) desorption and ammonium metavanadate is carried out according to the procedures described in the literature [119, 120].



The movement of vanadium pulp is shown by red arrows, the movement of resin is shown by blue arrows.

Scheme 1 - Countercurrent pulp sorption and desorption of vanadium. 1- slag pulp tank, 2 – sorption apparatus, 3 – desorption tank, 4 – drainage grid, 5 – ionite recharge tank.

3 RESEARCH ON THE EXTRACTION OF RARE AND RARE EARTH METALS FROM TECHNOGENIC WASTE USING MANGANESE ORE INTO PRIMARY PRODUCTIVE MATERIALS (ROUGH CONCENTRATES)

Currently, in many countries, research has been launched to improve chemical processes in the following areas:

- pretreatment of refractory and non-concentrate materials or intermediate products for the formation or removal of surface films on grains of ore minerals, segregation of fine particles and other chemical changes in waste components in order to increase the difference in the physical and physicochemical properties of raw materials and create the possibility of separating them by conventional methods of concentration;
- fine-tuning of rich concentrates, in terms of substandard content of the main component or impurities, by partial or complete removal of some accompanying minerals from them by chemical methods;
- processing of rough, bulk concentrates or hard-to-feed industrial products for the purpose of almost complete selective extraction of useful components into products of the same name.

In the case of chemical processing of materials at the opening operation, usually, all valuable components and some of the impurities are transferred into solution from the starting material. As a result, technological schemes become much more complicated. Moreover, their implementation requires large expenditures of reagents. However, the use of chemical processing of enrichment products makes it possible to increase the extraction of the main components from raw materials into final products, as a rule, with a higher content of them and a lower content of harmful impurities than in other chemical processes. So, in the final products, impurity content of less than 0.1% can be achieved, which significantly increases the profitability of chemical technology.

The choice of a chemical process depends on the material composition of the feedstock, the content and mineral forms of useful components, their cost, and quality requirements for the final product.

Hydrometallurgical processes have received the greatest industrial application; their advantages, for example, when compared with pyrometallurgical processes, are the possibility of processing more complex, poorer polymetallic products with the implementation of an almost complete separation of metals and a more rational solution to the problem of environmental protection, using relatively low temperatures in the decomposition of processed samples - 293-473 K.

The ability of minerals to enter into chemical reactions with the leaching of metals and their transition to a solution determines the possibility of using various hydrometallurgical processes. This ability depends on the type of chemical compound, its degree of oxidation, the amount of isomorphic impurities and many other reasons and varies widely.

For the most complex mineral raw materials, the scheme of hydrometallurgical processing may include the following operations: additional grinding of the source material, decomposition of extracted minerals, leaching of useful components, purification of the obtained solutions from harmful impurities, separation and sedimentation of the extracted components, and others. In addition, some operations are often combined: for example, additional grinding of products, their decomposition and leaching (in ball mills or in horizontal autoclaves); decomposition of mineral components and leaching of the formed compounds; use of waste solutions as circulating ones; sorption leaching in the pulp (the dissolved element in the pulp is sorbed immediately onto the sorbent, which is added to the pulp).

To extract rare and rare-earth metals, it is necessary to develop technologies for converting these metals into primary productive materials containing such concentrations of these elements for their industrial and economically profitable production to increase the percentage of direct extraction into finished products. When studying the processes of chemical decomposition and leaching of minerals, several thermodynamic functions are used: the internal energy of the system, enthalpy, entropy, Gibbs free energy, Helmholtz free energy, redox potential.

The bulk of the ore, except for minerals containing recoverable components, must be preserved in its original or insignificantly changed state during leaching. Therefore, an important task of thermodynamic research is to obtain data on the comparative chemical stability of raw material minerals, including concerning certain leaching agents.

The redox systems of rare and rare earth metals are diverse. Having different redox potentials, rare metals can leach out depending on the solution medium and the solution potential. For this purpose, it was necessary to consider the ionic state of rare metals depending on the pH of the solution and the potential. Figures 3-13 show the ionic state of rare and rare earth metals in various media. For example, the ionic state of rare earth metals in phosphogypsum-cerium, lanthanum, yttrium; rare metals – tellurium, selenium, thallium, indium, rhenium, cadmium, wolfram.

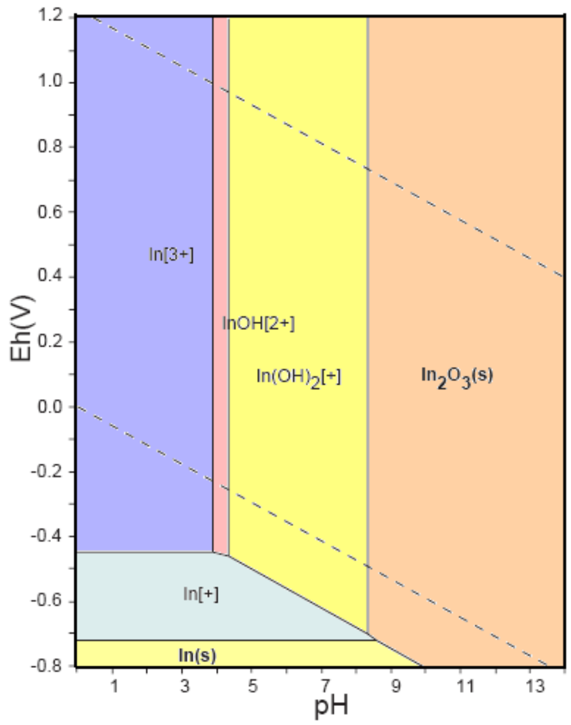
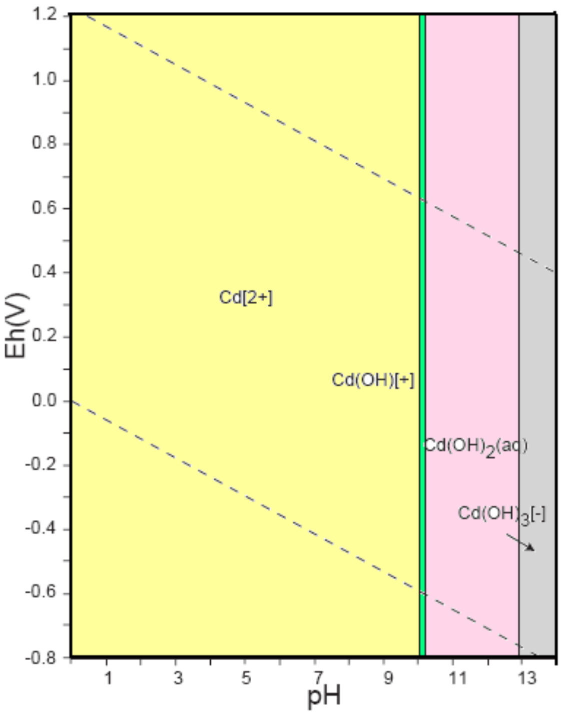


Figure 3



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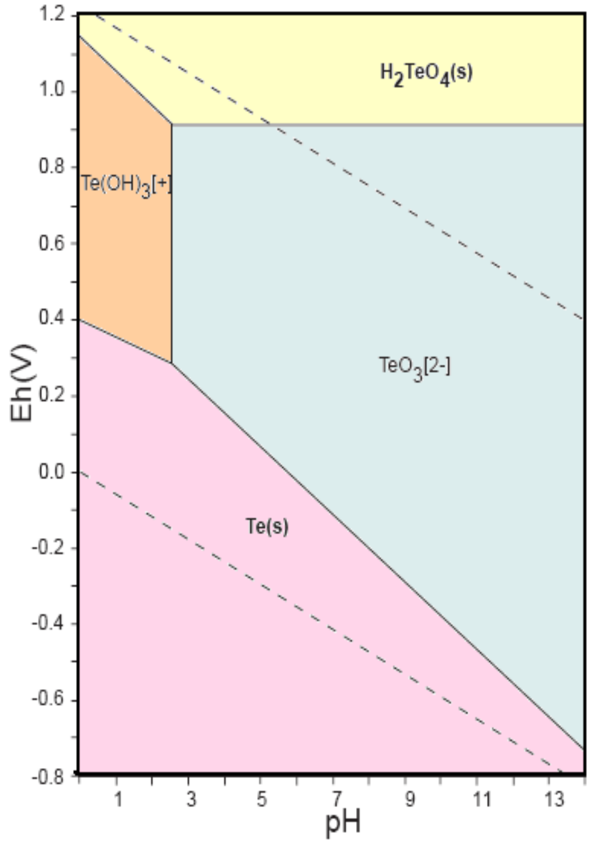


Figure 5

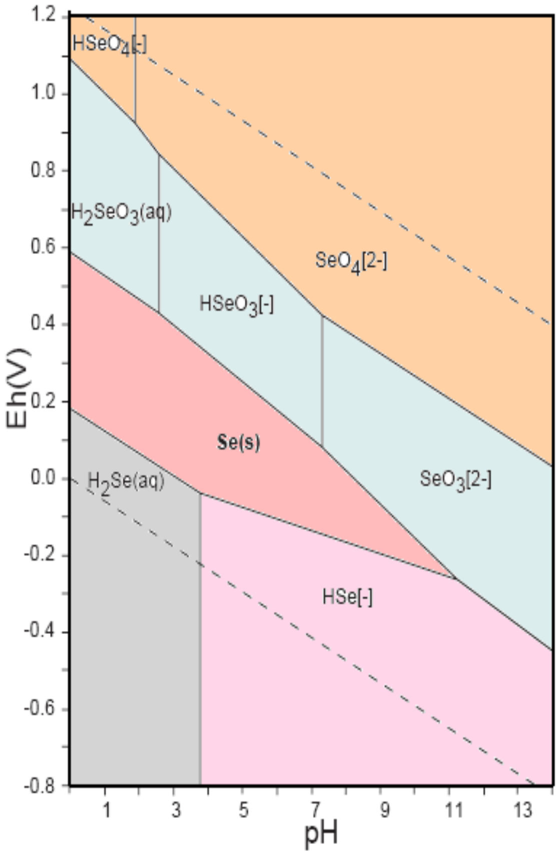


Figure 6

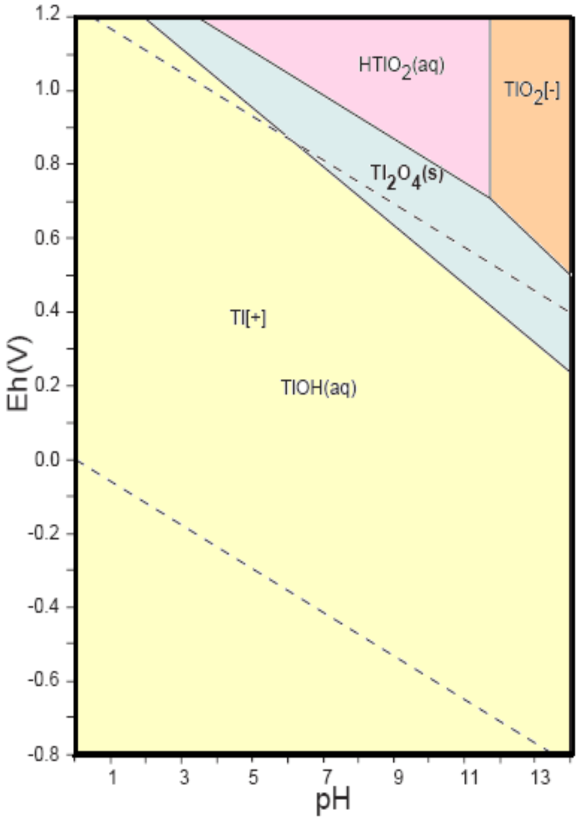


Figure7

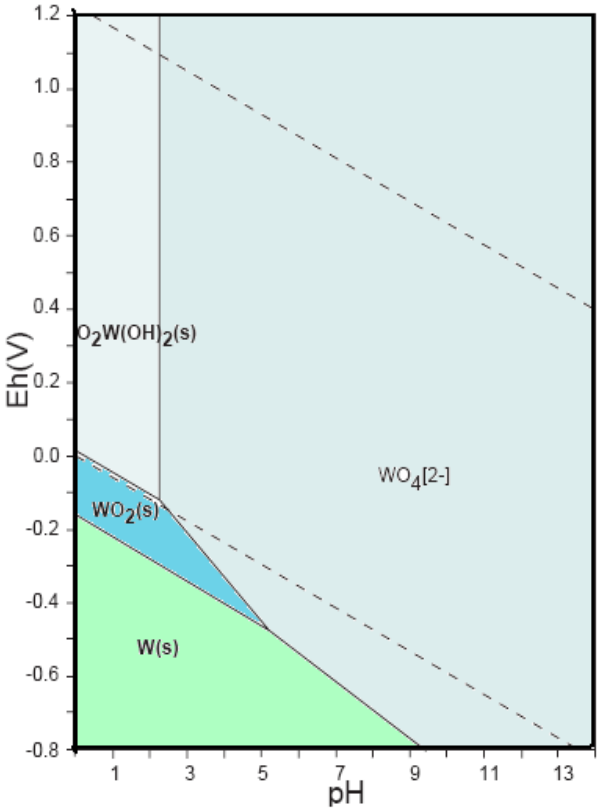


Figure 8

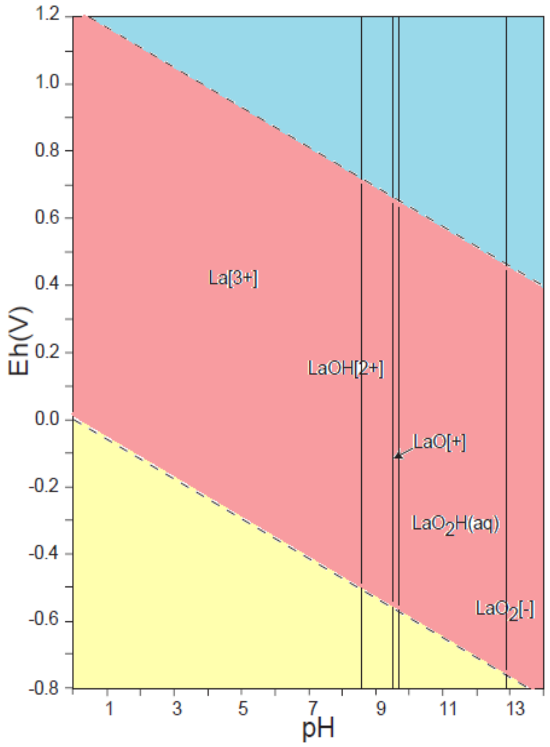


Figure 9

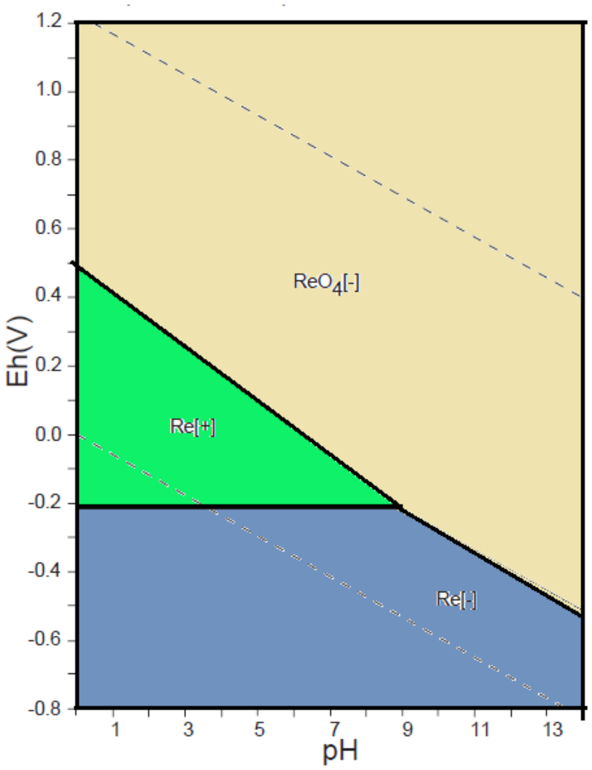


Figure 10

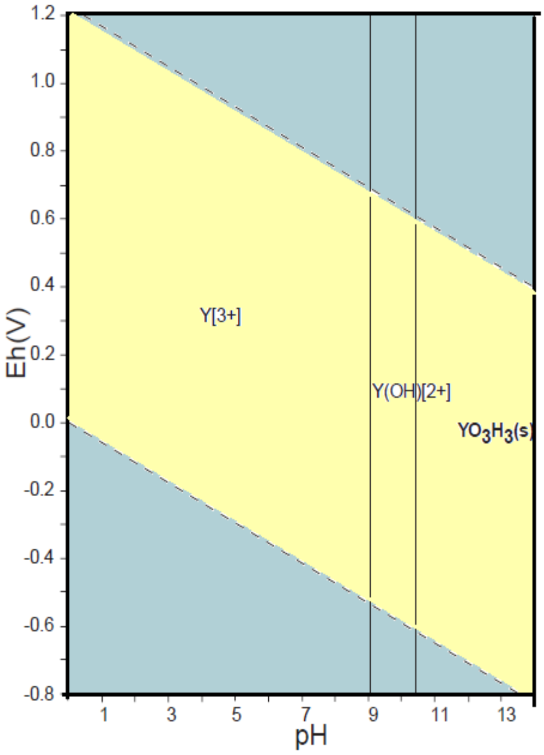


Figure 11

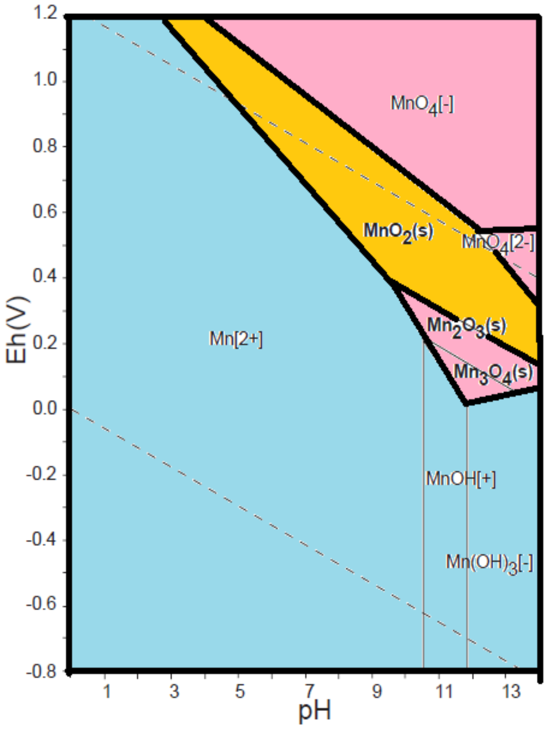


Figure 12

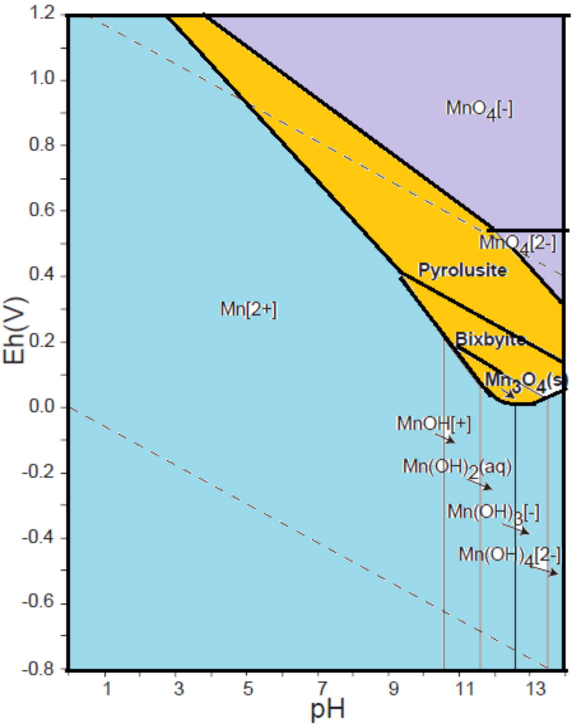


Figure 13

As can be seen from Figures 3-13, at the production parameters of the uranium industry, the group of rare earth metals and rhenium, regardless of the redox potential, are in the highest degrees of oxidation.

The essence of oxidation-reduction reactions, as is known, consists of the transition of electrons from the atoms of the reducing agent to the atoms of the oxidizer.

A measure of the oxidizing ability of an oxidizer (atom, ion) is the affinity for an electron, which is the energy (work expressed in electron volts) that is released when an electron is connected to it.

The measure of the reducing ability is the ability of atoms to give away external electrons, determined by its ionization potential (Y) [48].

Higginson [49] proposed the following semi-empirical rules:

a) complexes of transition elements react with each other, passing through a number of stages, in each of which the valence changes by one;

b) complexes of non-transition metals react with one another, changing the valence by two units, if at least one of the reacting substances is not a free radical (in the latter case, the valence changes by one);

c) transitive and non-transitive elements react with each other with a change in valence by one.

Yatsimirsky [50] believed that all redox processes with the transfer of one electron proceed by a three-stage mechanism:

a) formation of the primary complex;

b) electron transfer with the formation of a subsequent complex;

c) the decay of the subsequent complex.

Using the example of the oxidation reaction of n-phenetidine with vanadium using the method of electron paramagnetic resonance and optical spectra, he traced all three stages. A similar point of view on the mechanism of oxidation-reduction reactions was held by Maciejevsky, Dorfman, et al., Lavrentiev and Hidekel [51].

Many elements involved in oxidation-reduction reactions are found in solution in the form of complex oxygen-containing ions: first of all, this applies to acid-type oxidizers. In these cases, an increase in the concentration of hydrogen ions in aqueous solutions leads to a shift in ionic equilibria towards the appearance of non-ionized acids, to their decomposition with the formation of active intermediate compounds of lower valencies. Since the oxidized forms are unstable in an acidic medium, their free energy, expressed by the redox potential, is high. At the same time, the lower the valence of the central atom of the oxidizing molecule, the wider the pH range in which its oxidizing properties are manifested. In an alkaline environment, the oxidizing abilities are reduced, and in most cases, with multivalent central atoms (except for low-stability compounds), they do not appear at all.

The indicated dependence of the manifestation of the oxidative activity of substances on the pH of the medium directly follows from the mechanisms of the oxidative action of compounds through their decomposition with the formation of intermediate compounds and the role played by hydrogen ions in this case.

In the framework of the electrostatic theory, the higher the ion charge, the greater the ionization potential and the stronger the ion "grabs" oxygen electrons in oxygen compounds, hence the greater strength of the compounds with the highest valence of the element. A decrease in the charge on oxygen atoms during the transition from the lowest to the highest valence of the central atom entails weakening the attraction of protons. This is the reason for an increase in the degree of electrolytic dissociation acids. Compounds of higher valences of the central atom also have a greater symmetry of the molecular structure, leading to greater stability. Therefore, for the activation of molecules with a higher valence of the central atom, a more energetic influence of external factors is also necessary, for example, a higher concentration of hydrogen ions, a higher temperature, etc. It is not difficult to understand that the selectivity of the oxidation and dissolution processes is directly related to these factors. This is of paramount importance in applied issues, in particular in hydrometallurgy.

Manganese compounds are of considerable practical interest for the implementation of redox processes. Manganese ions have a large range of ionic radii (0.091, 0.070, 0.052 and 0.046 nm, respectively, for Mn^{2+}, Mn^{3+}, Mn^{4+} and Mn^{7+} [52] and differ in wide limits of fluctuations in the values of ionic potentials. This determines the great opportunities for the formation of its various chemical compounds. In nature, manganese is contained in the form of two -, three-and four-valent compounds. Inorganic substances, it is possible to find manganese is higher (+5, +6, +7) degrees of oxidation. Due to the presence of several degrees of oxidation (valence states) – 0, 2, 3, 4, 5, 6, and 7-the corresponding chemical compounds of manganese (except divalent) can effectively perform the role of oxidizing agents, for example, when leaching metals of variable valence from materials in acidic and carbonate (alkaline) solutions. Thus, manganese dioxide, a relatively strong oxidizer, can convert elemental sulfur to SO_2, HCl to Cl_2, NH_3 to N_2, carbon to CO_2 [52]. Manganese dioxide can also act as an oxidizer in neutral non-aqueous media [53].

The oxidation states of manganese and some mutual transformations of its compounds are presented below in Table 15.

Table 15 - Mutual transformations of manganese compounds

Oxidation state	Mutual transformations	reaction environment
7	$MnO_4^{-} \to e \to MnO_4^{2-}$	strongly alkaline
6	$MnO_4^{2-} \to 2e \to MnO_2$	slightly alkaline
5	$MnO_4^{2-} \to e \to MnO_4^{3-}$	Very strongly alkaline
4	$MnO_2 \to 2e \to Mn^{2+}$	acidic
3	$Mn^{3+} \to e \to MnO^{2+}$	acidic
2	MnO^{2+}	-

As oxidizing agents during acid leaching of rare metals, manganese oxide ores are primarily of practical interest as the most affordable and economically acceptable raw materials for industrial production. About a quarter of the total 45% of the confirmed reserves of manganese ores are accounted for by Europe. A significant part of which is contained in the deposits of the CIS: Ukraine

(Nikopolskoye, Bolshetokmakskoye), Kazakhstan (Atasuyskaya group of deposits), Georgia (Chiaturskoye field). Zhayremskoye (Zhanaarkinsky district, Karaganda region, Kazakhstan) is a stratiform pyrite-polymetallic deposit discovered in 1959, developed since 1971. The main feature is the spatial combination of syngenetic iron-manganese and zinc ores with the superposition of hydrothermal-metasomatic barite-lead-zinc mineralization. Mineralization of both types is associated with the siliceous-carbonate strata of the Upper Devonian. Ore textures are layered, interspersed, striped and breccia. Main minerals: ore-pyrite, sphalerite, galena, chalcopyrite, hematite, marcasite; non-metallic – quartz, barite, calcite, dolomite. Minor minerals: pale ores, $CuPbSbS_3$ burnonite, NiS millerite, bravoite, jamsonite, boulangerite, albite, fluorite, kalishpat, sericite. Only relatively poor manganese ores of the Zhayrem deposit (Karaganda region) are used as hydrometallurgy of rare metals.

The use of manganese concentrate as an oxidizing reagent determined the need to study its chemical composition. At our request, the Zhayrem Mining and Processing Plant sent a batch of manganese concentrate, which was crushed in a ball mill and analyzed.

The concentrate is a dark-colored powder with high specific gravity, containing 63.2 wt—% of manganese (Table 16) In addition to manganese, silicon oxide (IV) – 23.4%, iron oxide (III) – 11.71% and zinc 3.62% are contained in tangible quantities.

Table 16-Chemical composition of manganese concentrate (Zhayremskoye deposit)

Name	Content, wt.%	Name	Content, wt.%
Мп	63,20	Na_2O	0,4500
Мп (IV)	26,40	Pb	0.3400
Fe	8,200	Zn	3,6000
Fe_2O_3	11,71	Cu	0,0060
Al_2O_3	4,120	BaO	0,3700
CuO	2,950	As	0,0390
MgO	0,540	TiO_2	0,2100
$S_{общ}$	0,051	Te	0,0008
K_2O	1,140	ппп	8,4100

The oxide minerals of the pyrolusite and psilomelane groups (a mixture of Mn^{2+}, Mn^{4+} oxides and other oxides of non-constant composition) that are most often found in the works have a significant industrial value. These include todorokite $(Mn^{2+})(Mn^{2+}, Mn^{4+}\ldots)_6O_{12}*H_2O$, asbolane $(Mn^{4+}O)_2(Mn^{2+}(OH)_2*nH_2O$, birnessite $Mn^{3+}[Mn^{4+}(O, OH)](O, H_2O)_6$, buserite $Mn^{4+}[Mn^{2+}\ldots(OH, H_2O)]O_2$, vernadite MnO_2*nH_2O (Mn_2O, MnO, Mn_2O_3) – are the main components of Fe – Mn nodules, pyrolusite, psilomelane and manganin MnO(OH) – the main minerals of sedimentary and volcanogenic-sedimentary and other types of manganese deposits.

Among the most industrially valuable minerals containing Mn (IV), pyrolusite (β-MnO_2) is the most satisfying technological and economic requirement for oxidizing agents for industrial use in acidic environments. The content of Mn,%, in minerals, is given in Table 17.

Table 17-The content of manganese in its own minerals

Mineral name	Chemical formula	Content, %
Pyrolusite*	β-MnO_2	60-63,2
Psilomelan	$(Ba, Mn^{2+})_2(O, OH)_6Mn_8^{4+}O_{16}$	45-60
Vernadite	MnO_2*H_2O	44-52
Todorokit	$(Mn^{2+}, Ca, Mg)Mn_3^{4+}O_7*H_2O$	47-54
Rancieite	$(Ca, Mn^{2+})Mn_4^{4+}O_9*3H_2O$	43-50

* Natural γ-MnO_2 - ramsdelite is rare

The normal potential (E°, V) of the redox system $Mn^{2+} + 2H_2O/MnO_2 + 4H^+$ with respect to the normal hydrogen electrode (at 25 ° C) is 1.28 V. To determine the redox potential of all manganese compounds, and it can be represented in the Purbe diagrams (Figure 14).

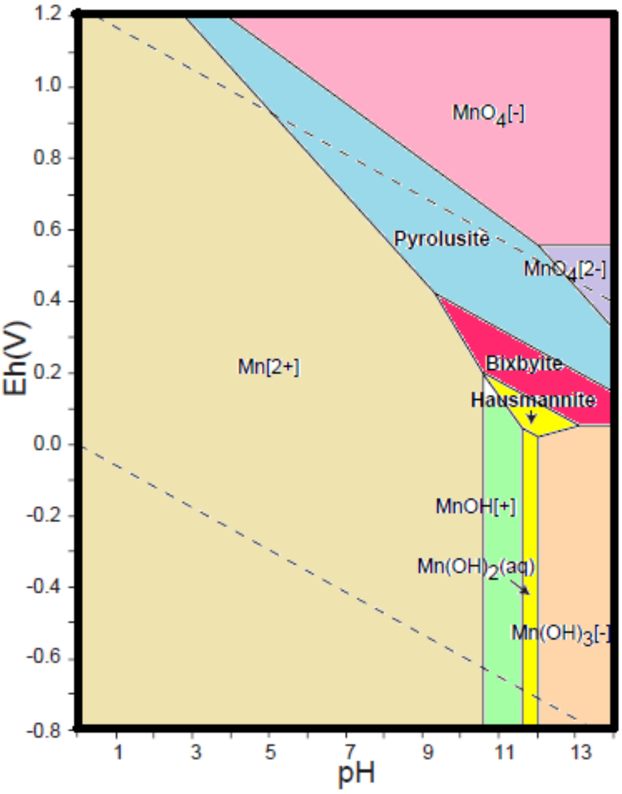


Figure 14-Redox potential of manganese

As shown from the diagram (Figure 14), manganese dioxide or the ore mass of this compound – pyrolusite has a high degree of redox potential above 1.2 V.

3.1 Technogenic waste of the uranium industry containing rare and rare earth metals

In modern industry, due to the lack of rich uranium ores (the exceptions are the Canadian deposits of disagreement, where the uranium concentration reaches 30% and the Australian ones with uranium content of up to 3%), the method of underground leaching of ores is used. This is one of the most cost-effective and environmentally friendly mining methods that do not require either quarries or mines. Preliminary preparation takes place directly underground. The method is applicable in severe climatic conditions and permafrost. The technology is closed, sealed. The subsoil is practically not destroyed and even completely restored within a few years.

Underground borehole leaching – a method of developing ore deposits without raising ore to the surface by selectively transferring natural uranium ions into a productive solution directly in the depths. This method is carried out by drilling wells through uranium ore bodies, supplying solutions to uranium ore bodies, lifting uranium-containing solutions to the surface and extracting uranium from them in sorption ion-exchange installations, adding acid to mother liquors and pumping them back into the bowels.

The entire area of the deposit is "pierced" by wells (columns). Sulfuric acid (1-2% solution) is pumped into one well, sometimes with the addition of ferric salts (to oxidize uranium U (IV) to U (VI)). However, the ores often contain iron and pyrolusite, which facilitate oxidation. The uranium leaching process is in progress. Through another well, the productive solution is pulled upward by means of a pump. Then it goes directly to sorption, hydrometallurgical extraction and simultaneous concentration of uranium.

The method of underground borehole leaching is the most attractive method of uranium extraction from the point of view of simplifying technological operations. With this method, there is no change in the geological state of the subsurface since the mining mass is not excavated. The total land surface occupied by the underground leaching landfill and the processing plant for producing 500 metric tons of U / year U_3O_8 is 3-4 times less than the area occupied by a typical hydrometallurgical plant for the same productivity. In the process of borehole leaching, less than 5% of radioactive elements are transferred to the mobile state in the subsurface and brought to the surface, compared with 100% with traditional methods of uranium extraction. Sulfuric acid in contact with the rock turns into gypsum, so there are no elements left in the ground that are not there with this technology. And if there is any blurring, they are quickly eliminated because the technology does not work with leaks. Therefore, there is no need to build tailings dumps for storing waste with a high level of radiation.

There are small sandpits that are easy to reclaim after mining is completed. Note that the natural hydrogeochemical environment in uranium deposits is often capable of self-recovery from technogenic impact. Due to the gradual restoration of natural redox conditions, a slow but irreversible process of reclamation of underground waters of ore-bearing aquifers occurs. Furthermore, an intensification of this process is possible, which accelerates reclamation tenfold. An example of natural demineralization of residual solutions is the result of 13 years of observations carried out at the Irkol field (South Kazakhstan).

The complexity of extracting associated components from productive solutions of the uranium industry, enriched with rare and rare earth elements, is a rather complicated problem in methodological and practical terms. This is due to the lack (for the subsoil user - the complete absence) of information on the technical and economic indicators of the extraction of associated useful components and the variety of their possible marketable forms (collective product, oxides, salts, metals of varying degrees of purification, characterized by different yield, price and other technical and economic indicators).

At present, when putting on the balance of associated components in terms of reserves, they are guided not only by the achieved level of industrial development of ores as a complex raw material but also by the results of pilot industrial or technological laboratory tests. In addition, the economic feasibility of extracting these components was assessed from the condition of the complete consumption of all by-products from the entire mass of mined ores, which many times (for a number of components dozens of times) exceed the country's need for it, in some cases, the volume of world consumption and, therefore, leads overestimation of the calculated performance indicators for the complex processing of ore and concentrates.

In addition to the above, the limiting factors in processing rare metals (hereinafter - RM) are environmental, especially high requirements for liquid effluents. Completely zero waste schemes will undoubtedly have advantages over time.

The solution of the intersectoral problem of rational, integrated use of unique uranium concentrates enriched with rare and rare earth metals is an urgent problem and should be carried out with the involvement of a wide range of specialists – geologists, technologists, chemists, economists, for example, within the framework of the Development Program of «NAC «KAZATOMPROM» JSC to create a collective concentrate of rare earth metals.

The growing interest in rare earth products around the world is confirmed by a number of documents signed in Astana on October 22, 2009, within the framework of the tenth joint meeting of the Kazakh-Japanese and Japanese-Kazakh committees for economic cooperation aimed at creating joint ventures with major Japanese corporations in the field of rare and rare earth metals and products based on them on the territory of Kazakhstan:

"Protocol of intent on cooperation in the field of rare metals" with Toshiba Corporation;

"Memorandum of Understanding and Mutually Beneficial Cooperation on the Project for the Development of Rare Earth Metals in the Republic of Kazakhstan" with Sumitomo Corporation;

"Agreement on the main provisions of joint activities for the development of a feasibility study for the production of rare-earth metals" with Sumitomo Corporation.

The documents were signed by the management of «NAC «KAZATOMPROM» JSC, Toshiba Corp. and Sumitomo Corp. in the presence of representatives of the MEMR of the Republic of Kazakhstan, the Ministry of Economy, Trade and Industry of Japan (METI) and the Japanese National Oil, Gas and Metals Corporation (JOGMEC).

To assess the economic feasibility of the extraction of rare earth metals and the development of effective technology for their extraction, it is necessary to have quantitative characteristics of the content of rare earth metals in solutions of underground leaching (IS). To this end, in November 2008, a program was initiated, the goals of which are: development of new highly sensitive methods for the analysis of REM content in PV solutions, obtaining reliable quantitative data on the content of REM, and development of technologies for the extraction of rare earth metals from PV solutions.

As a rule, deposits of these rare elements and their increased concentrations are associated with the final phases of acid magmatism (pegmatites, albuminized, reionized granites), to a lesser extent with rocks enriched with aluminosilicate, silicate and oxygen compounds (feldspar, mica, etc.), in the form of accompanying components they are present in polymetallic, fluorite, uranium deposits, in deposits of non-ferrous metals, in sedimentary deposits of iron and coal. In particular, in the endogenous deposits of Uzbekistan and Kazakhstan, many rare elements are either in high concentrations or are extracted simultaneously with the complex use of ores. Their gross content in ores does not play a significant role in the latter case since their industrial concentrations are formed in intermediate processing products. The published information on the contents of the above-mentioned rare elements in gold, gold-bearing and uranium-ore deposits is very fragmentary. Due to the important task of the complete extraction of rare and trace elements from copper, poly metals, uranium, etc., data on their distribution in endogenous deposits are theoretical. With the prospect of developing new technologies, they may also have practical significance.

Technological methods used in the rare metals industry have a number of features associated with the nature of the feedstock and the requirements for the quality of the finished product. These features include a low concentration of rare metals in natural raw materials or industrial waste, the complexity of their composition, the chemical resistance of most rare metal minerals and very high requirements for the purity of the final product. Therefore, the technology for the production of pure and high-purity rare metals from ores or other types of raw materials always has a multistage nature and usually consists of the following main stages:

1) beneficiation of ores or various wastes;
2) decomposition (opening) of concentrates;
3) obtaining pure chemical compounds of the mono element;

4) their restoration to metal;

5) metal refining;

6) obtaining compact ingots of metals and alloys and products from them.

Usually, when obtaining pure compounds of one metal, the greatest difficulties are caused by purification from analogous metals, for example, zirconium-hafnium, niobium-tantalum, tungsten-molybdenum. For the separation of these metals and their effective reduction, physicochemical methods are used, including fractional crystallization and sedimentation, distillation and sublimation, ion transfer, chromatographic method, liquid extraction, and zone recrystallization. However, in ion exchange technology concerning the separation of rare earth elements, the greatest success has been achieved.

Rare earth metals in their chemical properties are very similar to each other due to the peculiarities of the structure of the electron shell. In aqueous solutions, all REM is in the trivalent state. Therefore, when reactions occur in an aqueous medium and sedimentation is formed in one operation, only a slight enrichment of one of the rare-earth metals of others is achieved. In anhydrous solutions, the difference in the properties of rare earth metals is more pronounced.

In technologies for producing rare and rare earth metals in the metallic state, pyrometallurgical processes (sodiumthermia, calciothermy, magnesiumthermia, alumothermy, carbothermy), electrolysis and the method of decomposition of halide vapors, etc. are developing and practically applied.

Methods of arc melting, electron-beam vacuum melting, distillation, zone melting and electric transfer have been developed for refining rare and rare-earth metals, scandium and yttrium.

The technical level of equipment is a very important component of any technological process and includes the following components:

- equipment for the beneficiation of ores to concentrate (separators with high-energy permanent magnets, flotation processes, gravity processes, radiometric beneficiation);
- Corrosion-resistant equipment for leaching (autoclaves, containers), mixing pulp, pumping sorbent.

Obtaining high-purity substances is associated with high energy and material costs. Therefore, when receiving them, it is necessary to first answer the following questions: what is the degree of purity of the final product; whether there is an optimal concentration of impurities for a given substance.

Thus, the involvement of secondary noble and rare metals in industrial use is an urgent task. Prospective from the point of view of ecology and economically feasible are electrochemical processes of processing of technogenic raw materials, the main advantages of which are the production of pure metals; the minimum amount of reagents involved in the process, which greatly simplifies the solution of the problems of the circulation of industrial solutions and environmental protection; the possibility of full-scale automation. In addition, the use of electrochemical methods for the processing of technogenic raw materials is based on the possibility of using them at many stages of processing: the preliminary stage is concentration, the final stage is refining.

3.2 Phosphogypsum and agglomeration shop dust containing rare and rare earth metals

The effective use of pyrolusite as an oxidizing agent is possible for solving various chemical-technological and environmental problems. For example, the possibility of using pyrolusite MnO2 as an oxidizing agent to extract gold (and silver) in hydrochloric acid or sulfuric acid solutions containing chloride ions is noted [54, 55].

$MnO_2 + 4H^+ = Mn^{4+} + 2H_2O$
$Mn^{4+} + 2Cl^- = Mn^{2+} + Cl_2$
$2Au + 8Cl^- + 3Mn^{4+} = 2AuCl_4^- + 3Mn^{2+}$
$2Au + 3Cl_2 + 2Cl^- = 2AuCl_4^-$
$2Au + 8Cl^- + 3MnO_2 + 12H = 2AuCl_4^- + 3Mn^{2+} + 6H_2O$

At the same time, an effective method has been developed for the complex hydrometallurgical processing of mattes from lead plants by means of sulfuric acid leaching using manganese dioxide as an oxidizing agent.

To elucidate the role of individual components of the system in establishing redox potentials, let us consider, for example, the change in E ° in the $UO_2 – MnO_2$ Fe(II) – H_2SO_4 system with a gradual complication of its composition. As follows from these data, the highest potential is observed when the system contains only manganese dioxide. At the same time, the oxidation state of uranium dioxide under these conditions is low. Considering that manganese dioxide is practically insoluble in dilute solutions of sulfuric acid at 40 ° C [56, 57], it becomes clear how small amounts of this oxidizing agent in solution or on the electrode surface are sufficient to establish a high value of E °.

From our point of view, the most acceptable method for opening rhenium-containing lead dust is the method of direct hydrometallurgy, as it is more economical. In addition, the use of oxidizing agents makes it possible to significantly increase the extraction of metals into the solution. However, nitric acid, hydrogen peroxide, and potassium permanganate did not bring success either because of the high cost or because of the additional introduced impurities into the solution, which complicate its further processing. Therefore, it became necessary to find an inexpensive, affordable and sufficiently effective oxidizer. Manganese compounds can be oxidizing agents.

The use of various natural manganese-containing materials as an oxidizing agent for the extraction of rare and non-ferrous metals from lead-containing industrial products was considered in [24].

Attempts to use manganese ore to open up lead dust at the Ust-Kamenogorsk lead-zinc plant did not go beyond laboratory tests [25]. The following leaching regime is proposed: L: S = 2: 1, temperature - 75-85 ° C, initial concentration of sulfuric acid - 200-220 g / dm3, amount of manganese ore - 3.4 g per 1% sulfide sulfur, leaching time - 2 hours. The degree of extraction into the solution was,%: zinc 76-82, cadmium 66-89.5, thallium 60-62, arsenic 69-78, no data on rhenium.

The authors of [22] also used manganese concentrate with a content of 30-40 wt—% Manganese as an oxidizing agent to extract rhenium from sulfuric sludge of the Zhezkaz-Gan copper smelter. The technological parameters of leaching were studied: temperature, L: S, time, oxidant consumption. On the basis of experimental data, the optimal model was selected: L: S = 5: 1, temperature - 90 ° C, initial concentration of sulfuric acid - 200-250 g / dm3, leaching duration - 2 hours, consumption of manganese ore - 10% by weight of the sludge. The extraction of rhenium into the solution was 70-72%. Industrial tests have shown a lower extraction of rhenium (50%) in solution compared to laboratory experiments. The authors explain this situation by a lower leaching temperature (70 ° C). Along with rhenium, 51% of cadmium and 63% of zinc are extracted into the solution. The solutions after leaching were sent to the extraction of rhenium by extraction. There are no proposals for the extraction of cadmium and zinc.

There is data on the use of manganese-containing material for the leaching of lead-zinc prompt scraps [15]. The authors of the article studied and proposed the following leaching regime: temperature - 70-80 ° C, L: S = 5: 1, time - 8 hours. The consumption of the oxidizing agent has a significant effect on the extraction of metals into the solution, as well as on the quality of the resulting zinc sulfate. At an oxidizer consumption of 0.8-1.6% (based on the mass of the leached material), the extraction into the solution was,%: zinc 67.5, cadmium 77.1, indium 68.0. An increase in the consumption of the oxidizing agent from 5 to 20% significantly increases the extraction of rare metals, according to the authors (unfortunately, there are no numerical data), but it reduces the quality of zinc sulfate. The reason for this lies in the unacceptably high level of impurities additionally introduced with the oxidizing agent into the main process solution. It is known that the purification of solutions from manganese is complicated by the fact that manganese, along with potassium, sodium, and magnesium, is one of the impurities that are practically not removed from the zinc solution.

Thus, an analysis of the scientific, technical and patent literature on the extraction of rare and non-ferrous metals from lead production byproducts using manganese-containing compounds as oxidants revealed a positive effect of these oxidants on the degree of conversion of some metals into solution, but information on this issue is limited and scattered. , there are no judgments and points of view of the ongoing processes. The conducted research can be characterized as exploratory.

In the process of oxidative agglomerating, roasting of the lead charge, rhenium, cadmium and thallium are concentrated mainly in the dust of electrostatic sediments. This dust is the source of these metals. In light of this, studies have been carried out to study the behavior of rhenium, cadmium and zinc in the process of opening agglo dust with sulfuric acid solutions in the presence of manganese concentrate, depending on various physicochemical factors.

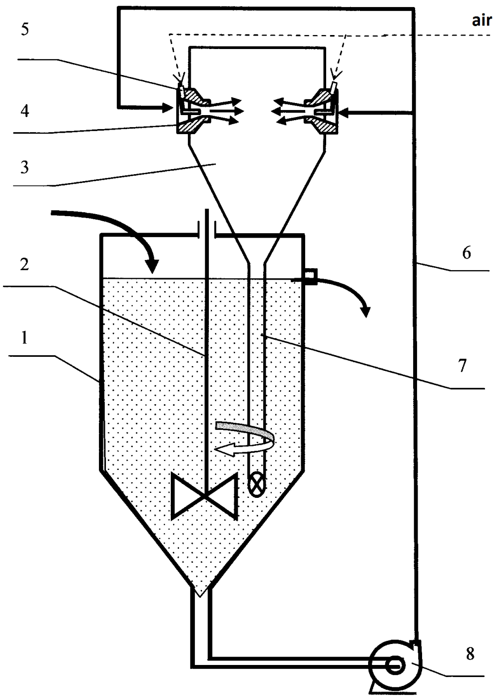
The experimental setup consisted of a thermostatically controlled cell with a working capacity of 0.25 L, equipped with an MR-25 stirrer with an adjustable speed and a reflux condenser. Temperature constancy was controlled using a U-10 thermostat. Sulfuric acid of "KhCh" grade of a given concentration was poured into the cell. A sample of dust was poured into a solution previously brought to the operating temperature. Thereafter, the required amount of oxidizing agent was supplied. After the end of the experiments, the pulp was filtered, and the resulting cakes were washed and dried at a temperature of 105 ° C.

The studies used:

- dust of the sintering shop of ShSZ;
- manganese concentrate, the elemental composition of which is given in Table 13, for conducting experiments to determine the optimal mode of metal leaching and testing in laboratory conditions;
- manganese (IV) oxide or "analytical grade" qualification for carrying out experiments to identify the kinetic regularities of metal leaching from dust, to study the interaction in systems: ReO_2-MnO_2-H_2SO_4, ReO_3-MnO_2-H_2SO_4, ReS_2-MnO_2-H_2SO_4;
- sulfuric acid of "chemically pure" qualification.

Solid and liquid products obtained in the course of the experiments were analyzed for rhenium, zinc, cadmium, and manganese according to generally accepted methods. Rhenium in solid products and in solutions was determined by the mass spectral method described in Section 2. Small contents of manganese, cadmium, zinc were determined by the atomic absorption method, large ones - by the volumetric method.

Leaching in a laboratory unit with the addition of manganese dioxide was carried out in the unit shown in Figure 15.



1 - PMS-6 converter; 2 - bath body; 3 - stirrer; 4 - electric motor; 5 - loading device.

Figure 15-Pulp leaching bath

The influence of the parameters characteristic of the hydrometallurgical process is studied: the consumption of manganese concentrate, the concentration of sulfuric acid, the duration of leaching, the ratio of solid to liquid.

The amount of manganese concentrate.

Experimental conditions: temperature-80 °C, duration-1 hour, mixing speed-200 revolutions per minute, initial concentration of sulfuric acid-1.0 mol/dm3, ratio S: L=1:3. The amount of manganese concentrate was changed from 0 to 30 % of the weight of the initial dust with an interval of 5 %. The results of the studies are shown in Table 18.

Table 18 - Influence of the amount of manganese concentrate on the extraction of metals into solution

Quantity of manganese concentrate, % of dust weight	Content in the solution, g/dm^3				Extraction into solution, %			
	Re	*Cd*	*Zn*	*Mn*	*Re*	*Cd*	*Zn*	*Mn*
0,0	0,106	5,380	2,63	-	50,50	39,9	87,60	-
5,0	0,151	8,910	3,23	9,300	80,10	66,0	91,37	98,15
10,0	0,158	10,80	3,75	18,58	84,01	80,0	91,95	98,02
15,0	0,159	11,23	4,25	27,01	84,27	83,2	92,03	94,97
20,0	0,165	11,89	4,75	34,99	87,58	88,1	92,03	92,28
25,0	0,167	11,89	5,25	43,52	88,55	88,1	92,20	91,81
30,0	0,169	12,06	5,78	51,56	89,73	89,3	92,70	90,65

From the obtained dependencies presented in table 17, it can be seen that in the absence of manganese concentrate rhenium is leached by 50.5%, cadmium by 39.9%, zinc by 87.6%. This extraction can be explained by the forms of finding the studied metals in the agglomerate: 50% of rhenium is represented by water-soluble compounds - perrhenates. The extraction of cadmium into the solution is about 40%, which is due to its presence in the agglomerate in the form of sulfate and oxide, readily soluble in water and aqueous solutions of acids. The high degree of zinc extraction into solution (87%) is also explained by the presence of zinc sulfate and zinc oxide in the dust. And also the introduction of an oxidizing agent into the pulp in an amount of 5-30% by weight of the dust helps to increase the degree of extraction of metals into the solution. Moreover, the extraction of cadmium increases on average by 50%, rhenium by 40, and zinc by only 5, and amounts to the total extraction from the solution by 89.3, 89.73, 92.7, respectively. A sharp jump in the increase in the degree of extraction of rhenium and cadmium into the solution (30%) occurs with the introduction of 5% concentrate, with a further increase in the amount of concentrate (up to 30%), the extraction of rhenium increases by only 9%. The amount of concentrate practically does not affect the degree of zinc extraction into solution: its equivalent values are within 91-92%. The extraction of manganese into the solution decreases from 98.65 to 90.65%. The high degree of transition of rhenium and cadmium into the solution upon the addition of manganese concentrate is probably explained by the occurrence of redox reactions between the compounds of rhenium, cadmium and manganese. It is likely that the sulfides and oxides of the lower oxidation states of the elements are oxidized.

The optimal amount of manganese concentrate (15%) by weight of dust), allows to achieve high extraction rates of Re, Cd, Zn, Mp.

Sulfuric acid concentration.

Experimental conditions are similar to the previous series, except for the amount of manganese concentrate and sulfuric acid. In the experiments carried out, the amount of manganese concentrate by weight of dust was 15%, the concentration of sulfuric acid was 0.25; 0.5; 1.0; 1.5; 2 mol/dm^3. The obtained experimental data are presented in table 19.

Table 19 - Influence of the concentration of sulfuric acid on the extraction of metals into solution

H_2SO_4, mol/dm^3	Content in solution, g/dm^3				Extraction into solution, %			
	Re	Cd	Zn	Mп	Re	Cd	Zn	Mп
0,25	0,167	5,40	4,07	17,65	88,20	40,0	82,13	62,07
0,50	0,167	8,29	4,29	27,22	88,15	61,42	92,85	95,73
1,00	0,166	10,86	4,25	27,65	88,18	80,46	92,08	97,22
1,50	0,168	11,73	4,27	27,77	88,85	81,89	92,50	97,64
2,00	0,168	11,61	4,49	27,66	88,90	86,01	92,3	97,27

The concentration of sulfuric acid has a different effect on the behavior of metals during their leaching from agglomerates. So, the extraction of rhenium does not depend on the acid concentration in the original pulp and is 88%. This is in good agreement with the ability of rhenic acid and its salts to dissolve in aqueous solutions. Obviously, during the oxidation of rhenium compounds - ReO_3, ReO_2, ReS_2 (practically insoluble in water, in aqueous solutions of alkalis and mineral acids that do not have oxidizing properties), when agglopyls are leached with sulfuric acid solutions in the presence of manganese oxide, rhenic acid is formed.

In contrast to rhenium, the extraction of cadmium with an increase in the concentration of sulfuric acid increases from 40 to 86%. Obviously, when the acid content in the solution is 0.25 or 0.5 mol/dm3, it is not enough to convert the poorly soluble cadmium oxide present in the dust into highly soluble cadmium sulfate.

The extraction of manganese, as well as cadmium, depends on the concentration of sulfuric acid. With an increase in its content from 0.25 to 2.0 mol/dm^3, the degree of manganese extraction also increases from 62 to 97%. Probably, at low acid concentrations (0.25; 0.5 mol / dm^3), it is not enough to obtain a well-soluble MnSO4 salt. The formation of manganese sulfate can be represented by the following reaction:

$$MnO_2 + H_2SO_4 = MnSO_4 + 1/2\ O_2 + H_2O$$

The influence of the concentration of sulfuric acid insignificantly affects the indicators of zinc extraction into solution. Its recovery rate is quite high (82-92%). This is due to the fact that zinc in the dust is mainly in the form of soluble zinc sulfate and partly - ZnO, when interacting with an acid, zinc sulfate is also formed.

Thus, the concentration of sulfuric acid in the leaching solution is determined by the quantitative content of cadmium and zinc oxides in the dust and manganese in the concentrate.

The ratio of solid to liquid.

In this series of experiments, the S: L ratio was changed in the range from 1: 2 to 1: 8 (Table 20). The rest of the studied parameters are constant and similar to the previous series.

Table 20 - Influence of S: L on the extraction of metals into solution

S:L	Content in solution, g/dm^3				Extraction into solution, %			
	Re	*Cd*	*Zn*	*Mn*	*Re*	*Cd*	*Zn*	*Mn*
1:2	0,160	10,66	4,17	22,49	86,13	78,95	90,36	79,1
1:3	0,120	7,560	2,81	17,64	88,20	84,10	91,58	93,1
1:4	0,090	5,730	2,12	13,50	88,20	85,03	92,20	95,0
1:5	0,070	4,700	1,70	11,06	87,20	87,10	92,40	97,3
1:6	0,050	3,970	1,42	9,210	87,20	88,30	92,50	97,2
1:7	0,050	3,410	1,22	7,870	88,70	88,40	92,70	97,0
1:8	0,047	2,970	1,07	6,910	88,70	88,00	92,70	97,3

From the data in table 19 it can be seen that an increase in S: L from 1: 2 to 1: 8 has practically no effect on the rates of extraction of rhenium and zinc. They are high and range from 86.1 to 88.7% for rhenium; from 90.4 to 92.7 for zinc. The observed deviations can be explained by the error in the methods for determining these elements.

The main amount of cadmium and manganese (approximately 80% each) is extracted at S: L = 1: 2. Starting from S: L = 1: 3, the degree of cadmium extraction monotonically increases and reaches 88.0%. Unlike cadmium, the extraction of manganese at S: L = 1: 3 increases by 13.0% compared to S: L = 1: 2, and then increases insignificantly, rising to 97%. The different influence of S: L on the transfer of Re, Cd, Zn and Mn into solution is determined by the amount and solubility of compounds of these elements present in the dust and concentrate and formed during the leaching process.

The optimal S: L ratio is 1: 3, at which the degree of extraction into the solution of rhenium is 88.2%, cadmium - 84.1, zinc - 91.5 and manganese - 93.0%. An increase in the S: L ratio above 1: 3, as can be seen from Table 19, leads to dilution of the solutions for the metals under study, to an increase in fluxes, and, consequently, to an increase in the cost of obtaining commercial products of rhenium, cadmium, zinc and manganese.

Temperature.

The temperature in the experiments was varied from 40 to 90 ° C while other parameters were constant. The initial temperature of 40 ° C is due to the heating of the pulp at the time of its preparation, i.e. when feeding sinter dust and manganese concentrate into sulfuric acid solutions. There is no noticeable effect of the temperature of the leaching process, as can be seen from Table 21, on the conversion of zinc into solution. Its recovery is 91-92% over the entire temperature range.

Table 21- Influence of the process temperature on the extraction of metals into solution

T, °C	Content in solution, g/dm^3				Extraction into solution, %			
	Re	Cd	Zn	Mп	Re	Cd	Zn	Mп
40	0,167	9,42	4,22	23,91	88,61	69,76	91,30	84,07
60	0,172	10,37	4,22	25,16	90,89	76,80	91,41	88,48
70	0,171	11,91	4,26	25,59	90,60	86,00	92,20	90,01
80	0,172	11,61	4,26	25,67	91,19	88,20	92,10	90,28
90	0,177	11,96	4,25	25,61	93,93	88,60	92,00	90,07

As can be seen from table 20, the degree of extraction into solution of rhenium and manganese slightly increases (by about 6% each) as the temperature rises from 40 to 90 ° C. The maximum amount is extracted into the solution - 94% of rhenium and 90.3% of manganese.

An increase in temperature from 40 to 80 ° C has a positive effect on the extraction of cadmium. It increases by about 20% and reaches a maximum value of 88.2%. The analysis of the data obtained showed that in order to more fully extract all the studied elements from the dust, the leaching process must be carried out at a temperature not lower than 80 ° C.

*Duration of leaching.*The experiments were carried out in the following time intervals: 5, 10, 30, 60, 90, 120 and 180 min. The results are shown in Table 22.

Table 22 - Influence of leaching duration on the extraction of metals into solution

Time, min	Content in solution, g/dm^3				Extraction into solution, %			
	Re	Cd	Zn	Mп	Re	Cd	Zn	Mп
5,0	0,034	3,120	2,61	5,740	18,00	23,1	56,60	20,20
10	0,105	6,070	3,60	10,89	55,60	45,0	78,00	38,30
20	0,149	7,830	3,93	17,66	79,00	58,0	85,00	62,10
30	0,169	11,47	4,44	22,38	89,51	85,0	96,19	78,70
60	0,170	11,52	4,44	22,84	90,12	85,3	96,21	80,32
90	0,170	11,56	4,31	22,36	90,20	85,7	93,30	80,40
120	0,140	11,73	4,45	23,88	90,19	86,9	96,34.	83,97
180	0,172	11,65	4,47	23,94	91,05	86,3	96,73	84,18

As can be seen from Table 21, increasing the leaching time has a positive effect on the transfer of metals into solution. So, in the first 20 minutes, the following is extracted into the solution, %: rhenium 79, cadmium 58, zinc 85 and manganese 62; and in the next 10 minutes, respectively, 89.5; 84.98; 96.1; 78.7. An increase in the process time from 30 to 180 min does not affect the degrees of extraction of the studied metals.

Based on the foregoing, it can be assumed that soluble compounds of rhenium, cadmium and zinc - perrhenates and sulfates, then - sulfates of cadmium and zinc, formed during the interaction of their oxides with sulfuric acid, go into the solution first. Starting from 30 minutes, hardly soluble sulfide and oxide compounds of rhenium and sulfides of cadmium and zinc pass into the solution.

Thus, on the basis of the studies carried out, it was found that the parameters under study (consumption of manganese concentrate, L: S, concentration of sulfuric acid, temperature, duration) have different effects on the extraction of rhenium, cadmium and zinc into the solution during leaching of agglomerates with sulfuric solutions, acid in the presence of manganese concentrate, which plays the role of an oxidizing agent.

The optimal leaching conditions have been determined: the concentration of sulfuric acid is 1.0 mol / dm^3, the consumption of manganese concentrate is 15.0% of the weight of the initial sinter dust, the duration is 1 hour, S: L = 1: 3, temperature is 80 ° C. The resulting solutions can be processed using sorption technology to obtain ammonium perrhenate and metallic cadmium.

3.3 A brief analytical review of the composition of technogenic waste from the uranium industry, and methods for extracting valuable components

The successful solution of the problem of protecting the biosphere, reducing the negative impact of industrialization on the state of the natural environment and many other global problems are directly related to the development of effective methods of analysis. There is a constant need for easy-to-follow, accurate, sensitive methods that would allow the determination of a component in a mixture of complex composition. To solve this problem, concentration methods are used, which have largely eliminated difficult situations. Moreover, in some cases, concentration expanded the range of applicability of instrumental methods (atomic absorption spectrometry, chromatography, spectrophotometry, voltammetry).

The study of the distribution of metals among coexisting forms in productive solutions and industrial waters of metallurgical plants requires a deep understanding by the analyst of the object of analysis, the correct choice of detection methods, and adequate interpretation of the results obtained. Steps such as sampling, storage and transportation are equally important. It is clear that the most reliable results are obtained in situ, at the sampling site. But in practice this is not always possible. To preserve samples during transportation to a stationary laboratory, they are frozen, preservatives and stabilizers are added. These operations inevitably lead to a change in pH, oxidation-reduction potential (Eh), ionic strength, cause imbalance between the coexisting forms of metals. As a rule, most analytical methods, including arbitration ones, allow determining only the total content of metals in water, and not their individual forms. To the factors complicating the determination of individual forms of metals, it is also necessary to add low concentrations of the metals being determined in productive and technogenic solutions, the presence of the so-called "background electrolyte" (macrocomponents of water - Na^+, K^+, Ca^{2+}, etc.) and various, including high-molecular organic compounds of natural origin (for example, humic substances, proteinaceous compounds, polypeptides, etc.). Thus, the complexity of the direct determination of individual forms of metals in productive and technogenic solutions is due to both the complexity of the object of research and a wide variety of their compounds in water, insufficient sensitivity and limited selectivity of many analytical methods. At this stage, this problem is solved by developing and using various research schemes based on a combination of methods for separating individual forms of metals with methods for determining their concentration in the resulting fractions. Such a separation can be based on various properties of the physicochemical forms of metals: size, solubility, affinity for the solid phase or ability to complex formation, charge, hydrophobicity, etc. In addition, each of these schemes provides for a reasonable sequence of performing the most important stages of research, compliance with which is a prerequisite for obtaining objective data on the distribution of metals among coexisting forms in natural waters. Especially important is the maximum preservation and minimization of the disturbance of the equilibrium state established between the coexisting forms of metals in productive and technogenic solutions.

Metals can be sorbed by suspended particles and / or hydroxides of iron and manganese, undergo hydrolysis, oxidized or reduced, and form complexes with inorganic and organic ligands. Listed in Figure 16 - the processes significantly affect the state of metals in natural and technogenic waters, productive leaching solutions and determine a wide variety of their forms of migration.

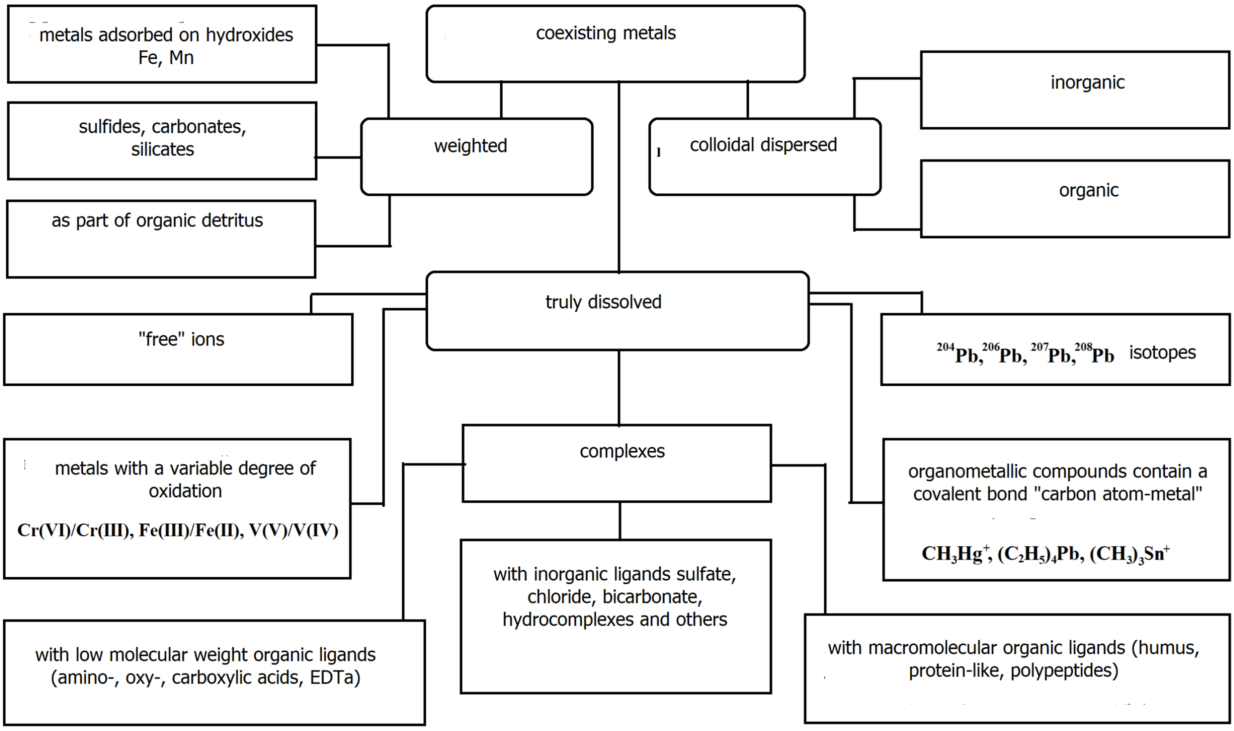


Figure 16 - Coexisting forms of metals in natural waters and productive solutions of underground leaching [58]

Low concentrations of rare earth metals in productive solutions and tail waters, as well as in fractions after separation of coexisting forms, necessitate their preliminary concentration. For this purpose, methods of both absolute (evaporation, freezing) and relative (sedimentation, extraction, ion exchange, and sorption) concentration can be used. The choice of one method or another is determined, first of all, by the properties of individual forms of metals and the method of their subsequent detection. The optimal case is when the concentration of individual forms of metals is combined with their separation. One of the most important conditions for using a particular method for concentration is the minimum impact on the equilibrium established in the system between coexisting forms.

Higher concentration ratios are achieved using co-sedimentation with different reservoirs. Concentration in this way is more expedient to use in combination with methods for detecting an analytical signal directly in the solid phase, for example, with X-ray fluorescence, atomic emission, or neutron activation.

Extraction with organic solvents is undoubtedly considered one of the most common methods for concentrating metals in samples. The use of the method provides not only high concentration efficiency and the possibility of combining with many detection methods, but also allows the separation of some forms of metals. Thus, extraction is successfully used for the separation and concentration of metals in different oxidation states, for example, Cr (VI) [59], V (IV and V) [60], metal complexes with natural organic ligands, and organometallic compounds. The disadvantages of extraction concentration include the need to work with toxic organic solvents, as well as technical difficulties arising in the separation of the organic and aqueous phases due to the formation of stable emulsions. There is also a risk of imbalance between coexisting metal forms if additional reagents are used for extraction.

Many disadvantages of liquid extraction are avoided by solid-phase extraction (SPE) and solid-phase matrix extraction (SPME), which, respectively, are based on the use of hydrophobic alkylated silica gels and polymer-coated fibers. Both methods are widely used to concentrate organometallic compounds during their gas chromatographic separation, as well as to determine the content of metals in different oxidation states. The conditions for the extraction of substances using these methods are similar to the conditions for their separation in liquid extraction. At the same time, the advantages of SPE and SPME in comparison with traditional liquid-liquid extraction are greater environmental safety, ease of automation and combination with on-line detection methods. Unfortunately, some methodological aspects of the use of SPME for preconcentration, including the main mechanisms of the interaction of substances with the coating of fibers, the stability of the extracted compounds on the surface of the carrier, etc., remain unclear.

High values of concentration coefficients and the possibility of selective separation of metals are combined in the case of sorption methods. Sorbents are especially convenient for obtaining metal concentrates directly at the sampling site. Activated carbons, cellulose, aluminum oxide, ion exchangers based on various materials are widespread. The efficiency of metal extraction by such sorbents substantially depends on the properties of the solid phase surface. The main disadvantage of these sorption materials is their insufficient selectivity with respect to metal ions. The problem can be solved by a directed change in the chemical and analytical properties of sorbents by modifying their surface with chelating reagents. Both covalent and non-covalent attachments of organic reagents with different functional groups to the support surface are possible. In this case, ion exchangers based on polymers of various types can serve as materials for modification: polyurethane foams, cellulose, polymer fibers, membranes and filter paper, aluminum oxide, silica. The latter, in contrast to synthetic polymers and ion-exchange resins, are characterized by high thermal, mechanical and chemical resistance, lack of their own color, high rate of mass transfer and ease of regeneration.

Silica with various complex-forming functional-analytical groups covalently fixed on the surface has proven themselves well for the extraction and concentration of metals from aqueous solutions. The main advantage of such sorbents is their high resistance to desorption of immobilized analytical reagents. Among the disadvantages should be noted the complexity of obtaining such sorbents and their regeneration and, as a consequence, high cost.

A less complicated method of midification is the impregnation of silica with organic reagents. However, the sorbents obtained in this way are characterized by a high degree of desorption of the modifier from the silica surface, especially at low pH values. To solve the problem, alkylated silica gels LiChroprep RP-8 and LiChroprep RP-18 and nitroso-P-salt in the form of an ion pair with methyltrioctyl ammonine chloride (Aliquat 336) are used for impregnation. The degree of desorption of the reagent from the surface of the sorbents obtained in this way turned out to be 40-80% less than in the case of hydroxylated silica gel impregnated only with nitroso-P-salt.

Adsorption is a more effective and at the same time simple way of fixing organic reagents on the surface of silica. At the same time, adsorptively modified silicas retain such advantages of chemically modified materials as mechanical and chemical stability, high rate of establishment of sorption equilibrium, etc. Both hydroxylated and alkylated silica gels are used to immobilize organic reagents. A number of sorbents have been obtained for the concentration of metals on the basis of various analytical reagents. Among them are immobilized 1-nitroso-2-naphthol, 1,10-phenanthroline, dithizone, xylenol orange, diphenylcarbazone, 8-hydroxyquinoline, quaternary ammonium salts, etc. Immobilized hetarylase compounds proved to be the most promising for the determination of sd-metals, in particular 1- (2-pyridylazo) -2-naphthol (PAN), 4- (2-pyridylazo) -resorcinol (PAR), 4- (2-thiazolylazo) -resorcinol (TAP), 1- (2-thiazolylazo) -2-naphthol (TAN), 1 - (4-adamantyl-2-thiazalylazo) -2-naphthol (ATAN). For example, TAN immobilized on silica turned out to be sufficiently sensitive and selective for the extraction and concentration of Cu, Zn, and Co. Unfortunately, the high degree of desorption of the reagent from the silica surface limits the use of the sorbent for the analysis of highly mineralized waters.

The extensive experimental results of recent years on the methods of concentration and separation are summarized and presented in the monographs of Yu.A. Zolotova, N.M. Kuzmina, Moskvina L.N., Tsaritsina L.G., Mitsuike A. As follows from these works, the same methods are usually used for separation and concentration. The most common ones are:

1 Extraction (including extraction chromatography).
2 Sorption methods (sorption, ion exchange and chelate chromatography).
3 Sedimentation and co-sedimentation.
4 Electrochemical methods.
5 Membrane methods.
6 Physical and physicochemical methods.
7 Flotation.

3.4 Physicochemical basis for the extraction of rare and rare earth metals from technological solutions

Sedimentation is generally used to separate inorganic substances. Sedimentation of microcomponents with organic reagents, and especially their co-sedimentation, provide a high concentration coefficient. These methods are used in combination with determination methods that are designed to obtain an analytical signal from solid samples, for example, atomic emission and X-ray fluorescence.

Almost all selective inorganic and organic inorganic ion deposition reagents are suitable for separation. Several groups of sedimentation can be distinguished:

1) Acids and hydrated metal oxides (silicon, stannous, tungstic acids, hydrates of iron (III) oxides, aluminum, etc.);

2) Poorly soluble compounds of some acids (sulfates, chlorides, carbonates, sulfides, phosphates, oxalates);

3) Sediments with organic reagents (poorly soluble chelates and ionic associates);

4) substances released in the elemental state (mercury, tellurium, selenium, gold).

Sedimentation concentration usually isolates the matrix rather than the microcomponent. It is important to obtain sediment free from trace impurities; for this it is better to use organic sediments. The concentration of microcomponents by sedimentation is rarely used: their content is so small that a solid phase is not formed. For these purposes, it is more expedient to use the method of cosedimentation of microcomponents.

Cosedimentation can be considered in two aspects: as an undesirable effect accompanying the sedimentation process and leading to contamination of the sediment, and as a process of directed release of trace impurities.

According to the experimental technique, the cosedimentation method has much in common with conventional sedimentation. Usually, a reagent capable of forming a poorly soluble compound with one of the macrocomponents of the mixture to be separated or a substance specially introduced into the solution is introduced into the solution, which acts as a carrier or collector of trace impurities.

In our case, ammonia water was used as a co-precipitant, which completely sedimentates all impurities from the solution. This operation is necessary for a one-time purification of technological solutions from ions of iron, aluminum, chromium, etc. An ammonia solution NH_4OH sedimentates iron (II) hydroxide, like alkalis. However, in the presence of ammonium salts, ammonia does not sedimentate iron (II).

Rare earth metal hydrates are easily formed by the interaction of solutions of the corresponding salts with alkalis. Scandium oxide hydrate has a weakly expressed acidic character and dissolves slightly in alkali solutions; B.N. Ivanov-Emin and EA Ostroumov established [61] that a noticeable dissolution of $Sc(OH)_3$ occurs only when boiling with concentrated solutions of alkalis. Vickery [62] believes that the solubility of NaOH - in NaOH depends on the relative amounts of reagents. In fig. 28 shows the dependence obtained by Vickery between the pH of dissolution of NaOH and its concentration. It should be borne in mind that if the sedimentation of scandium hydroxide is carried out not with caustic soda, but with ammonia, then complete sedimentation does not occur due to the formation of complex ammonoscandiates.

Yttrium oxide hydrate forms in alkaline solutions only colloidal solutions that quickly coagulate; hydroxide lanthanum does not react with alkalis at all, having a pronounced basic character.

Hydrates of oxides of other rare earth elements are also basic and do not interact with alkalis, which is of great practical importance, that allows to highlight rare earths in the form of oxide hydrates from alkaline solutions other connections.

B. N. Ivanov-Emin and JI. A. Niselson [63] showed that under certain conditions, ytterbium and lutetium hydroxides exhibit amphotericity. If air-dry ytterbium or lutetium hydroxides with a sodium hydroxide solution saturated at 20° C are heated in an autoclave at 180 ° C, the hydroxides are completely dissolved; when the solution is cooled, crystalline sedimentates with the composition $Na_3[Yb(OH)_6]$ and $Na_3[Lu(OH)_6]$ sediment. With cold water, these crystals completely decompose with the formation of a hydroxide sediment and the release of free alkali.

The pH of the beginning of sedimentation of scandium hydroxide is, according to E. A. Ostroumov's data [64], 4.9 if the sedimentation is carried out from nitrate solutions; according to other data, the pH of $Sc(OH)_3$ sedimentation from acetate solutions is 6.1 [65]. In general, the pH of the onset of sedimentation of hydroxides of all elements of the scandium subgroup noticeably depends on the solution from which sedimentation is carried out and varies between 6 and 8.

Table 23 shows the data they received. The color of the formed sedimentation is also indicated there, since it is characteristic of the REE.

Table 23 - pH sedimentation of REE hydroxides from sulfate solutions

Hydroxide	pH of sedimentation from sulfate solutions	Sediment color
Lantana	7,41	White
Ceria	7,35	White
Praseodymium	7,17	Gray-green
Neodymium	6,95	Mauve
Samaria	6,70	Yellowish
Europia	6,68	Pinkish White
Gadolinium	6,75	White
Yttria	6,83	White
Erbia	6,50	Pinkish
Tulia	6,21	Greenish White
Ytterbium	6,18	White
Lutetia	6,18	White

The solubility products of hydroxides are given in Table 24 according to the data of Miller and Kremers [67, 65] and Meller and Vogel [66]. For comparison, the same table shows the data obtained by I. M. Korenman [68] by calculation based on the equation $p\Pi p = 42{,}39 - 3\ pH - [Me^{3+}]$ obtained using the expression for the product of solubility $[M^{3+}]*[OH-]^3 = Pr$, in which $[OH-]^3$ is expressed in terms of the ionic product of water. The concentration of REE ions in the calculations of M. I. Korenman was assumed to be 10^{-6} mol/l, and the pH of sedimentation of hydroxides was taken from the literature data.

Table 24-Product of solubility of lanthanide hydroxides

Hydroxide	Calculated data on Latimer [67]	Calculated data on I.M. Korenman [68]
Lanthanum	$1*10^{-19}$	$5*10^{-21}$
Cerium	$1,5*10^{-20}$	$5*10^{-23}$
Praseodymium	$2,7*10^{-20}$	$7*10^{-24}$
Neodymium	$1,9*10^{-21}$	$5*10^{-24}$
Samaria	$6,8*10^{-22}$	$2*10^{-24}$
Europium	$3,4*10^{-22}$	-
Gadolinium	$2,1*10^{-22}$	-
Yttrium	$8,1*10^{-23}$	$1*10^{-24}$
Erbium	$1,3*10^{-23}$	-
Thulium	$3,3*10^{-24}$	-
Ytterbium	$2,9*10^{-24}$	-
Lutetius	$2,5*10^{-24}$	-
Scandium	$1*10^{-28}$	-

There are no data for promethium hydroxide in this table; however, I. E. Starik and M. S. Lambet [69], working with micro amounts of promethium in an aqueous solution, found that at pH below 3, promethium is in solution in an ionic state (adsorbed on quartz glass), and at a pH of about 6, hydrolysis begins, and during ultrafiltration through a cellophane filter, up to 80% of the promethium present in the solution is retained on the latter. The solubility product of promethium hydroxide should be, according to the assumptions of the above-mentioned researchers, of the order of 10^{-33}, but, of course, still needs to be clarified, as well as the composition of the compound retained by the filter, which is supposedly taken for hydroxide.

As can be seen from the data in Tables 23 and 24, the pH and Pr values obtained by the same researchers, by the same method and from the same starting materials, are not the same for solutions of different salts of the same element. Moreover, it is obvious that the pH and Pr values obtained by different authors under different conditions from salts of different purity levels can differ from each other. Therefore, the values given in the extensive literature on the sedimentation of REE hydroxides should be treated with caution, always bearing in mind the conditions in which the data was obtained.

In addition, it should be borne in mind that during the sedimentation of REE hydroxides, basic salts of various compositions are usually formed first of all, which transform into normal hydroxide after different periods of time, sometimes rather long. This is clearly shown in a series of works by I.V. Akselrud and V.B. Spivakovsky [70], who carried out a potentiometric study of the sedimentation of hydroxides from solutions of cerium [71], yttrium and lanthanum chlorides [72], samarium [73], dysprosium [74], erbium and ytterbium [75]. These works showed that the pH of sedimentation and the composition of the sediment depend on the ratio of the concentrations of Me^{3+} and $C1^-$; the composition of the sediment gradually changes with time towards the elimination of the chlorine ion and turns into normal hydroxide $Me(OH)_3$, and the rate of this transition is very different. So, in the case of lanthanum it was 166 days, in the case of yttrium 125 days, samarium 33 and dysprosium 50 days; in the case of erbium and ytterbium, basic salts of the composition $Me(OH)_{2,5}Cl_{0,5}$ were found after 50 days.

Cerium hydroxide sedimentates were studied only freshly prepared, since when left for a prolonged time they are oxidized to Ce (IV). I.V Tananaev and M. Ya. Bokmelder [76], investigated sedimentation of cerium oxide hydrate from sulfate solutions, found that the formation of $Ce(OH)_3$ proceeds through the intermediate basic salts $Ce_3(OH)_5*(SO_4)_2$ and $Ce_2(OH)_4S0_4$, and some small amount of sulfate ion is firmly retained by the sediment. The sedimentation reaction of $Nd(OH)_3$ from solutions of its sulfates or nitrates proceeds in exactly the same way: first, a basic salt of the composition $Nd_2(OH)_5NO_3$ or $Nd_2(OH)_4SO_4$ is formed, which, with an increase in the concentration of alkali, transforms into $Nd(OH)_3$; a certain amount of sulfate or nitrate ions is always found in the hydroxide sediment [77].

Thus, the process of sedimentation of REE hydroxides, with all its external simplicity, is, in essence, a very complex and far from fully studied process.

$Ce(OH)_4$ tetravalent cerium oxide hydrate also has a basic character, but weaker than $Ce(OH)_3$. Cerium tetravalent salts are very easily hydrolyzed in aqueous solutions. Even cerates are known, i.e., salts of Me_2CeO_3.

Hydrates of oxides of all rare-earth elements, as well as yttrium and scandium, are readily soluble in acids, forming salts of the corresponding trivalent cations.

Based on the above given information the best sedimentating agent for industrial operations should be considered dissolved in water or gaseous ammonia. This is due to economic indicators. For example, let's consider some of the most commonly used inorganic precipitants in industry. In the example, the consumption of the precipitant for rare and rare earth metals is negligible, since in solutions of the uranium industry its amount is not more than 50 mg / l. The main components were taken into account according to the salt background, where the amount of aluminum and iron corresponds to 1 g / l.

Calculation of reagents per 1 liter of test solution

Σ Fe, Al = 1g/l +1g/l= 0,06n + 0,1n= 0,16n

Na_2CO_3 = 53 * 0,16 = 8,5gm

NaOH = 40 * 0,16 = 6,4gm

NH_3 = 17 * 0,16 = 2,72gm or NH_4OH = 2,72/0,25 = 11 ml

Fe*** = 0,06n

Na_2CO_3 = 53 * 0,06 = 3,2gm

NaOH = 40 * 0,06 = 2,4gm

NH_3 = 17 * 0,06 = 1,0gm or NH_4OH = 1,0/0,25 = 4ml

This method of sedimentation not only allows to clean solutions from undesirable salt background, but to concentrate scanty amounts of rare earth metals. Along with this, the features of the extraction of REE from uranium ore middlings include, as a rule, their insignificant content against the background of high concentrations of macrocomponents (Al, Fe, Ca, Mg, etc.). In this regard, many industrial technologies for the concentration and extraction of rare earth metals are unsuitable and ineffective. In addition, the choice of a method for extracting, for example, from productive solutions from underground leaching of uranium, in the overwhelming majority of cases, is associated with the impossibility of changing the chemical composition of productive solutions [78]. Scientists propose sorption or extraction extraction of REE, which they consider to be the most expedient at the stage of primary concentration. But a serious problem, both in sorption and in the extraction of rare earth metals from productive uranium sulfate solutions, will be the presence of a large amount of ferric iron in them, since it is known that the sulfuric acid medium is poorly selective for the separation of Fe (III) and rare earth metals [79] ... In practice, the task of separating rare earth metals from such solutions is solved by hydrolytic sedimentation of iron with alkaline agents, with further organization of the process of extracting rare earth metals from clarified solutions or from hydrated pulps [80]. Another way is the preliminary reduction of ferric iron to ferrous iron shavings, urea, sodium sulfite or other reducing agents. With such an organization of the process, the choice of extraction and sorption systems with significant separation coefficients of Fe (II) and REM (III) is much wider [81, 82].

Sulfuric acid is currently used almost exclusively to extract uranium from underground ores. Uranium forms soluble uranyl sulfate, UO_2SO_4, and complex anions such as $UO_2(SO_4)_2$-^{2} and $UO_2(SO_4)_2$-^{4}.

There are a number of technological parameters that affect the leaching of uranium. They include the granulometric composition of the ore, acidity, oxidative potential, temperature, time and pulp density. The oxidation potential is usually regulated by the divalent/trivalent iron ratio and the presence of trivalent iron ions is required to influence the oxidation to soluble uranium (IV) sulfate compounds.

$$UO_2 + 2\ Fe^{+3} \rightarrow UO_2^{+2} + 2\ Fe^{+2}$$

Although the ferric ion is an effective oxidizing agent, the pentavalent vanadium ion is also effective in this role. Since these oxidative ions are reduced by oxidizing uranium, they can be re-formed by the addition of other oxidizing reagents such as oxygen, sodium chlorate, Caro's acid (H_2SO_5) or pyrolusite (MnO2).

$$6\ Fe^{2+} + NaClO_4 + 6\ H_2 \rightarrow 6\ Fe^{3+} + NaCl + 3\ H_2O$$

$$2\ Fe^{2+} + MnO_2 + 4\ H_2 \rightarrow 2\ Fe^{3+} + Mn^{2+} + 2\ H_2O$$

It has been shown that chemical oxidants, including oxygen, are generally ineffective in oxidizing uranium in the absence of iron in solution. The ratio of ferric to ferrous ions in solution also affects the rate and degree of uranium dissolution; the recovery decreases with an increase in the number of ferrous ions, even if the concentration of ferric ions remains constant. A large ferrous / ferric ion ratio is especially important when leaching more refractory uranium ores.

In the Elliot Lake ore type, brannerite is the main uranium mineral and contains uranium already in an oxidized form. High acidity and temperature are mandatory for the dissolution of this refractory mineral. However, oxidizing agents are still required to oxidize a small amount of uranite and to neutralize the reducing effect of metallic iron from the grinding material. The latter necessity was of course eliminated, since the use of semi-self-grinding has become more common.

Stoichiometric iron is not required in the oxidative reaction because iron is only an intermediate in this reaction. The minimum requirements for ferric ions were found to be about 0.5 g / L Fe^{3+} for low-grade ores; low concentrations of Fe^{3+} limit the rate of the dissolution reaction. For the rich ores of Saskatchewan, Fe^{3+} concentrations of about 3 g / l are more typical. It was also noted that the concentration of free ferric ions is a critical parameter, so the presence of complexing ions such as phosphate, arsenate or fluoride restores the effective concentration of ferric ions. It is believed that even chlorate combines with trivalent ions and can inhibit the oxidative reaction if chlorate is present in excess.

The oxidizing power of a solution is indicated by determining the ratio of Fe+ 3 to Fe + 2 or by directly measuring the redox potential using platinum and saturated calomel electrodes. Therefore, the degree of completion of uranium oxidation can be determined and used as a process control measure for the addition of an oxidant. Satisfactory leaching is usually achieved with a redox potential in the range of 400 to 650 mV, oxidizing relative to a standard calomel electrode. However, for a particular type of ore, laboratory tests are usually required to determine the optimal conditions for EMF, temperature, ferric / ferrous ratio, total iron concentration and type of oxidant, all of which are somewhat interrelated.

Iron is usually present in solution in sufficient concentrations to act as a catalyst for the added oxidizing agent, due to its presence in the starting minerals, in the accompanying vein minerals, and / or from wear of the steel grinding material. However, there are cases where there is a lack of iron for acceptable leach recovery, unless iron is specifically added. The Rössing uranium plant in Namibia showed for the first time that ferric ions are required to dissolve the dominant uranium mineral, uraninite. It was later found that, depending on the local source of the ore, there were subtle variations in leach recoveries. Despite this, if the concentration of ferric ions remained high, above 3 g/l Fe, these deviations were largely eliminated and uranium recovery in excess of 93% could be achieved in the usual way. Since iron oxide was produced as a calcined material by roasting pyrite to form sulfuric acid, a scheme was put in place to dissolve the calcined material in concentrated sulfuric acid, producing ferrous sulfate, which is added to the lye. The introduction of iron ions in this way also reduces the consumption of MnO_2, which is added to maintain a high ratio of iron ions trivalent / bivalent.

At the Hartebeestfontein factory, ferric ions are also formed from the fired material. After the reaction of roasted iron oxide with concentrated sulfuric acid, the resulting slurry is combined with the filtrate obtained from the extraction of uranium. The mixture reacts with sulfur dioxide in flotation cells, and the self-oxidation reaction leads to the conversion of ferrous ions to ferric with the formation of sulfuric acid. A number of South African factories use a milder form of decomposition of the fired material by adding sulfuric acid to the calcined pulp in pouches at a temperature of 70 to 90 °C.

Research has shown that pyrite can be oxidized in situ, but this approach has not been used commercially. Oxidative autoclave leaching is advantageous due to the fact that if a pyrite-bearing yranium ore slurry is saturated with air at a pressure of about 150 psi and a temperature of 1500 ° C, the pyrite is oxidized, thus producing the sulfuric acid required for the leach. The Anglo American Corporation's pressure leaching method was carried out in the 1950s, but was considered unprofitable at the time. With the increase in prices for uranium and sulfuric acid, experiments were resumed. This exploration work showed that with the presence of 0.2 to 2% pyrite in the ore, enough acid was produced to dissolve the uranium, but this approach was not put into production with pyrite as a sulfur source.

Even with the selective extraction of uranium using tertiary amines, there may still be significant amounts of co-extracted iron, co-sorbed on organic droplets, or simply involved in the organic phase. The transfer of iron for separation can cause stable emulsions or clots from the deposition of iron hydroxides/oxides at these stages. The introduction of water purification stages between extraction and separation has been confirmed as effective in controlling the transfer of iron and other impurities. A good example of such a technology is water purification for removing ammonia in the uranium dissolution extraction scheme at Key Lake [83].

It was found that for some rich uranium ores, the extraction by dissolution or ion exchange could be replaced by the iron deposition stage. The sedimented iron hydroxide tends to collect impurities and form a solution from which it is possible to obtain a uranium concentrate corresponding to the usual characteristics. Very careful monitoring of the pH in the 3.4-3.6 range is required to avoid co-deposition of too much uranium. Even in this case, a certain amount of uranium is jointly deposited and it is necessary to re-leach the prompt scrap, with a return to the main leaching, for an acceptable total extraction of uranium.

But it should be noted that we will be studying technogenic solutions, i.e. sorption mother liquors with traces of uranium and containing REE 15-50 mg / l. At such concentrations of recovered components, sorption methods for the extraction of REE are unsuitable and ineffective, and extraction methods are economically inexpedient due to the high cost of the process reagents. Therefore, sedimentation methods of rare earth metals are not only economically beneficial, but also effective with such amounts of valuable components. Along with this, this method makes it possible to clean up from accumulated salt systems in circulating solutions of the uranium industry, which undoubtedly makes the use of the developed method attractive against the background of other methods for extracting rare earth elements.

3.5 Obtaining rough concentrates from solutions of the uranium industry, containing rare and rare earth metals

Laboratory studies were carried out to extract rare earth metals from the spent solution of the PV-19 deposit. The content of the total REM in the initial solution is on average 30 mg / l, the iron content is 1.0 g / l, the aluminum content is 0.9 g / l (900 mg / l); and iron by a hydrolytic method by neutralizing the solution to pH = 9, a collective concentrate was obtained containing 1.5-2.5% of the total REM. Ammonia solution, caustic and soda ash, magnesite and partially slaked lime were used as a solution neutralizer. The decrease in the concentration of the total REM in the concentrate is caused by the sedimentation of aluminum hydroxide. The use of manganese ore as an oxidizer of iron to a trivalent state saves sulfuric acid by 25-30% when neutralizing the solution. The resulting product was analyzed on a two-beam scanning spectrophotometer Cary-50 Scan in the regional engineering testing laboratory "Structural and biochemical materials" at SKSU named after M.O. Auezov (Figure 16).

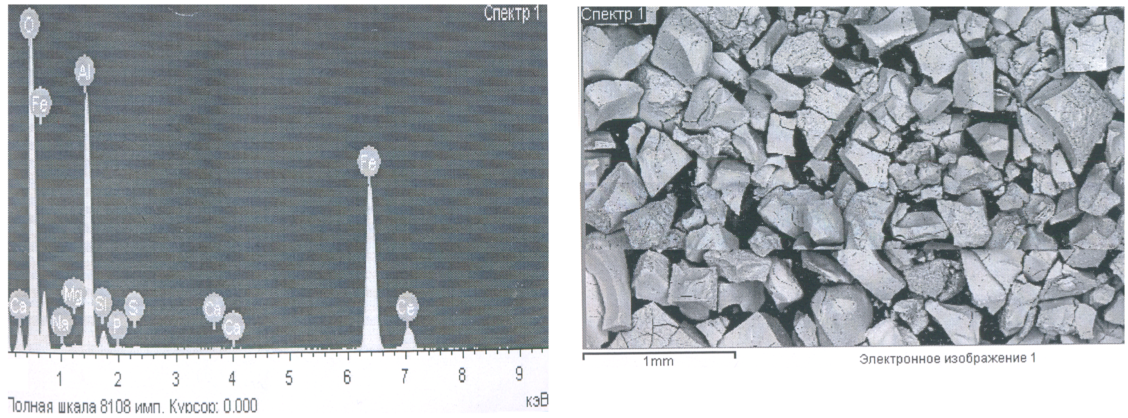


Figure 16 - The resulting primary product containing rare earth metals

As can be seen from Figure 16, the resulting sediment is hydrates of iron, aluminum and rare earth elements, which is confirmed by the chemical analysis of the product.

It was decided to investigate a method for extracting rare-earth metals by the method of preliminary selective sedimentation of iron at pH = 3.8, and then co-sedimentation of rare-earth metals and aluminum at pH = 9.5. When the pH of the solution was raised to 3.8, the iron was sedimented to traces, while the aluminum content in the solution decreased by half. With an increase in the pH of the solution to 9.5, aluminum was completely sedimentated, the content of rare-earth metals in the solution decreased by 90-97% and a collective concentrate was obtained containing 2.5-3.5% of the total amount of rare-earth metals. The work requires further research.

It was decided to investigate a method for extracting rare-earth metals by the method of preliminary selective sedimentation of iron at pH = 3.0-3.5, and then co-sedimentation of rare-earth metals and aluminum at pH = 9.5.

The concentrate is being enriched by removing aluminum by leaching with an alkaline solution. The conducted series of laboratory studies on the extraction of rare earth metals from the spent solutions of the PV-19 deposit by the method of preliminary deposition of iron at pH=4 and further co-deposition of rare earth metals with aluminum and its purification will make it possible to adjust the basic scheme for processing solutions with a low content of rare earth metals and obtaining a concentrate richer in rare earth metals.

A method for extracting rhenium from masterbatch solutions of uranium sorption is also considered. Methods that can be divided into four groups are currently used to isolate rhenium from solutions:

- methods of sedimentation of poorly soluble rhenium compounds (potassium perrenate, sulfides, organometallic rhenium compounds, etc.);
- cementation methods;
- electrolytic deposition;
- sorption and extraction methods.

Currently, sorption-extraction methods have become dominant in rhenium technology, which have practically displaced the rest from factory practice. In general, the current technological extraction of rhenium from various solutions is characterized by complexity, multi-stage and labor intensity. They usually include a combination of processes such as liquid extraction, ionite sorption, electrodialysis, etc.

Sedimentation of poorly soluble rhenium (VII) compounds. Currently, in factory practice, two methods are mainly used for the sedimentation of rhenium from solutions obtained during the processing of rhenium-containing raw materials: sedimentation of rhenium sulfides (from poor solutions) and in the form of potassium perrenate from rich solutions [84].

Rhenium (VII) sulfide is practically insoluble in water, alkaline and acidic solutions [85]. It is decomposed by hydrogen peroxide and nitric acid to form rhenium acid. From acidic media, rhenium (VII) sulfide is sedimented by the reaction:

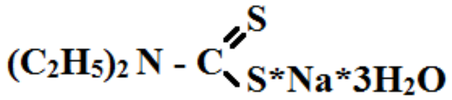
$$2HReO_4 + 7H_2S = Re_2S_7 + 8H_2O$$

Sodium sulfide, ammonium sulfide, polysulfides, etc. can be used as sedimentators. In practice, the sulfide sedimentation of rhenium from acidic solutions is most often carried out with sodium thiosulfate [86]. Usually, a 20% solution of sodium thiosulfate is used. The concentration of $Na_2S_2O_3$ in the solution is 1.0-2.0 g/l, the temperature is > 60 ^{0}C, the duration is 0.5-1.0 h. The extraction of rhenium into the sulfide product exceeds 90 %. Rhenium sulfide deposition is used on an industrial scale for pre-concentration from poor solutions that do not contain molybdenum in significant quantities.

Chemical purification of the obtained primary product is used mainly for separation from alkaline and alkaline-earth impurities. It consists in the sedimentation of REM hydroxides from their solution in mineral acid with an ammonia solution. Washing hydroxides, dissolving them in nitric acid, sedimenting oxalates, washing them, drying and calcining REM oxalates to oxides. Optimal conditions for this process: the concentration of REE in a solution of 20-30 g/l of oxides, sedimentation with 25 % ammonia at 80 °C, triple washing of hydroxides with hot water at S:L =1: 1. Double sedimentation of hydroxides allows achieving deeper purification from impurities, but significantly complicates the technology and requires a large consumption of reagents.

Further separation of impurities of alkaline and alkaline earth metals, as well as purification from coloring impurities is carried out in the process of sedimentation of REM oxalates. The filtered hydroxide sediment is dissolved in nitric acid to a concentration of 50-60 g/l Ln_2O_3 and pH = 1-2, after which the REM oxalates are sedimented from the solution with a saturated solution of oxalic acid. The oxalate sediment is washed twice on the filter with hot water containing 0.2 % $H_2C_2O_4$, at S: L=1:1. Next, oxalates are calcined to REE oxides according to the well-known method [87].

A more effective method of purification from impurities of coloring transition metals is the sedimentation of impurities using organic complexing agents, in particular sodium diethyldithiocarbaminate (DDTC), which has the following formula:



$$(C_2H_5)_2N - C\overset{\displaystyle \nearrow S}{\searrow S*Na*3H_2O}$$

DDTC is an available group reagent for all elements that form stable sulfides with it in aqueous solutions. It is successfully used to separate impurities of coloring transition metals from REM, since stable REM sulfides are not formed. The advantages of DDTC over other organic complexing agents (ditizon, xanthogenate) are that reactions with heavy metals take place in an acidic environment. This is especially important when working with solutions of REM salts that are prone to hydrolysis in a neutral and slightly alkaline environment. Transition metals form intra-complex compounds with DDTC of the type. For more complete deposition of impurities and improved filtration, polyacrylamide is introduced into the solution in the form of an aqueous 0.1% solution. The introduction of polyacrylamide into the cleaned solution significantly improves the quality of cleaning due to the flocculating effect on colloidal particles of DDTC complexes with impurity metals. In the process of sedimentation of impurities with the help of DDTC, it is possible to purify REM oxides from impurities of coloring transition metals up to $(0,2 \div 3)*10^{-4}$ %.

The possibilities of sedimentation of micro-impurities with the help of organic complexing agents are significantly expanded when using the adsorption-complexing method, which consists in sorption of micro-impurities in the form of their complex compounds with organic reagents on substances with a developed specific surface area. One of the most common types of sorbents are activated carbons – dense crystalline aggregates with a high degree of porosity. The adsorption-complexing method is widely used for deep purification of elements [88].

Based on the above, we have obtained primary productive materials containing rare and rare earth metals. Further, the primary concentrate will be purified to obtain pure compounds in the form of mish-metals of rare earth metals, which will be presented in the following sections of this report.

4 METHODS FOR THE DETERMINATION OF RARE AND RARE EARTH METALS IN LIQUID AND SOLID SAMPLES

The purpose of this section of the research work is to develop methods for measuring the content of rhenium and rare earth metals for certification of data obtained by inductively coupled plasma with mass separation, neutron activation analysis and X-ray fluorescence analysis, and obtaining their metrological characteristics.

The results of studies on the study of the total and individual contents of rare-earth metals and rhenium in solutions and resins of underground leaching, taking into account a one-time sampling at uranium deposits, preliminary data are of an estimate nature. At the same time, for the used instrumental methods NAA, ICP MS and XRF, methodological work was not carried out to determine their metrological characteristics. In this regard, the analytical data obtained can be considered only estimates. An example of this is the content of rhenium in solutions of underground leaching; the data on the content of this element obtained by two independent methods have significant differences, which can be determined both by the peculiarities of the behavior of rhenium compounds during drying of samples, and by the possible influence of spectral overlays. To a lesser extent, similar effects can be characteristic of other elements as well. Considering that on the basis of these data the expediency of extracting rhenium and rare-earth metals from technological products should be determined and a decision should be made on the development of technologies for their extraction, the obtained data on the content of rare-earth metals and rhenium in solutions and resins of underground leaching should be as objective as possible. At the same time, it was decided not to restrict the development of techniques only to the objects of underground leaching, ,the prospects for the development of the rare-earth direction, by expanding their area of applicability to rocks, ores, minerals, which allows using the developed techniques when carrying out geological exploration.

4.1 Method of determination of rare and rare-earth metals using mass separation with induction-coupled plasma

Purpose and scope of application. The method is intended for the quantitative analysis of rare earth elements (La, Ce, Nd, Pr, Pm, Sm, Eu, Gd ' Tb, Dy, Ho, Er, Tm, Yb, Lu) and rhenium in water samples, solutions and liquid technological products of uranium production and establishes the procedure for determining the mass contents of the elements to be determined using the method of induction-coupled plasma with mass separation.

Characteristics of the error of the analysis results. The calculation of the errors of the analysis results (σ_M, % rel.) Is similar to similar procedures for the XRF method and is described in detail in paragraph 1.2 of this report.

Determination of relative errors. Based on the experiments, the relative errors were obtained for different ranges of the contents of the determined elements, which are shown in Table 25.

The essence of the technique. The ICP-MS method combines the use of inductively coupled plasma as an ion source with a quadrupole mass spectrometer, which acts as a mass analyzer (filter), and a discrete dynode detector, which is used to register individual ions and their fluxes. Inductively coupled plasma, maintained in a special burner, is capable of effectively exciting singly charged ions from the atoms of the injected sample. Then the ions are focused by an ion-optical system (they are separated from polyatomic and isobaric ions in special models of devices) and enter the analyzer of the mass spectrometer, where they are separated according to the ratio of mass to charge (M / Z). The corresponding ion flux is recorded by the detector.

Table 25 - Obtained relative errors for REM and Re

The element	Content interval, mg/l	σ_M, % rel. P = 0.95
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	0.0001 – 0.0100	40
	0.01 – 0.10	20
	0.1 – 1.0	20
	1.0 - 10	11.4
	10 - 100	10.3
	100 - 1000	8.6
Re	0.0001 – 0.01	40
	0.01 – 0.10	30
	0.1 – 1	25
	1 - 10	15
	10 - 100	12
	100 - 1000	9,6

Ions with a strictly defined ratio (M / Z) are passed through the mass spectrometer at each time point, which then enter the detector for quantitative registration. The number of collisions per unit time is proportional to the number of atoms of each determined isotope in the initial sample. The linear range of the dependence of the signal intensity on the concentration on modern devices exceeds six to eight decimal orders of magnitude, making it possible to register both single pulses from low concentrations and ion currents from high concentrations of elements in one scan cycle of the mass spectrum.

To achieve such a wide dynamic range, modern ICP-MS devices use double signal registration: the pulse mode of one segment of the detector is used to count individual ions and the analog mode of the other is used to register ion currents. Thus, modern ICP-MS devices make it possible to determine the concentrations of elements and individual isotopes at a level from hundredths of nanograms to hundreds of milligrams per liter (10-11% - 10-3%).

The achievable detection limits, high sensitivity and selectivity of the ICP-MS method allows quantitative determination of up to 40-50 elements in many objects within 2-3 minutes (excluding sample preparation time).

To prepare samples of solid samples for analysis by the ICP-MS method, it is allowed to use two methods of decomposition: 1) acid dissolution in open vessels, without complete destruction of the matrix; 2) acid decomposition ("wet ashing") using microwave sample preparation systems.

The open decomposition method is characterized by the following features: a)in productivity with a small consumption of reagents, which is attractive with a small correction for the idle experiment; b) the method is not applicable for the decomposition of materials containing a lot of fatty matter and concretions; c) the possibility of partial or sometimes complete loss of volatile elements (such as rhenium, for example); d) the organic matrix preserved in sample solutions after decomposition can be a source of serious matrix interference during ICP-MS measurements, limiting the determination and isotopic analysis of some elements.

The microwave decomposition method provides the following advantages: a) high decomposition productivity; b) more complete oxidation of the organic matrix of almost any samples; c) a significant reduction in the loss of volatile elements during decomposition.

To achieve the best detection limits up to the level of hundredths (mg/l) and eliminate polyatomic overlaps caused by the sample matrix and the solvent matrix, as well as plasma gases, it is recommended to carry out measurements on devices with a dynamic reaction system (DRS). The best detection limits on these devices are achieved by reducing the background level and focusing the ions in an additional gas-filled quadrupole located in front of the quadrupole of the mass analyzer. The elimination of polyatomic and isobaric overlaps is carried out by removing interfering ions as a result of reactions and interactions with molecules of the reaction gas released into the cell (ammonia, methane, etc.). The mass spectrometer software should provide the following functions: 1. Support for the following analysis methods: quantitative, semi-quantitative (survey), isotope ratio and isotope dilution methods; 2. Automatic measurements without operator participation; to carry out automatic measurements, the spectrometer must be equipped with an automatic sampling device; 3. Automation of calibration procedures and adjustment of the mass scale and operating parameters of the spectrometer; 4. Statistical processing and saving of results in generally accepted formats; 5. The possibility of re-processing data without additional measurements; 6.The possibility of using a quality control device for operational automatic control of the measurement progress in accordance with specified quality criteria and calculation of statistical quality parameters.

- Characteristics of a mass spectrometer with inductively coupled plasma. A mass spectrometer with the following characteristics is used for measurements:
  - mass scanning range, a.e.m.: 2 - 270.
  - dynamic range of the detection system: 10-1 109 imp./s.
  - resolution range, amu: 0.3 - 3.0.
  - short-term stability, RMS: <3%.
  - long-term stability, RMS: <4%.
  - doubly charged ions, Ba / Ba: <3%.

- oxide ions, CeO / Ce: <3%.
- background level at a mass of 220: <25 pulses / s.
- standard deviation of the background level on a mass of 220: <5 imp./s.

Equipment ,materials, reagents. To minimize the laboratory background level, all operations for preparing samples for measurements and the measurements themselves should be carried out in a clean room in which dust does not accumulate. For the analysis of ultra-low concentrations, environmental contamination is the main limiting factor for detection and determination by ICP-MS. For the quantitative determination of elements common in the environment, such as Na, Mg, K, Ca, Fe and others, at concentrations of the order of and below 1 μg / L, sample preparation and measurements should be carried out in rooms of class 1000 (<1000 suspended particles per 1 m3 of air). To prepare samples, use fluoroplastic (PTFE, Viton, Teflon) or perfluoroalkoxypolymer (PFA) vessels. For temporary storage of samples and working calibration solutions, it is recommended to use disposable polypropylene glassware (tubes with a capacity of 15 - 20 ml for storing samples and 50 ml with a screw cap for storing working standards). When performing measurements, the following measuring instruments and other technical means are used:

1. Quadrupole mass spectrometer with inductively coupled plasma, certified by the State Standard of Kazakhstan, registered in the State Register of Measuring Instruments.
2. Analytical balance with a tolerance limit of +/- 0.0005 g, meeting the requirements of GOST 24104.
3. Electric one-stage water distiller, GOST 28165.
4. Installation for obtaining deionized water, providing water with a specific resistance of 15 - 18 Mohm per cm2.
5. Manual or electronic automatic liquid dispensers with disposable tips with a capacity of 0.5 - 10 μl ,50 - 200 μl and 200 - 1000 μl, providing a total dosing error of +/- 1%.
6. Thermoblock for fluoroplastic cylinders with the ability to heat up to 120ºC and automatically maintain at this temperature.
7. Cylinders are fluoroplastic (PTFE, Viton, Teflon, PFA) with a capacity of 20 ml.
8. Microwave decomposition system with temperature and pressure control.
9. PTFE autoclaves with a capacity of 20 - 50 ml for microwave decomposition.
10. Disposable 15 ml uncapped polypropylene centrifuge tubes for storing dissolved samples.
11. Disposable 50 ml screw-capped polypropylene graduation centrifuge tubes for storing working standards.
12. Ultrasonic cleaner UZV-9.5 l or similar.

When performing measurements, the following materials are used:

1. Concentrated nitric acid, v.s.h. (GOST 11125) or purified by isothermal distillation in a heat-resistant polypropylene system (GOST 446).

2. Argon, compressed or liquefied, of high purity (GOST 10157).
3. Deionized water with a resistivity of 15 - 18 MΩ per cm2.
4. Acetone ,o.s.ch. (TU 2633-039-44493179-00).
5. Standard samples of the composition of solutions, single and multi-element for mass spectrometry manufactured by Perkin-Elmer or similar, certified.
6. Surgical scalpel.
7. Filter paper.
8. Plastic washers for deionized water and diluted nitric acid.
9. Laboratory sealing film Parafilm "M" or similar.

Requirements for the qualifications of performers. To perform measurements on the mass spectrometer, persons who have undergone training in the skills of working with the ICP-MS device, confirmed by a certificate of the company - the manufacturer of the device, are allowed; who have studied the technical description of the measuring device and the measurement procedure; trained in accordance with GOST 12.0.004-79 and having a qualification group of at least 1 in accordance with the "Rules for the technical operation of electrical installations of consumers", approved by the State Energy Supervision Agency on 12.21.84; trained in workplace safety and familiarized with the maintenance rules of the spectrometer.

Persons who have undergone appropriate training are allowed to work with sources of flammable and toxic gases.

Operators with the qualification "Laboratory Assistant" who have experience in a chemical laboratory are allowed to carry out sample preparation.

Analysis conditions

The measurements are carried out under normal climatic test conditions in accordance with GOST 15150. The room should not contain toxic vapors and gases. The ambient temperature in the laboratory is 18 - 25 ºC. Atmospheric pressure 84 - 106 kPa (630 - 800 mm Hg). Relative air humidity 75% +/- 5%. The temperature gradient should not exceed 1.5 ºC / h. When using electrical appliances, the alternating current frequency is 50 +/- 1 Hz, the mains voltage is 220 +/- 10 V. Room lighting, natural or artificial, is not limited by special requirements.

Preparation for taking measurements.

All procedures for preparing samples for analysis must exclude the possibility of contamination. The fluoroplastic dishes used for sample preparation are thoroughly washed in an ultrasonic bath in diluted 1: 1 nitric acid and rinsed three times with deionized water.

Sampling, storage and preparation of samples

Sampling is carried out by the customer in accordance with the regulatory documents for sampling in force at the customer's enterprise or regulatory documents in force in the territory of the Republic of Kazakhstan and approved by the authorized bodies.

Samples are stored at temperatures from 15ºC to 25ºC and humidity exceeding 80%.

Solid samples. Open decomposition.

On an analytical balance, take a weighed portion of a sample weighing 0.01-0.10 g. The weighed portion is placed in a fluoroplastic cylinder (PTFE, Viton, Teflon, PFA), 0.2-1.0 ml of concentrated nitric acid is poured, covered with a protective laboratory film and placed in a thermoblock, heated to 115ºC, incubate for 0.5 - 1.0 h until the sample is completely dissolved. The dissolved sample is quantitatively transferred into a volumetric polypropylene tube, rinsing three times from the walls of the cylinder, and brought to 10 ml with deionized water. Sealed with a protective laboratory film, mixed and transferred for analysis.

Liquid samples. Open decomposition.

A sample of the analyzed object 0.1 - 0.5 g (0.1 - 0.5 ml) is taken on an analytical balance into fluoroplastic cylinders (PTFE, Viton, Teflon, PFA), determining the weight of the sample by the difference in the mass of the test tube before and after taking the sample. 0.3 - 1.0 ml of concentrated nitric acid is poured into the cylinder, covered with a laboratory film and placed in a thermoblock heated to 115 ° C. Incubate in a thermoblock for 0.5 - 1.0 h until the sample is homogenized and then proceed as described above to decompose solid samples

When working with homogeneous aqueous media, simple dilution of the sample with 2 - 3% nitric acid is allowed immediately before analysis. For this, 5 - 7 ml of deionized water is poured into the weighed portion of the sample in a measuring tube, then 0.3 - 0.5 ml of concentrated nitric acid and the sample is brought to 10 - 15 ml with deionized water. In this case, it is not recommended to reduce the sample dilution factor below 1: 100.

Microwave sample preparation.

A weighed sample is placed in a fluoroplastic insert and 5 ml of nitric acid is added. The autoclave with the sample in the insert is placed in a microwave oven and the sample is decomposed using the decomposition program recommended by the oven manufacturer. In general, the following heating mode is used: raising the temperature to 200 ° C within 5 minutes, holding for 5 minutes at 200 ° C, cooling to 45 ° C. The cooled autoclave is shaken to mix the contents and the lid is opened slightly to equalize the pressure. A qualitatively decomposed sample after distilling off nitrogen oxides should be a colorless or yellowish transparent solution without undissolved particles on the bottom and on the walls of the insert. The dissolved sample is quantitatively transferred into a 15 ml test tube by shaking the insert with a lid with 1 ml of deionized water three times and transferring each wash to a test tube, adjust the volume to 10 ml with deionized water, close and mix. An aliquot of 1 ml is taken with an automatic dispenser with a replaceable tip and adjusted to 10 ml with 0.5% nitric acid, covered with a protective laboratory film, and transferred for analysis. The data on the volume of the aliquot part and the volume of the dilution are entered into the spectrometer software along with the name and weight of the sample. Direct sampling of 0.1 - 0.5 ml aliquots from a decomposed sample in an autoclave is allowed. To compensate for the dilution error, an internal standard solution (In or Rh) must be added to the sample before digestion so that the internal standard concentration in the final solution sent for analysis is approximately 10 µg / L (for example, add 100 µL of solution to the sample, containing 10 mg / L Rh, then take an aliquot of 0.5 ml from 5 ml of the decomposed sample and make up to 10 ml). Internal standard solution must be added to all blanks and calibration solutions. The target concentration of the internal standard (10 µg / L) in blanks and standard solutions must be strictly observed. A blank sample solution is prepared with the performance of all the above operations, with the exception of the operation of taking a sample.

Preparation of standard calibration solutions

Working standard solutions are prepared by mixing several standard multielement standard solutions for mass spectrometry, manufactured by Perklin-Elmer or similar, containing different groups of elements. To calibrate the spectrometer, two or three working standards are used, containing, for example, 10, 40 and 100 µg / L of all elements, except for mercury, the content of which is 1 and 4 µg / L in the first two standard solutions. A standard solution containing 100 µg / L of elements is used to calibrate the spectrometer for the determination of matrix elements such as Na, Mg, Al, P, K, Ca, Fe, and Zn. For a more accurate determination of matrix elements, it may be necessary to use a standard solution in which their concentrations would be of the same order of magnitude with the upper limits of the range of element concentrations in the test object, taking into account the dilution factor used. The prepared working solutions are stored in 50 ml polypropylene centrifuge tubes. It is recommended to use working standards for calibration within 3 to 5 days after preparation. An example of the composition of working calibration solutions is shown in Table 26.

Table 26 - Example of the composition of working standard solutions for a methodology based on ICP MS (concentration is indicated in µg / L (ppb))

Stock standard solutions	The elements	Working standard solutions		
		10 ppb	40 ppb	100 ppb
PE ICP-MS standard #3 10 mg / l	Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Ni, Pb, Rb, Se, Na, Ag, Sr, Tl, V, U, Zn	10 mcg / l	40 mcg / l	-
PE ICP-M4 standard #3 10 mg / l	B, Ge, Mo, Nb, P, Re, Si, Ta, Ti, W, Zr	10 mcg / l	40 mcg / l	-
PE ICP-M5 standard #3 10 mg / l	Sb, Au, Hf, Ir, Pd, Pt, Rh, Ru, Te, Sn	10 mcg / l	40 mcg / l	-
PE single element standard solutions, 10 mg / l	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	10 mcg / l	40 mcg / l	-
PE single element standard solutions, 1000 mg / l	Fe, K, Ca, Al, Mg, Na, P, Zn	-	-	100 mcg / l

Preparing the device

The mass spectrometer is prepared for operation in accordance with the manual, the technical parameters are shown in Table 27. For a specific type of device, the optimal modes can be established experimentally. After starting the device, the performance of the device is checked, including a sensitivity check over the entire mass range, a background level check, the level of secondary oxide and doubly charged ions, and reproducibility (by calculating the root-mean-square deviation from 5-6 successive signal measurements).

Table 27 - Conditions for the analysis on the ELAN 9000 mass spectrometer

Parameter	Meaning
Cooling flow, l / min.	15
Auxiliary flow, l / min.	1.2
Spraying flow, l / min.	0.94
Power input	1150 Wt
Spray	Cross-flow, material - PEEK, sapphire tips
Spray chamber	Uncooled two-way, Scott type, material - rhyton
Sample feed rate, ml / min.	1.5
Sampler and skimmer cones	Nickel or platinum
Scan mode	1 point per peak
Integration time, ms	50 - 100 per mass
Number of scan cycles	20 per replica
Number of replicas	2, for operational control of reproducibility
Spectral resolution	0.8 ± 5% amu for 7Li, 9Be
Total time of sample measurement, with washing, min	~ 1

Correction of isobaric overlays

Examples of applied corrections for overlaps from isobaric ions are shown in Table 28. In software packages of modern mass spectrometers, such correction procedures are offered automatically. The exact correction factors are determined experimentally.

Table 28 - Examples of isobaric overlays

Isotope to be determined	Isobaric ion	Correction expression
^{74}Ge	^{74}Se	$-0.1166\cdot{}^{77}$Se
^{82}Se	^{82}Kr	$-1.0078\cdot{}^{83}$Kr
^{114}Cd	^{114}Sn	$-0.0273\cdot{}^{118}$Sn
^{120}Sn	^{120}Te	$-0.0217\cdot{}^{125}$Te
^{138}Ba	^{138}La, ^{138}Ce	$-0.0009\cdot{}^{139}$La $0.00284\cdot{}^{140}$Ce

Correction of spectral isobaric overlaps (correction of polyatomic overlaps caused by matrices of samples, reagents and plasma gases, correction of transport noise)

Correction of the three main types of interference in traditional ICP-MS analysis with injection of a liquid sample (without the use of dynamic reaction systems) is carried out using three different methods, differing in both complexity and reliability. The identification of interference during debugging of the method is carried out by determining the standard additives and measuring a series of serially diluted samples.

Correction of spectral aliasing from polyatomic ions

Correction of spectral aliasing from polyatomic ions from different sources requires more attention. Several methods are used to eliminate and correct spectral overlaps from polyatomic ions in ICP-MS. Elements in parentheses are defined for which a specific option is applied:

- exclusion from the sample preparation process of reagents that cause spectral overlaps, for example, the use of nitric acid instead of hydrochloric acid, which causes the formation of chlorine-containing polyatomic ions (for V, Cr, As, undergoing superposition from polyatomic ions ClO^+, $ArCl^+$);
- Removal of components causing polyatomic overlays, for example, by oxidation or evaporation (removal of an organic matrix that interferes with the determination of Cr, Al, Si due to polyatomic ions ArC^+, CN^+, CO^+);
- Taking into account overlaps using empirical relationships for superimposed ions (for example, taking into account the effect of $^{40}Ar\ ^{35}Cl +$ at a mass of 75 by $^{40}Ar\ ^{37}As +$ ion at a mass of 77 in determining as);
- Application of the "cold plasma" method for the analysis of elements that are strongly interfered with by polyatomic ions from the plasma gas (at an input power of <900 W, it is possible to determine ^{56}Fe, ^{40}Ca and ^{40}K at a level of <1 μg / L in solution);
- the use of desolvation devices for dehydration and drying of the aerosol of the sample before entering into the plasma (the method requires the purchase of additional equipment, desolvation systems have an increased memory effect - they require a longer washing between samples, the method eliminates the presence of polyatomic ions caused only by the solvent matrix - ArO^+ ions, NO^+, $ArCl^+$, etc.);
- the use of electrothermal atomization (ETA) or laser ablation (LA) for sample introduction (the ETA method is well applicable for eliminating chlorine and oxygen-containing interference, however, it is significantly inferior in cost and capabilities to the modern method of correction with DRS; the LA method is used to work with solid homogeneous samples, difficult to calibrate);
- The use of ion-molecular reactions for the destruction and filtration of polyatomic ions when working on devices with dynamic reaction cells (the method eliminates the influence of polyatomic ions and improves the detection limits by 1 - 3 decimal orders).

Table 29 lists examples of common polyatomic overlays. The most severe interferences from the sample matrix and from impurities in plasma-forming argon are caused by polyatomic NN and CO ions when analyzing silicon. All three silicon isotopes undergo superposition, which reduces the ability to determine Si in organic matrices. When determining arsenic in samples with a high chloride content, it is necessary to use the equation for correcting the effect of the polyatomic ion ^{40}Ar ^{75}Cl + on a mass of 75. The most serious interference from the matrix of the samples and from impurities in plasma-forming argon are caused by polyatomic ions NN and CO during the analysis of silicon. All three silicon isotopes undergo superposition, which reduces the possibility of determining Si in organic matrices. When determining arsenic in samples with a high chloride content, it is necessary to use the equation for correcting the effect of the polyatomic ion ^{40}Ar ^{75}Cl + on a mass of 75, which uses the ratio of polyatomic ions ^{40}Ar ^{35}Cl + / ^{40}Ar ^{37}Cl +, approximately equal to the natural ratio ^{35}Cl / ^{37}Cl, also taking into account the contribution from ^{77}Se to mass 77 (by ^{82}Se).Where: massNN is the measured signal at the corresponding mass; I (^{75}As) East. - true signal As.

Table 29 - Examples of common polyatomic overlays

Isotope	The relative abundance of the isotope,%	Interfering ion	Source of interference
$^{32}S^+$	95.0	^{16}O, $^{16}O^+$	Water
$^{32}K^+$	93.3	$^{38}ArH^+$	Argon plasma ,water
$^{40}Ca^+$	96.9	$^{40}Ar^+$	Argon plasma
$^{56}Fe^+$	91.7	^{40}Ar, $^{16}O^+$	Argon plasma ,water
$^{80}Se^+$	49.6	^{40}Ar, $^{40}Ar^+$	Argon plasma
$^{28}Si^+$	92.2	^{12}C, $^{16}O^+$	Organic matrix carbon
$^{44}Ca^+$	2.0	^{12}C, ^{16}O, $^{16}O^+$	Organic matrix carbon
$^{48}Ti^+$	73.8	^{32}S, $^{16}O^+$	Sulfur organic matrices
$^{51}V^+$	99.7	^{35}Cl, $^{16}O^+$	Chlorides of the matrix ,HCl solvent
$^{64}Zn^+$	48.6	^{32}S, ^{16}O, $^{16}O^+$, ^{32}S, $^{32}S^+$	Sulfur organic matrices
$^{75}As^+$	100	^{40}Ar, $^{35}C^+$	Chlorides of the matrix ,HCl solvent

The coefficients in the equation are refined experimentally during the debugging of the working method. To determine Ti, V, and Cr in samples with a high chloride and / or carbon content by the traditional ICP-MS method, rather high sample dilution factors (from 1: 300 to 1: 500) are required to reduce the level of polyatomic ions ClO $^+$ and ArC (in the presence of organic matrix) or carry out measurements by the method of standard additions.

The problems associated with polyatomic ions caused by the matrix of samples, reagents and plasma gases are radically eliminated by using instruments with a dynamic reaction system (DRS) for measurements. The DRS system uses an additional quadrupole - the DRS cell located in front of the mass analyzer quadrupole. The influence of polyatomic ions is eliminated by their selective destruction as a result of interactions with molecules of a neutral and / or reaction gas admitted into the DRS cell. The reaction gas is usually anhydrous ammonia or methane. In addition to carrying out reactions, the quadrupole of the DRS cell provides dynamic separation of a narrow transmission range of ions of interest and prevents the propagation of parasitic reaction products to the quadrupole of the mass analyzer. Thus, the DLS system efficiently filters polyatomic ions, reduces the overall background and increases the stability of signals. These features of ICP-DRS-MS devices allow achieving better detection limits, confidently determining traditionally difficult elements for ICP-MS determinations in organic matrices (Si, K, Ca, Ti, V, Cr, Fe, As, Se), as well as performing more accurate isotopic analysis of matter.

Elimination and consideration of transport obstacles

Transport hindrances arise from differences in viscosity and surface tension between calibration standards and samples. The viscosity of solutions affects the efficiency of spraying and, as a consequence, affects the signal of each analyzed isotope in the solution, ideally proportional to its concentration. The viscosity of aqueous solutions depends on the concentration of the acid and on the concentration of the matrix components. By using fairly high dilution factors for samples with a residual organic matrix (1: 300 - 1: 500) and by normalizing the acid background in standards, blanks and test samples, the effect of transport interference can be reduced to an insignificant level. When working with smaller dilution factors, it is recommended to ensure that there is no interference by analyzing a series of serial dilutions of one sample (e.g. 1:10, 1:50, 1: 100, 1: 200) and select a compromise dilution factor that does not compromise the detection sensitivity items of interest. If transport interference cannot be eliminated, internal standardization should be applied by adding an internal standard solution of Rh or in to all blanks, standard solutions and test samples to obtain a final concentration of 10 μg / L in all solutions. Internal standardization can also compensate for sample dilution errors and account for many matrix effects on plasma and ion flux.

Mass spectrometer calibration

Calibration of the spectrometer is performed before starting measurements of fully prepared samples using calibration solutions with the instrument parameters set in 4.14. Determination of the calibration dependence, processing and storage of the calibration results are performed by the software of the spectrometer.

Calibration check is carried out before starting the analysis of samples. Verification consists of the measurement of an internal verification standard or CRM of the matrix under investigation. Modern software packages for ICP-MS systems allow you to set criteria for the acceptable quality of calibrations based on the accuracy and reproducibility of results for verification standards, as well as on the correlation coefficient, and program an automatic measurement algorithm, which can include repeated checks of calibrations and recalibrations without operator intervention.

To identify and take into account the drift of the instrument sensitivity, repeated measurements of the verification standards and / or complete recalibration are recommended to be carried out every 1 - 2 hours of operation (every 15 - 30 samples), depending on the stability of the ambient temperature, supply voltage and other conditions in the laboratory.

Taking measurements

A prepared sample is introduced into the mass spectrometer and the isotope signals are measured under normal climatic test conditions in accordance with the requirements of the manual (instruction) for the operation of the device. The optimal mode of registration of mass spectra and measurements is established in accordance with the recommendations of the manufacturer of this device. Typical settings of operating parameters during measurements are shown in Table 29. Primary signal processing and concentration calculations are performed by the software automatically based on the parameters of the method used and the data of the performed calibration.

For measurements, isotopes are used that are most preferable in terms of a set of characteristics. The most important of them are the relative abundance, absence or low level of spectral polyatomic overlays, and the attainable detection limit. When debugging the software method, measurements are carried out in the peak scan mode to determine possible influences from adjacent peaks and to set the optimal resolution for each isotope. Examples of the choice of optimal masses and the detection limits achieved in this case are shown in Table 30.

Table 30 - Examples of the selection of optimal masses and the detection limits achieved

Element	Isotope	Method limit ng / L (ppt)	Concentration ,equivalent background, ng / L (ppt)
Re	185, 187	4	6
La	139	3	2
Ce	140	3	2
Pr	141	3	2
Nd	146	5	2
Sm	147	5	2
Eu	151, 153	4	2
Gd	157	5	2
Tb	159	3	2
Dy	163	5	2
Ho	165	3	2
Er	166	4	2
Tm	169	3	2
Yb	172	5	2
Lu	175	3	2

Note. The limits of determination were calculated according to the standard methodology at 98% confidence interval, as 3 RMSfon / ES, where 3 is the value of the Student's distribution for the 98% interval and seven degrees of freedom, RMSD is the standard deviation of the background signal (imp./s), calculated for eight replicas of reading, ES is the isotope sensitivity, expressed in counts / s x µg x l [12].

Processing of measurement results

Analytical signals are processed by the software of the mass spectrometer, based on the constructed calibration linear regressions calculated by the least squares method, taking into account the background correction, the signal of internal standards, and also taking into account the influence of isobaric and polyatomic spectral overlays. The result of determining each element is presented as the average of several (at least two) parallel measurements of the analyzed sample. Processing of measurement results complies with GOST 8.207. The measurement results are displayed on the monitor, printed out and / or saved as a file on the hard disk of the computer.

Internal operational control

The method error control is carried out in accordance with GOST R ISO 5725-6-94. Internal quality control of the results of the determination of microelements (convergence, reproducibility, accuracy) is carried out in order to obtain operational information on the quality of analyzes and, if necessary, to take prompt measures to improve it. Operational quality control is carried out by analyzing the test samples and a standard sample, the chemical composition of which should not differ from the composition of the test sample so that it is necessary to change the analysis procedure.

Operational control of reproducibility

The frequency of control of the reproducibility of the analysis results is determined by the number of working measurements for the controlled period and depends on the control plans. 2 analysts are involved in the work. Samples for control are representative samples, each of which is analyzed in strict accordance with the prescription, varying the conditions of the analysis as much as possible: two results are obtained using different sets of volumetric glassware, different lots of reagents and different copies of standard samples for calibration of the device. The control results are considered satisfactory if the following condition is met:

$| X1 - X2 | <= 0.01D X$,

Where: - X1 is the result of the analysis of the working sample, µg / g;

X2 is the result of the analysis of the same sample obtained by another analyst using another device, another volumetric glassware and another batch of reagents, µg / g;

D - Permissible discrepancies between the results of the analysis of the same sample, %.

If the standard for operational control of reproducibility is exceeded, the experiment is repeated. If the specified standard D is exceeded again, the reasons leading to unsatisfactory results of work and control are found out and eliminated.

Operational accuracy control

The frequency of control of the reproducibility of the analysis results is determined by the number of working measurements for the controlled period and is determined by the control plans. Use the standard addition technique or, if available, run the analysis. It is recommended to use reference materials produced by reference materials agencies (NCCRM - China, NIST - USA, IRMM - United Europe, NIES - Japan), as well as specialized firms (Bio-Rad, Seronorm, Sigma-Aldrich, Merck, etc.).

Standard addition method.

Two samples are taken and an additive is made to one of them in the form of a solution so that the content of the element to be determined increases in comparison with the initial one by 50 - 150%. Each sample is analyzed in strict accordance with the protocol of the method and the result of the analysis of the original working sample X and the working sample with the addition of X` is obtained. The results of the analysis of the initial working sample X and the working sample with the addition of X` are obtained under strictly identical conditions, i.e. they are received by one analyst using one set of volumetric glassware, one batch of reagents, etc. The control results are considered satisfactory if the following condition is met:

$| X` - X - C | < CD$,

Where: K is the standard of operational control of the error, µg / g;

C - additive to the sample in the form of a solution with a concentration, µg / g.

With external control (P = 0.95), take:

Where ΔX and ΔX 'are the characteristics of errors for the original sample and the sample with the addition, µg / g.

$\Delta X = 0.165\ X$ and $\Delta X' = 0.165\ X'$

With intralaboratory control (P = 0.90), it is assumed that:

$CD' = 0.84\ CD$

If the standard of operational control of the error is exceeded, the experiment is repeated. If the specified standard is exceeded again, the reasons leading to unsatisfactory control results are found out, and they are eliminated.

Standard sample method.

A sample prepared from a standard sample is analyzed according to the method and its results are compared with the certified content of elements. The error of attestation should not be more than 1/3 of the error of the method. The control results are considered satisfactory if the following condition is met:

$| C - A | < K$,

Where: C is the found content of an element in a sample prepared from a standard sample; A = ΔA - certified content of an element in a standard sample.

With intralaboratory control (P = 0.90), it is assumed that:

$K = 0.84\ \Delta$

With external control (P = 0.95), take:

$K = \Delta$,

Where Δ is the total error of the analysis result according to the method.

If the standard of operational control of the error is exceeded, the experiment is repeated. If the specified standard is exceeded again, the reasons leading to unsatisfactory control results are found out, and they are eliminated.

Operational convergence control

The frequency of control of the convergence of the analysis results is determined by the number of working measurements for the controlled period and is determined by the control plans. Use the results of parallel analyzes.

The standard of operational control of convergence is calculated by the formula:

Cmax - Cmin <= D,

Where: Cmax, Cmin - the largest and the smallest values of parallel definitions;

D - standard for operational control of reproducibility,

D = 2.77 σ (Δ)

Where σ (Δ) is the characteristic of the random component of the error.

If the standard of operational control of the error is exceeded, the experiment is repeated. If the specified standard is exceeded again, the reasons leading to unsatisfactory control results are found out, and they are eliminated by corrective actions.

Registration of test results

The results of the quantitative determination of chemical elements in samples are presented in the form: the results of the analysis - X, mg / L or%, depending on the contents of the elements obtained, the characteristic of the error - Δ ,% with a confidence level of P = 95%, or the result of the analysis - (X ± Δ), mg / L or% depending on the obtained contents of elements. The values of the contents of the element in the sample and the error must contain the same number of decimal places.

Checking the correctness of the technique

In order to verify the correctness of the data obtained by the ICP MS method when analyzing solid samples, in accordance with the developed methodology, the contents of REM in standard ore samples SG-1A, ST-1A, SG-3 and SGD-1A were investigated. The results are shown in Table 31.

Table 31 - REM contents in ore standard samples obtained by ICP MS (μg / g)

Element	Standards used							
	SG-3		ST-1A		SG-1A		SGD-1A	
	$C_{ср}\pm2\sigma$	$C_{серт}\pm2\sigma$	$C_{ср}\pm2\sigma$	$C_{серт}\pm2\sigma$	$C_{ср}\pm2\sigma$	$C_{серт}\pm2\sigma$	$C_{ср}\pm2\sigma$	$C_{серт}\pm2\sigma$
La	44±2	45±5	11.9±0.6	14±2	27±1	32±8	85±4	80±20
Ce	90±4	90±10	27.0±0.9	26±7	64±3	62±6	175±6	150±10
Pr	13.6±0.9	-	4.0±0.2	2.7±0.6	6.1±0.2	5±1	24±1	15±5
Nd	55±4	50±10	19±1	15±5	13.5±0.6	18±5	93±6	70±10
Sm	11.1±0.8	10±1	5.1±0.4	5±2	2.6±0.1	5±2	16±1	17±1

Eu	0.38±0.06	0.4±0.1	1.6±0.2	2.3±0.6	0.07±0.01	0.1*	3.9±0.5	5±1
Gd	9.4±0.8	-	5.8±0.4	5*	3.1±0.2	7*	12.4±0.5	10±3
Tb	1.55±0.09	1.7±0.3	1.00±0.09	1*	0.77±0.04	0.8*	1.40±0.06	1.4±0.2
Dy	9.9±0.8	10*	6.2±0.5	58	6.6±0.3	6*	7.02±0.03	6±1
Ho	2.1±0.1	-	1.31±0.09	1.3*	1.82±0.09	1.5±0.5	1.10±0.06	1.2±0.3
Er	6.7±0.4	6*	3.8±0.3	4*	7.4±0.6	6*	2.8±0.2	3.2±0.7
Tm	1.16±0.09	-	0.60±0.02	0.7*	1.6±0.2	1.1±0.3	0.47±0.03	0.5±0.2
Yb	8.1±0.8	7±1	3.7±0.2	3.8±0.8	12±1	12±6	2.7±0.2	2.9±0.5
Lu	1.3±0.2	0.9±0.2	0.54±0.07	0.5±0.1	1.8±0.2	1.9±0.5	0.30±0.01	0.30*

* In the table Ccp - the average content of an element based on the results of five measurements; Ssr - Certified Content Element Value. * - Estimated value.

As can be seen from Table 31, the relative errors for REM and Re vary on average ± 1%. It is recommended to format the results of measurements and calculations in the form of a table. The characteristic of the error Δ is determined on the basis of the values of the error limits of the determined element in the required range of contents obtained during the analysis of standard samples.

The main dependence studied in spectrophotometry is the dependence of the absorption intensity of incident light on the wavelength. The method is based on measuring not the absolute value of the optical density, but the difference between the optical densities of the test solution and the solution, the optical density of which is taken as zero (reference solution). Spectrophotometry is widely used in the study of the structure and composition of various compounds (complexes, dyes, analytical reagents, etc.), for the qualitative and quantitative determination of substances (determination of trace elements in metals, alloys, technical objects).

One of the modern devices in the field of spectrophotometry is the VARIAN Cary-50 spectrophotometer, which allows determining the concentration of rhenium in a large number of samples and in a short time.

In solutions, rhenium is usually found in the form of heptavalent oxide Re_2O_7. To detect it, it is necessary first of all to convert it into a complex compound, which allows it to be stained in a certain color for further comparison with a standard solution and subsequent calibration of the obtained data using a spectrophotometer. Based on the readings of the standard solution, a calibration graph is built, with which the data of the analyzed solution is compared. The measurement procedure applies to productive (technological) solutions obtained in the process of leaching waste from the metallurgical and chemical industries, and establishes a photocolorimetric method for determining the mass fraction of rhenium in the concentration range of 0.006 - 0.03 g / dm^3.

The technique is intended for the quantitative analysis of rare earth elements (La, Ce, Nd, Pr, Sm, Eu, Gd ,Tb, Dy, Ho, Er, Tm, Yb, Lu) and rhenium in samples of rocks, ores, minerals and technological products of uranium production and establishes the procedure for determining the mass content of the analyzed elements.

When performing analyzes of samples of productive and leaching solutions for the content of rare earth metals and rhenium, the methods described above were used. Analyzes using the ICP MS method were carried out at the M. Auezov South Kazakhstan State University on its own material and technical base in the regional engineering testing laboratory "Structural and biochemical materials". In this case, no special sample preparation was required except for the necessary dilution of the sample with bidistilled water.

4.2 Conducting analytical studies to determine the content of impurities in rough concentrates

Sampling was carried out by the services of uranium mining enterprises, responsible for the operational quality control of technological solutions, in accordance with the approved sampling regulations.

The transportation of the selected samples to the analytical laboratory was carried out in plastic bottles with a capacity of 5 liters with hermetically sealed screw caps. Before sampling, the transport containers were thoroughly rinsed with water and rinsed several times with the solution that was supposed to be taken.

The location of sampling and the conditions under which they were taken were indicated on the label and attached to the sampling container. The containers with samples were packed in such a way that the packaging did not affect the composition of the sample and did not lead to losses of the determined indicators during transportation, and also protected the containers from possible external contamination and breakage. Storage conditions excluded the effects of light and elevated temperatures on the samples. Joint storage of water and chemical samples is not allowed.

There was no special preservation of the taken samples, given the small time interval between the time of sampling and analysis, was not carried out.

Sources of sampling bias can include the following:

- pollution due to sampling equipment, cross-contamination of samples;
- instability of the sample itself and its storage conditions;
- inappropriate preservation, contaminated preservatives;
- contamination during transportation of samples;
- incorrect selection of the sampling point.

For a general assessment of contamination during water sampling (cleanliness of dishes, samplers, etc.), blank samples were analyzed.

The sampler is washed 2-3 times with distilled (or bidistilled in the analysis of heavy metals) water. The last portion of distilled water is filled into the sampler and then treated as with a normal sample. If required by the analysis method, the sample is filtered, then preservatives are added, stored, processed and analyzed as a normal water sample. The same batch of distilled water is analyzed in the laboratory (laboratory blank). Comparison of the results of the analysis of a blank field sample and a blank laboratory sample allows you to reveal the error that has arisen due to the selection, processing and transportation of samples.

To find out the source of contamination (sampler, dishes, preservatives, transportation), if necessary, individual blank samples are analyzed. A blank field sample is considered uncontaminated if the concentration of the analyte does not exceed the detection limit of the method.

Results of the analysis of the contents of rare earth metals and rhenium. When performing analyzes of samples of productive and leaching solutions for the content of REM and rhenium, the methods described in Section 5.1 of this report were used.

In this case, no special sample preparation was required except for the necessary dilution of the sample with bidistilled water.

The analyses using the SEM methods were carried out on the analytical base of the SKSU im. M. Auezov, the results of which are shown in Figure 17. In this case, the samples before analysis were pre-dried and prepared in accordance with the developed sample preparation procedure. The analysis results obtained are shown in table 32.

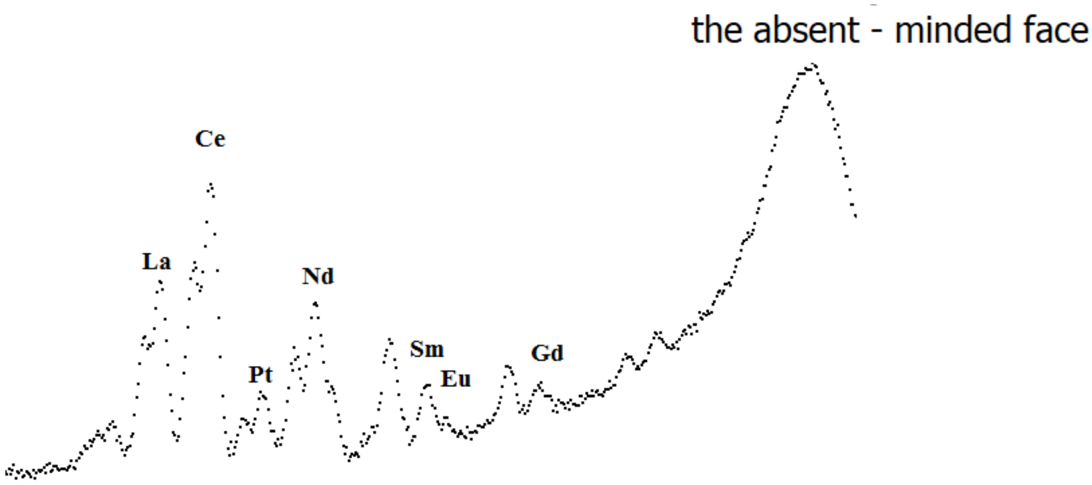


Figure 17 - Typical spectrum obtained in the analysis of REM using the Am241 source

Table 32 - Chemical composition of primary productive materials

Try	REE amount,%	Re,%	Fe,%	Al,%	others, %
Experience number 1	4,5	0,5	40,0	35,0	5,0
Experience number 2	3,8	0,2	44,0	32,8	19,2

Based on the chemical and material composition of waste, the most suitable method for determining rhenium in lead-containing materials - dust, cakes, sludge can be attributed to photocolorimetric. For indium and thallium, a volumetric, atomic absorption method of determination, due to the good sensitivity of the determination of indium 0.01% and thallium 0.01%.

5 DEVELOPMENT OF MODES OF PURIFICATION OF IMPURITIES IN ROUGH CONCENTRATES

Any simple or complex substance is a mixture of many substances, and the task of obtaining an individual substance is to isolate the main substance from this mixture. When a substance is obtained using a chemical reaction, the impurities contained in the reagents partially pass into the reaction products. In addition, in this case, side compounds are always formed, contaminating the resulting substance. Thus, obtaining simple and complex substances in a highly pure state consists in their deep purification and removal of impurities. The difference from conventional separation here is that when obtaining a substance of high purity, the depth of separation should be much greater, and the material of the walls of the apparatus should not contaminate the substance to be purified to any appreciable degree [50, 51].

The methods used for deep cleaning of substances are varied. The choice of the method is determined by the properties of the substance to be purified and the nature of the separated impurities. Although it is theoretically possible to assess the capabilities of the methods, nevertheless, in most cases, it is necessary to conduct special studies that make it possible to choose the optimal method or find a method that allows you to achieve the required degree of purity.

Methods of binding impurities with specially selected reagents into such chemical compounds that are relatively easily separated from the basic substance in one way or another (filtration, centrifugation, distillation, etc.) have proven themselves well. So, acting on aqueous solutions of sulfates of some metals with sodium diethyldithiocarbamate (selective complexation method), it is possible to convert the impurities of iron, cobalt, copper and other transition metals contained in these salts into poorly soluble compounds such as chelates. These compounds sediment and can be filtered off. This method makes it possible to reduce the iron content in the research materials to 10-5%, etc. [52,53].

It should be noted that the characteristic chemical property of rare earth metals is the formation of hydroxides insoluble in an alkaline medium and oxalates poorly soluble in an acidic medium. In a neutral and acidic environment with hydrogen sulfide, they do not form sedimentation. For a long time, it was believed that this combination of properties is sufficient to differentiate and separate rare earth metals in the course of analysis from other elements, with the exception of thorium and, to a lesser extent, zirconium and hafnium. But recently, various authors, including Vickery, have shown that even the sedimentation of hydroxides far from it is always so complete, as it is believed, especially of yttrium hydroxides, heavy yttrium earths (ytterbium, lutetium) and, to an even greater extent, scandium [54-59].

When ammonia or alkali metal hydroxide is added to a solution of a rare earth metal salt, a rare earth metal hydroxide sedimentation is formed. Depending on the nature of the rare earth metals, hydroxides of various oxidation states are obtained: trivalent type $Ln (OH)_3$, cerium hydroxide $Ce (OH)_4$, or bivalent type $Sm (OH)_2$.

The solubility of trivalent lanthanide hydroxides in water is extremely low (4.8 * 10-5 mol / l of water for $Nd (OH)_3$), therefore, the formation of hydroxides is used in the separation and determination of rare earth metals.

With a sequential transition from lanthanum to lutetium, the pH value of sedimentation (for the ratio OH: Ln^3 + = 0.4) changes from 8.18 to 6.55; this interval is sufficient for fractional separation. Scandium sedimentates at pH = 4.9, that is, significantly lower than yttrium earths or yttrium, during the deposition of which pH = 6.83; this makes the separation much easier.

Rare earth metal hydroxides have a hexagonal lattice, with the exception of scandium hydroxide, which differs sharply from other hydroxides both in crystal structure and in other properties. So, in the presence of an excess of alkali, scandium hydroxide partially dissolves with the formation of scandate or hexaminoscandium ions $[Sc (NH_3)_6]^{3+}$ and other complex ions.

It was found that as a result of the reaction of solid hydroxides of rare-earth metals with niobium hydroxide, new phases of the composition $Ln(NbO_3)_n$ are formed.

The formation of basic salts has been carefully studied all the time, since it can facilitate or interfere with some separation processes. In this case, the question of the catalytic activity of some hydroxides is also of interest. For example, under the action of air, $Ce (OH)_3$ hydroxide is oxidized to $Ce (OH)_4$; oxidation is also possible with hydrogen peroxide in an alkaline medium, when a reddish-brown sediment of metastable perhydroxide $Ce (OH)_3O$ * OH is sedimented, which slowly oxidizes $Ce (OH)_3$ to $Ce (OH)_4$ (this reaction is usually used in analytics to detect traces of cerium). After some time, trivalent cerium hydroxide is converted into $Ce (OH)_4$, which is also attributed to the formula $CeO_2 * 2H_2O$. in this case, the product of the solubility of $Ce (OH)_4$ is from 1.54 * 10-51 to 4.8 * 10-51, brief characteristics are described in table 33. Hydroxides of the $LnOH_2$ type are obtained from salts of divalent elements. The formation of the $Sm (OH)_2$ compound with a characteristic green color in a mixture of rare earth metal chlorides is used to detect the presence of samarium. Summarizing the general presentation of the properties of hydroxides of rare earth metals, we can consider the following formulation of the process.

Table 33 - Properties of hydroxides of some rare earth metals

REM hydroxide	Crystal structure				Free energy at 25 oC -ΔF	Solubility product, Kpr
	Type	Options, A				
		a	b	c		
$Sc(OH)_3$	G.ts.p.	7,882	–	–	294,66	–
ScO*OH	orthorhombic	4,01	13,01	3,24	–	–
$Y(OH)_3$	hexagonal	6,24	–	6,53	–	$1*10^{-24}$
$La(OH)_3$	Also	6,50-6,52	–	3,84-3,85	–	$5*10^{-21}$
$Ce(OH)_3$	– « –	6,48	–	3,80	–	$5*10^{-23}$

$Pr(OH)_3$	– « –	6,47-6,48	–	3,76	–	$7*10^{-24}$
$Nd(OH)_3$	– « –	6,42	–	3,74	–	$5*10^{-24}$
$Sm(OH)_3$	– « –	6,31-6,96	–	3,59-3,66	–	$2*10^{-24}$
$Gd(OH)_3$	– « –	6,26	–	3,54	–	–
$Dy(OH)_3$	– « –	6,27	–	3,53	–	–
$Er(OH)_3$	– « –	6,23-6,25	–	3,51-3,53	–	–
$Yb(OH)_3$	– « –	6,22	–	3,50	–	–
YbO*OH	orthorhombic	10,39	10,50	7,05	–	–
$Lu(OH)_3$	–	–	–	–	303,24	–

Hydrolytic sedimentation of impurities is based on the ability of metal cations in solution to interact with water to form sparingly soluble hydroxides. In this case, the concentration of the metal in the solution decreases - the solution is purified. In general terms, the reaction of hydrolysis of a metal cation is expressed by the equation

$$Me_n{}^+ + nH2O = Me\ (OH)\ n + nH\ +, \quad (6.8)$$

where $Me_n{}^+$ is a metal cation; n is the charge of the cation.

The direction of the reaction (6.8) depends on the pH of the solution: in an acidic medium, the metal hydroxide will dissolve, in an alkaline medium, it will sediment.

The equilibrium of the hydrolysis reaction for each metal occurs at a certain pH of the solution, called the pH of hydrate formation (pH ° g). Table 34 below shows the pH ° g for standard conditions ($aMe_n{}^+ = 1$ mol / l, t = 25 ° C).

Table 34 - pHg values under standard conditions of hydrate formation of impurity metals

Metal cation	Co^{3+}	Sb^{3+}	Sn^{2+}	Fe^{3+}	Al^{3+}	Cu^{2+}	Zn^{2+}	Co^{2+}	Fe^{2+}	Cd^{2+}
$pH_{г}$	1,0	1,2	1,4	1,6	3,1	4,5	5,9	6,4	6,7	7,0

Cations $Co^{3\,+,}$ $Sb^{3\,+}$, $Sn^{2\,+}$, $Fe^{3\,+}$, $Al^{3\,+}$ form hydroxides insoluble at pH 4.5-5.5. The $Co^{2\,+}$, $Fe^{2\,+}$, and $Cd^{2\,+}$ cations are not hydrolyzed and remain in solution. The $Cu^{2\,+}$ cation is partially hydrolyzed. Iron in acidic solution is in the form of ferrous sulfates $FeSO_4$ and ferric iron $Fe_2\ (SO_4)\ _3$. Ferrous iron under conditions of neutral leaching does not undergo hydrolysis (pH ° g = 6.7).

Therefore, to purify the solution from iron, it is necessary to oxidize all the iron in the solution to trivalent. For the oxidation of iron, an oxidizing agent must be specially introduced into the pulp. Manganese ore containing MnO_2 (pyrolusite) is introduced as an oxidizing agent:

$$2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$$

At pH 5.2-5.4, iron (III) sulfate hydrolyzes according to the reaction

$$Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4$$

Together with iron, antimony, arsenic, indium, germanium, gallium, tellurium pass into the sediment. During hydrolytic purification, silicic acid is neutralized and coagulated. The solution of neutral leaching after hydrolytic cleaning contains, mg / l: 2-10 Fe^{3+}; 40-50 Fe^{2+}; 0,3-0,6 As; 0,2-0,3 Sb; 0,1 Ge, 200-300 SiO_2; 500-1000 Cu and 200-500 Cd.

Chemical purification of the resulting primary product is also used to separate from alkaline and alkaline earth impurities. It consists in the sedimentation of REM hydroxides from their solution in mineral acid with an ammonia solution while washing the hydroxides, dissolving them in nitric acid, sedimenting oxalates, washing them, drying and calcining REM oxalates to oxides. Optimal conditions for this process: concentration of rare earth metals in a solution of 20-30 g / l of oxides, sedimentation with 25% ammonia at 80 ° C, three-fold washing of hydroxides with hot water at S: L = 1: 1. Double sedimentation of hydroxides makes it possible to achieve deeper purification from impurities, but significantly complicates the technology and requires a large consumption of reagents.

Further separation of impurities of alkali and alkaline earth metals, as well as cleaning from coloring impurities is carried out in the process of sedimentation of REM oxalates. The filtered hydroxide sediment is dissolved in nitric acid to a concentration of 50-60 g / l Ln_2O_3 and pH = 1-2, after which rare earth oxalates are sedimented from the solution with a saturated solution of oxalic acid. The oxalate sediment is washed twice on the filter with hot water containing 0.2% $H_2C_2O_4$, at S: L = 1: 1. Next, oxalates are calcined to rare-earth oxides according to a known method.

Based on the research done by the staff of the scientific sector "Chemistry and technology of rare and rare earth metals" of the South Kazakhstan State University named after M.O. Auezov, the following conclusion on the further direction of work was revealed. A feature of uranium deposits in Kazakhstan is a wide variety of types in terms of mineralogical and physicochemical compositions. Many types of uranium ores are complex in composition and contain such valuable components as molybdenum, vanadium, tungsten, zirconium, rhenium, rare earth elements, etc. [60–62]. Solutions of the uranium industry with pH = 2.0 (after the sorption extraction of uranium) are neutralized with ammonia, while a small amount of manganese-containing product is added for the complete oxidation of iron from the oxidation state +2 to +3. When neutralizing with ammonia water, the process should be precisely carried out to pH = 5.0. In this case, iron hydrates and a part of aluminum (50-60% of the initial content in the solution) sediment, which are filtered on a frame press filter under production conditions. The clarified solution contains a part of aluminum and the entire volume of the sum of rare earth metals. Spectral analysis of the sediment did not reveal the presence of rare earth metals. Then the solution after filtration is sent to the sedimentation of the primary material of rare earth metals. In this case, the content of rare earth metals corresponds to the original solution. If the sedimentation of Fe3 +, Al3 +, rare earth metals is carried out with ammonia water to pH = 7.5 before the sedimentation of Fe (OH) 2 begins, the sedimentation of rare earth metal hydrates is obtained by 97-98%. The hydrate sediment is obtained - 40 g from 1 liter of solution, that is, 25 times less than the original solution. The sediment is dissolved in concentrated sulfuric acid, 40-50 ml of a solution of Fe2 (SO4) 3 * (Al2SO4) 3 * Ln2 (SO4) 3 is obtained, that is, the concentration of Al3 + and rare earth metals increases 20-25 times depending on the moisture content of the hydration cake. The amount of Fe (OH) 3 depends on the content of Fe3 +; Fe2 + mostly remains in solution. Therefore, before sending this solution for leaching, a solution with pH = 7.5 is oxidized with Fe2 + or by blowing with air:

$$Fe^{3+} + H_2O + O_2 = Fe(OH)_3$$

and then acidification to 20 g / l of free H_2SO_4. Since Fe3 + increases underground leaching of uranium due to the oxidation of U4 + to U6 +.

The composition of the solution after dissolution of the total hydration cake is presented in table 35.

Table 35 - Components of the solution obtained after dissolving the hydrated cake

Ions in solution	Fe3+	Al3+	REE	pH
Content g / l	7,5	25	0,5	2,5

When excess Na_2SO_4 or K_2SO_4 is added at T = 60-80 ° C, double salts of the cerium subgroup sediment, the residual concentration is 25-30 mg / l of Ce3 +. La, Nd ~ Σ 50 mg / l, that is, the extraction was - 90%, however, the more expensive yttrium group of rare earths does not sediment and leaves with circulating solutions for underground leaching. Therefore, it is necessary to have the technology to extract all the lanthanides and yttrium. The content of elements of the yttrium subgroup in uranium solutions is much lower than that of cerium.

The recovery of the entire amount of lanthanides can be started after an increase in the underground leaching of elements of the yttrium subgroup in the circulating solution.

For this, it is necessary to study the separation of rare earths from aluminum.

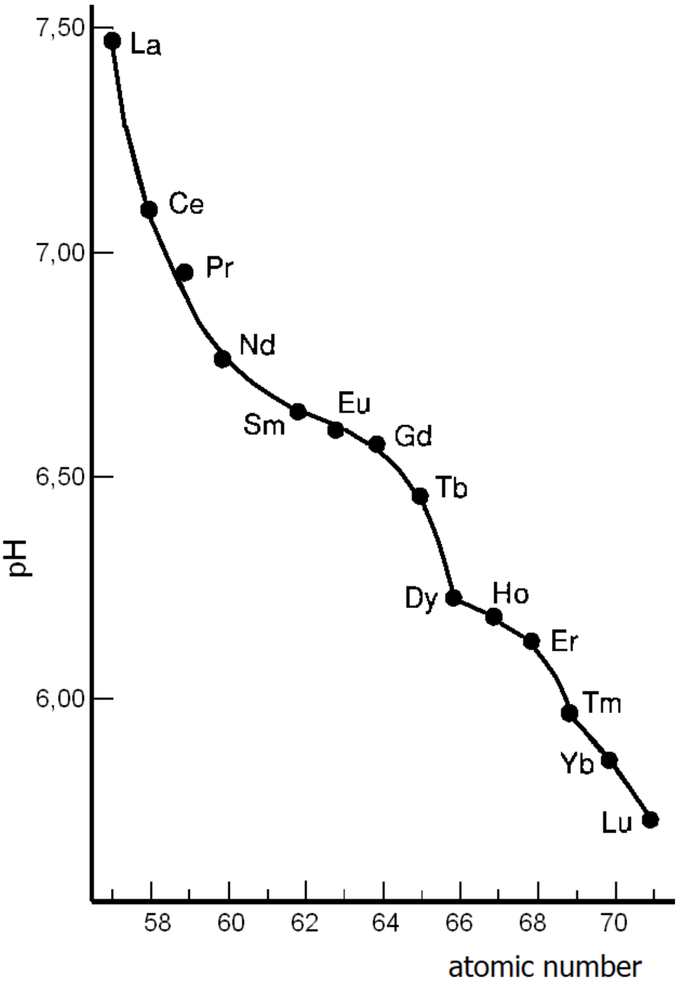


Figure 18 - Plot of pH of the beginning of sedimentation of rare earth metals, depending on the atomic number

The neutralization of the initial solution with ammonia must be carried out in such a way that with aluminum hydroxide there is a minimum co-sedimentation of rare-earth metals. In the process of neutralization in the range of pH = 3.5-5.0, determine the concentration of aluminum and the amount of rare earth metals. Achieve with the maximum deposition of Al (OH) 3 (more than 90%) the minimum cosedimentation of Ln (OH) 3 (less than 10%). Remove all lanthanides from the solution after separating the hydrated cake Fe (OH) 3 and Al (OH) 3. Figure 18 shows the pH section of the beginning of sedimentation of rare-earth metals in solution as a function of the atomic number.

As can be seen from Figure 18, the beginning of the sedimentation of lanthanides is pH = 5.5 and the end is pH = 7.48. To do this, use the sedimentation of lanthanide phosphates by adding Na3PO4, or bring the pH = 7.5 to the beginning of the sedimentation of Fe (OH) 2 by adding an alkali containing aluminum. The sediment Al (OH) 3 * Ln (OH) 3 or AlPO4 * LnPO4 is treated with a NaOH solution - 10%, obtaining a primary concentrate of rare earths, which is dissolved in H2SO4 and all Ln2 (C2O4) 3 free of impurities is sedimented with oxalic acid.

Thus, the obtained salts of rare earth metals - oxalates, hydrates, double sulfates - are further processed according to the well-known method of thermal decomposition of salts to obtain lanthanide oxides. The investigated topic of obtaining oxides of rare-earth metals from their salts is presented below.

The structure and body and kinetic stability of hydrated rare earth sulphates have been studied [63, 64]. In addition to lanthanum and cerium, sulfates tend to crystallize like octahydrates with all water molecules, coordinated with the central ion [65, 66]. The research results showed that the compounds Ce3 + and La3 + are the most stable sulfates with nine coordination hydrates. X-ray structural study of Ce2 (SO4) 3 * 9H2O indicates the presence of two crystallographically independent cerium ions, one of them is coordinated by six water molecules and three oxygen atoms of sulfate anions in a trigonal prismatic structure (9 coordination), and the other ion is coordinated by six water molecules and bidentate binding with oxygen atoms of three sulfate anions (12 coordination) [67-69]. The other three hydrate molecules bind to sulfate anions. Stable pentahydrates and tetrahydrates have also been isolated for the lighter lanthanides (La, Ce and Nd).

Studies of rare earth metal hydrates by differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) have shown (Figure 19) that initial decomposition involves the elimination of all water molecules by a multi-step process to form dihydrate and monohydrate intermediates. Further heating leads to the formation of stable oxysulfate, and then to sesquioxides [70, 71]:

$Ln_2(SO_4)_3{*}8H_2O$ (ж) = $Ln_2(SO_4)_3{*}\,xH_2O$(ж) + $(8-x)H_2O$(г)
$Ln_2(SO_4)_3$- H_2O (ж)> $Ln_2(SO_4)_3$ (ж) + H_2O (г)
$Ln_2(SO_4)_3$ (ж)> $Ln_2O_2SO_4$ (ж) +2 SO_3 (г)
$Ln_2O_2SO_4$ (ж)> Ln_2O_3 (ж) + SO_3 (г).

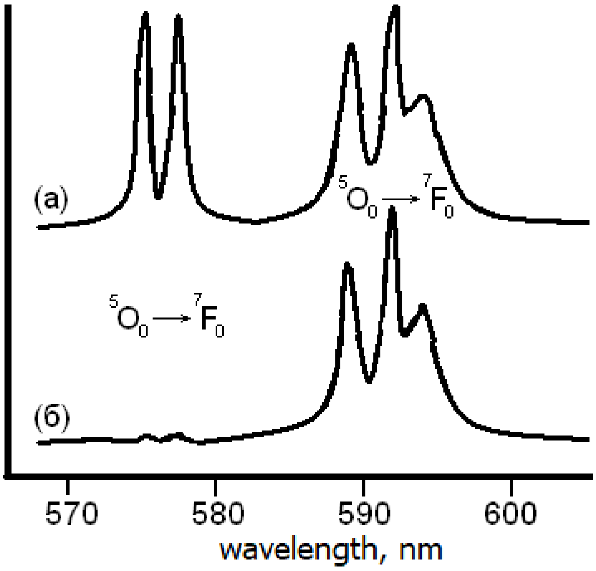


Figure 19 - Luminescence DTA 570 → 580 → 590 → 600, obtained in the analysis of Eu2 (SO4) 3 * 8H2O (a) at 25 ° C and (b) 110 ° C.

Measurements of the luminescence of the decomposition products of Eu2 (SO4) 3 * 8H2O (Britten 1983) confirm the initial conclusions. Figure 19 shows the spectra obtained for 570-700 transition regions for europium sulfate before (a) and after (b) drying at 110 ° C. For the original compound, the low intensity bands for the 570 → 700 transition were associated with a high symmetry of the structure. The intensification of these bands on heating to 110 ° C corresponds to a phase transformation in the form of lower symmetry, although there was no dehydration. In the temperature range from 175 to 350 ° C, complete dehydration occurs, which is duplicated at 580 nm of the DTA line, the transition in a wide asymmetric band is destroyed, indicating the presence of a number of species with different amounts of hydration [68].

Based on the above, the preparation of oxides of rare earth metals is not difficult. Rare earth metal salts are sent to complexes specialized for the production of high-purity concentrates or individual rare earth metals.

6 DEVELOPMENT OF TECHNOLOGICAL REGULATIONS FOR THE USE OF MANGANESE ORE AS AN OXIDIZER FROM MAN-MADE WASTES OF THE CHEMICAL AND METALLURGICAL INDUSTRIES

The use in leaching (opening) of various materials containing non-ferrous and rare metals of such oxidants as nitric acid, hydrogen peroxide, potassium permanganate, berthollet salt, copper sulfate leads either to a significant increase in the cost of technology, or due to additionally introduced impurities, complicates further processing.

A number of works have been carried out to develop a technology for using manganese ore as an oxidizer of industrial waste from the phosphorus and uranium industry:

- study of the chemical and material composition of industrial waste from the phosphorus and uranium industry;
- study of the kinetics of leaching of industrial waste from the phosphoric and uranium industry with solutions of mineral acids in the presence of manganese ore;
- study of the mechanism of redox reactions in systems rare, scattered metals - manganese dioxide - mineral acid;
- study of the influence of the nature of manganese-containing ions on the subsequent extraction of rare and scattered metals.

The influence of the parameters characteristic of the hydrometallurgical process was studied: the consumption of manganese concentrate, the concentration of sulfuric acid, the duration of leaching, the ratio of solid to liquid.

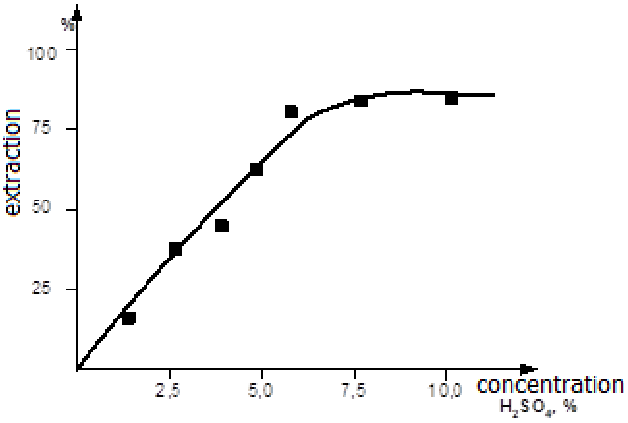


Figure 20 - Kinetics of rhenium leaching depending on the concentration of the lixiviant

Figure 20 shows the kinetics of leaching of rare metals depending on the concentration of sulfuric acid in the solution.

As can be seen from Figure 20, the kinetics of dissolution of the total of rare metals from the solid waste of the phosphorus industry increases with an increase in the concentration of sulfuric acid. The kinetics of rhenium leaching is also considered depending on the pyrolusite consumption is shown in Figure 21.

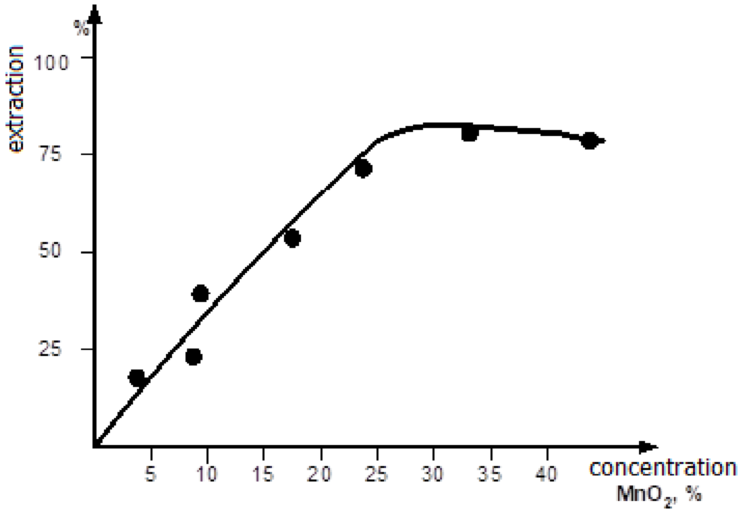


Figure 21 - Extraction of rhenium depending on the consumption of pyrolusite

As a result of the research, we had to abandon the previously presented principle technological scheme for obtaining rare and rare-earth metals from solutions of the uranium industry by sorption on a cation exchanger due to the high difference in the content of rare earth metals from iron and aluminum (the cation exchanger quickly gained the last metals without being saturated with rare earth metals).

Sorption extraction of the ion exchanger is shown in Figure 22.

Figure 22 - Sorption extraction of the amount of REE from technological solutions

Laboratory studies were carried out to extract rare earth metals from the spent solution of the PV-19 deposit. The content of the total REM in the initial solution is 30 mg / dm3, the iron content is 0.33-1.0 g / dm3 (330-1000 mg / dm3), the aluminum content is 0.6 g / dm3 (600 mg / dm3), Therefore, in the study of the method for extracting rare earth metals by the method of co-sedimentation of rare earth metals and iron by the hydrolytic method by neutralizing the solution to pH = 7.5, a collective concentrate was obtained containing 1.5-2.5% of the total amount of rare earth metals. An ammonia solution, caustic and soda ash, magnesite and partially slaked lime were used as a neutralizer of the initial solution. The use of manganese ore as an oxidizer of iron to a trivalent state allows saving sulfuric acid consumption by 25-30% when neutralizing the solution.

It was decided to sediment iron at pH = 3.5-4.0 (controlling the content of Fe + 3 by reaction with ammonium thiocyanate), then neutralize the solution to pH = 6 and pH = 7 (to avoid hydrolysis of magnesium and manganese salts) and selectively sediment REM with phosphoric acid in the form of a sediment of double salts and aluminum hydroxide. A collective concentrate was obtained with a content of 4.0-4.5% of the total REM. Work is underway to enrich the concentrate by removing aluminum by leaching with an alkaline solution. The work requires further research on the effect of impurities on the processes of leaching and sedimentation of rare earth metals.

The study of the cosedimentation of rare earth metals together with aluminum hydroxide showed that the complete cosedimentation of lanthanum and cerium occurs already at pH = 7 and their additional sedimentation in the form of phosphate is unnecessary. Under these conditions, the cosedimentation of magnesium and manganese is insignificant (1-2% of the initial content in the solution).

During the sedimentation of REM hydroxides, the elements of the yttrium group sediment somewhat more completely than the elements of the cerium group; therefore, the completeness of cosedimentation was checked by the behavior of lanthanum and cerium. When the pH of the solution was brought to 7, the residual content of thulium in the solution was 0.7 μg / dm3 (the conversion of thulium into the sediment was 98%), cerium with an initial content of 7 mg / dm3 in the solution at pH = 7 remained 0.04 mg / dm3 (the conversion of cerium into the sediment was 99%). The lanthanum content in the solution decreased from 2.3 mg / dm3 to 0.04 mg / dm3 at pH = 7 (the transfer to the sediment was 98%). With the addition of phosphoric acid, the pH of the solution decreased to 6 and the residual concentration of lanthanum increased to 0.05 mg / L. The neodymium content decreased from 3 mg / dm3 to 0.02 mg / dm3 (conversion to sediment was 99%).

The primary concentrate of the total of REM can, apparently, be obtained with a maximum extraction of 93-99% in the sediment of hydroxides by preliminary separation of iron hydroxide at pH up to 4.0 and cosedimentation of REM hydroxides with aluminum hydroxide at pH = 7. At a higher pH of the solution, magnesium hydroxide sediments. This is not desirable because in this case, firstly, the primary concentrate will be diluted with magnesium hydroxide;

secondly, the difficulty in dissolving Al (OH) 3 in a NaOH solution due to the presence of Mg (OH) 2 and the formation of Mg (AlO2) 2. A richer concentrate of rare-earth metals can be obtained by resedimentation in the form of oxalates or hydrates from a nitric acid solution.

Research has been carried out on the processing of phosphogypsum with a high content of impurities into complex concentrated fertilizers using methods of nitric acid decomposition.

The study of the influence of the concentration and rate of nitric acid, the duration of contact of the phases and temperature on the degree of transition of the main components of the test material into the liquid phase was carried out on samples of phosphogypsum, a product of processing of the Dzhambul phosphoric plant of the following composition (wt%): 31.0 CaO, 2.7 P2O5 , 1.3 MgO, 0.8 Fe2O3, 0.3 A12O3, 3.4 SiO2, 16.1 Stot- and 0.11 sum of rare earth elements. The experiments were carried out under periodic conditions. Phosphogypsum was decomposed with nitric acid in a glass reactor with a stirrer with vigorous stirring.

As shown by the results of the study, the leaching of phosphogypsum with nitric acid with a concentration of 5-15% HNO3 at a rate of 110 and 130% of the stoichiometric amount (based on CaSO4 in the raw material) proceeds quite intensively already at 40-50 ° C. The degree of extraction of rare-earth metals from phosphogypsum in the investigated range of concentrations and norms of nitric acid in 40-60 minutes is 95-98%. With an increase in the concentration of nitric acid from 5 to 25% HNO3, the degree of extraction of iron and aluminum into the liquid phase increases. At 50 ° C and an acid rate of 110% of stoichiometry (calculated as CaSO4) for 20 minutes, the degree of extraction of MgO into the solution in the studied concentration range changes from 71.2 to 79.9%, respectively. With an extension of the reaction time to 120 min, the transition of MgO to the liquid phase reaches 80.8 and 86.5%, respectively.

A change in the acid rate in the range of 110-130% has a significant effect on the extraction of MgO phosphogypsum into solution.

Figure 23 shows the effect of temperature on the degree of extraction of impurities into the solution during leaching of phosphogypsum with nitric acid containing 5% HNO3, taken in an amount of 130% of the stoichiometric norm. Decomposition time 2 h.

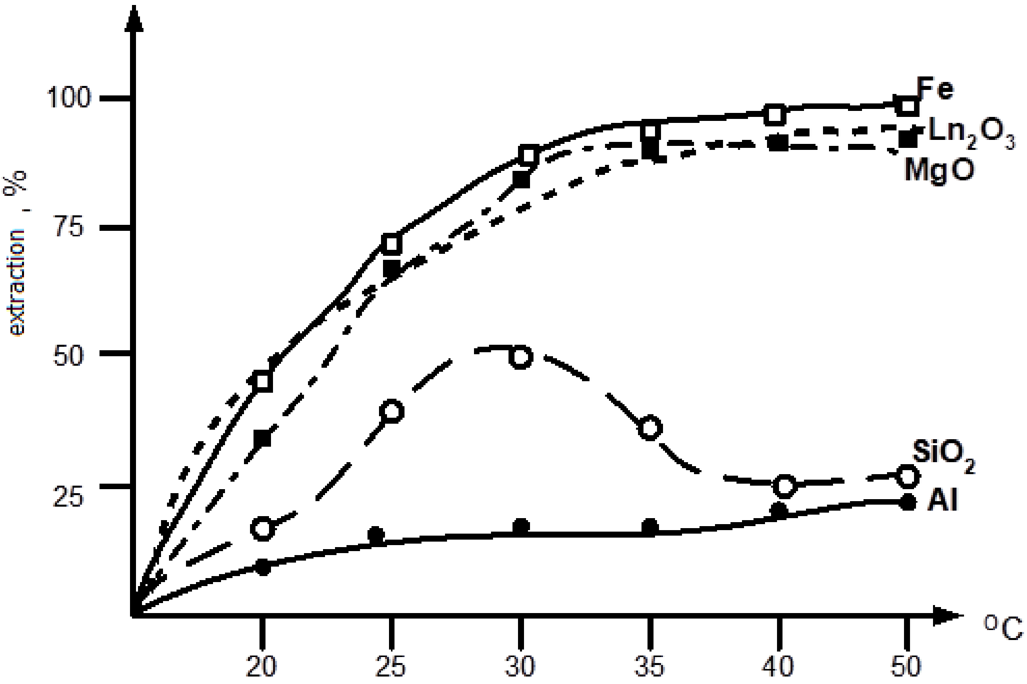


Figure 23 - Influence of temperature on the degree of extraction of impurities into the solution

Based on the studies carried out, it was found that the parameters under study (consumption of manganese concentrate, L: S, concentration of sulfuric acid, temperature, duration) have different effects on the extraction of rhenium, rare earth metals and other metals into solution during leaching of materials with solutions of mineral acids in the presence of manganese concentrate, which plays the role of an oxidizing agent.

Based on the results of the above studies, the optimal conditions for the use of manganese ore as an oxidizer for the processing of industrial waste from the phosphorus and uranium industries were determined and included in the technological regulations.

We have developed technological regulations for the processing of industrial waste from the chemical and metallurgical industries, namely, solutions of the uranium industry, phosphogypsum and by-products of metallurgical production - sinter dust.

1. Technological regulations for the use of manganese ore as an oxidizer of industrial waste - phosphogypsum. The procedure and recipe for conducting the developed technological process of phosphogypsum processing is as follows.

1.1 Sulfuric acid decomposition of phosphogypsum. Decomposition of phosphogypsum is carried out in vats or in leaching pads, with preliminary pulping of phosphogypsum with technical water. The density of the pulp is 1.40 g / cm3, at S: L = 1: 2. At the same time, a manganese oxidant is added in an amount of 0.5-1.0 kg / m3 for the complete oxidation of rare metals in phosphogypsum for further improved leaching. In addition, nitric acid is added at a rate of 2.25 kg / 100 kg of phosphogypsum. The temperature range is maintained at 60 ° C and the process duration is 1.5-2.0 hours. In this case, complete extraction of rare earth metals is observed. The solution is sent for filtration.

1.2 Filtration of the slurry on a frame press filter. The solutions are fed to the frame filter, the solution yield is 85-88%. The solutions are analyzed for the quantitative composition of the sum of rare earth metals, the acidity of the solution, and the total salt background. Then the solution is sent to the sedimentation of rare earth metal salts. The sediment is mainly calcium salts, which are sent to the tailings dump. It is supposed to be further processed into additives as a filler in building materials.

1.3 Sedimentation of rare earth metal salts. The clarified solution is fed into a vat for mixing with ammonia to pH 7.0, while up to 99% of the amount of REE is sedimented in the form of hydroxides. The slurry product is sent to the filtration department. Ammonia water consumption is 17.5 l / m3 of solution. Ammonia water in accordance with GOST 9-92, 10 / 21.5 / 31.5. added gradually at a rate of 5.0 l / min / m3 solution. The operation is carried out under the exhaust equipment. To keep alkali and alkaline earth metals in the solution, sodium hydroxide is added in an amount of 1.5-2.0 kg / m3.

1.4 Filtration of rare earth metal hydroxides. The solution is filtered on frame suction filters, here the complete sedimentation of rare earth metals in the form of hydroxides is carried out. A product with a moisture content of 20-25% is separated. After filtration, the solutions are analyzed for the general salt background and sent to the phosphogypsum pulping preparation workshop, that is, to the reverse start of the technological scheme. The primary concentrate of rare earth metals is then fed to the next operation for obtaining a secondary, purer product of the technology.

1.5 Dissolution of rare earth metal concentrates. The sediment is dissolved with sulfuric acid in the amount of 5 l / m3 of the sediment. The resulting solution has a pH of 2.0-2.5 and is heated during the dissolution process. In this case, the calcium contained in the concentrate is sedimented in the form of gypsum. Ions of rare-earth metals pass into the solution. The results of spectral analysis of gypsum deposits indicate the absence of rare earth metals in the gypsum. Then the solution is sent for filtration from impurity sediments.

1.6 Filtration of gypsum deposits. Filtration is carried out similarly to point 2. The solutions are fed to the frame filter, the solution yield is 95%. The solutions are analyzed for the quantitative composition of the sum of rare earth metals, the acidity of the solution, and the total salt background. The sediment is mainly calcium salts, which are sent to the tailings dump. Then the solution is sent to the sedimentation of rare earth metal salts.

1.7 Sedimentation of hydrates, oxalates or double sulfates of rare earth metals. The solution after sedimentation of potassium alum is mixed with a calculated amount of ammonia (12 l / m3) or sodium hydroxide (10 kg / m3) - to obtain hydrated forms, ammonium oxalate (20 kg / m3) - to obtain oxalates of rare earth metals, or sodium sulfate (6 kg / m3) - to obtain double sulfates of rare earth metals. After instant sedimentation when adding a precipitant (ammonia water) or after a short settling (ammonium oxalate, sodium sulfate).

1.8 Filtration of the pulp of crystals of rare earth metals. Rare earth concentrates, containing the main amount of 60-85% in the product, are sent to the pyrometallurgical department for the production of rare earth metal oxides. In this case, the solid sediment undergoes thermal decomposition, with the receipt of rare earth metal oxides of at least 95% purity.

1.9 Obtaining pure commercial products of rare earth metals in individual form. The process of obtaining is carried out in industries specialized in the industry of rare earth metals. Therefore, the obtained commercial product of REM concentrates with 95% purity is tared in special polyethylene dishes with tight-fitting lids.

Consumption of materials and reagents for processing 1000 tons of waste industrial waste from the phosphorus industry, with a total REE content of 0.08% (800 kg) are presented in Table 36.

Table 36 - Rate of consumption of materials and reagents

Materials and reagents	Quantity, t, m3
Phosphogypsum	1000 t
Manganese oxidant	1 t
Process water	1000 m^3
Nitric acid	22 t
Ammonia water 25%, technical according to GOST 9-92, 10 / 21.5 / 31.5	16,4 m^3
Caustic Sodium	1,6 t
Sulfuric acid H2SO4	14 t
Sedimentation of REE salts	
- ammonia water	9,3 m^3
- caustic sodium	7,8 t
- ammonium oxalate	15,6 t
- sodium sulfate	4,7 t

2. The procedure and recipe for the developed technological process of processing man-made waste from the uranium industry (waste solutions of underground leaching).

2.1 The first sedimentation of impurities dissolved in water with ammonia to pH 4.5-5.0. The solutions of the uranium industry are mixed in vats with ammonia water with a continuous supply and output of the solution, calculated by the necessary parameters for the further operation of the process. Mixing is done with an air pump. Ammonia water according to GOST 9-92, 10 / 21.5 / 31.5 is added gradually at a rate of 10.0 l / min / m3 of solution to pH 5.0. With an increase in the feed rate and the amount of ammonia water, the turbidity and its proportional value - the optical density of the medium - increase to a certain limiting value at which all useful components can be isolated from the solution in the form of a suspension. At the same time, iron ions (+3) are not detected in the solution, a reduced amount of aluminum is noticed. Ammonia water consumption is 7.5 l / m^3 of solution.

2.2 Primary filtration. Technogenic solutions of the uranium industry are filtered on suction filters with a capacity of m3 / hour. Filters operating under vacuum - Nutsch filters are made of thick-walled polypropylene pipes, the inner part of which is divided by a perforated partition with a filter cloth ("spunbond", non-woven polypropylene) attached to it. Suspension is poured into the upper part, the filtrate is collected at the bottom of the lower part. The vacuum is created under the partition using a vacuum pump connected to the suction filter through a receiver trap. The purpose of the receiver is to "smooth" the pump pulsations and prevent the ingress of an aggressive medium into its mechanisms. The capacitive filter is manufactured in an assortment of modifications: from an industrial one with a filtration area of S = 0.7 m^2. Polypropylene is used as the main material for the production of filters. The solutions are analyzed for the general salt background and sent to obtain the primary concentrate, the sludge is sent for further processing.

2.3 Secondary deposition. Obtaining a primary concentrate of rare earth metals with ammonia to pH 7.3-7.5. The clarified solution is fed into a vat for mixing with ammonia to pH 7.5, while up to 99% of the amount of REE is sedimented in the form of hydroxides. The slurry product is sent to the filtration department. Ammonia water consumption is 5.5 l / m3 of solution. Ammonia water in accordance with GOST 9-92, 10 / 21.5 / 31.5 added gradually at a rate of 5.0 l / min / m^3 solution. The operation is carried out under the exhaust equipment.

2.4 Secondary filtration. The solution is filtered on frame suction filters, here the complete sedimentation of rare earth metals in the form of hydroxides is carried out. A product with a moisture content of 20-25% is separated. After filtration, the solutions are analyzed and sent to the workshop for the preparation of the leaching solution for in-situ leaching, that is, to the turnover of the uranium production. The primary concentrate of rare earth metals is then fed to the next operation for obtaining a secondary, purer product of the technology.

2.5 Dissolution of rare earth metal concentrates. The sediment is dissolved with sulfuric acid in the amount of 7 l / m^3 of the sediment. The resulting solution has a pH of 2.0-2.5 and is heated during the dissolution process. Further, with rapid cooling, potassium alum is sedimented, while the amount of aluminum in the solution decreases from 6.0 to 1.5 g / l. The results of spectral analysis of potassium alum indicate the absence of rare earth metals in the salts. Then the solution is sent for planting rare earth metal salts.

2.6 Sedimentation of hydrates, oxalates or double sulfates of rare earth metals. The solution after sedimentation of potassium alum is mixed with a calculated amount of ammonia (12 l / m^3) or sodium hydroxide (10 kg / m^3) - to obtain hydrated forms, ammonium oxalate (20 kg / m^3) - to obtain oxalates of rare earth metals, or sodium sulfate (6 kg / m^3) - to obtain double sulfates of rare earth metals. After instant sedimentation when adding a precipitant (ammonia water) or after a short settling (ammonium oxalate, sodium sulfate).

2.7 Filtration of the pulp of crystals of rare earth metals. Rare earth concentrates, containing the main amount of 40-80% in the product, are sent to the pyrometallurgical department for the production of rare earth metal oxides. In this case, the solid sediment undergoes thermal decomposition, with the receipt of rare earth metal oxides with a purity of 95%.

2.8 Obtaining pure commercial products of rare earth metals in individual form. The process of obtaining is carried out in industries specialized in the industry of rare earth metals. Therefore, the obtained commercial product Misch metals with 95% purity is tared in special polyethylene dishes with tight-fitting lids.

The consumption of materials and reagents for processing 1000 m3 of waste solutions from the uranium industry, with a total REE content of 30 mg / l (30 kg), are presented in Table 37.

Table 37 - Rate of consumption of materials and reagents for processing 1000 m3 of waste solutions of the uranium industry

Materials and reagents	Quantity, t, m3
Solution	1000 m3
Sulfuric acid H2SO4, t	13 t
Ammonia water 25%, technical according to GOST 9-92, 10 / 21.5 / 31.5, m3	15.5 m3
Sedimentation of REE salts	
- ammonia water	12 m3
- caustic sodium	10 t
- ammonium oxalate	20 t
- sodium sulfate	6 t

3. Technological regulations for the use of manganese ore as an oxidizer of industrial waste - by-products of metallurgical production - sinter dust. The procedure and recipe for conducting the developed technological process for processing sinter dust is as follows.

Leaching of sinter dust is carried out with solutions of sulfuric acid (100 g / dm3) in the presence of manganese concentrate, the amount of which in terms of MnO2 is 15% of the weight of dust, at L: S = 3: 1, process temperature - 80 ° C, leaching time - 1 hour.

According to the technology existing in the workshop, before cementation of cadmium, the solution is purified from arsenic, iron, copper and lead. The solutions after extracting rhenium from them, containing 20 g / dm3 of sulfuric acid, are heated to 75 ° C, air is blown through and, when the mixer is running, neutralized with zinc igniters to pH 4-5. Taking into account the content of arsenic and iron in the solution, the calculated amounts of iron (II) and copper sulfates are fed. The process is carried out in three stages for 35-48 hours. At the first stage, the arsenic content in the solution is reduced to 1 g / dm3, at the second - to 0.05, and at the third - to "traces". These solutions are fed for further purification from copper and lead with suspensions of zinc sulfide and strontium carbonate.

Considering that manganese, which is an oxidizer of arsenic (III) and iron (II), as well as a high temperature of the solution (80 ° C), is present in solutions after leaching of agglomerate, we proposed to purify arsenic and iron at the end of the leaching process. dust. Before feeding iron (II) sulfate into it, the pulp is neutralized with zinc sublimates to pH 4.

As shown by preliminary experiments, within 30 minutes the content of arsenic and iron in solutions after their purification decreases to 0.005 g / dm3 and 0.03 g / dm3, respectively. The final purification from arsenic is carried out from solutions after the extraction of rhenium in accordance with the shop regulations.

By removing the main amount of arsenic in the "head" of the process, it will be possible to reduce the total amount of time for this operation by about 8 times. In addition, the operations of filtration and heating of solutions are reduced.

Pulp filtration. The resulting pulp is filtered from lead and iron-arsenic cakes on disk vacuum filters. After washing, the cakes are sent to the sinter shop, solutions for the extraction of rhenium, cadmium, zinc and manganese.

Sorption of rhenium. The extraction of rhenium is carried out in 4 stages at S: L = 1: 4. The phase ratio depends on the rhenium content in the initial solution. NH4NO3 250 g / dm3 dissolved in H2SO4 20g / dm3 was used as an extractant.

Obtaining RZO with a purity of ≥99.0% by separating RZK is a rather difficult task. The complexity of the separation of rare earth metals is due to the closeness of the properties of rare earth elements, especially praseodymium and neodymium, the ionic radii of which are practically the same.

Currently, to obtain high-purity individual REE compounds, liquid extraction is mainly used, which is the most widespread, extremely flexible and highly productive method for separating elements with similar properties.

The selection criterion for the extraction system for the separation of rare-earth elements are the coefficients of distribution (Kp) and separation (β) of neighboring elements, the capacity of the organic phase in terms of the extracted components, the rate of separation of the aqueous-organic emulsion during phase mixing, and the absence of a third phase. It is also necessary to take into account the factors affecting Kp, β and capacity: the content of REE and mineral acid in the initial aqueous solution, the concentration of the extractant, the effect of salting-out additives [48, 50, 54, 68, 69], etc.

In the majority of extraction systems known for the separation of rare-earth elements, the values of β are, as a rule, small; therefore, multistage extraction cascades are used to carry out the technological separation process. For the separation of compounds of elements exhibiting a different oxidation state from (+3) (for example, cerium (+4)), one to three steps are sufficient due to large β.

The largest β are observed when using undiluted extractants, which, as a rule, have a high viscosity, which reduces the productivity of the extraction equipment and increases the loss of extractants with aqueous solutions. Therefore, for dilution, inert non-polar solvents such as kerosene, dodecane, etc. are used, and their concentration is determined during an experiment that takes into account all the above factors.

Extractants of almost all main classes of organic compounds are used in the technology of separation of rare-earth elements, namely: neutral esters,

organic acids and organic bases. Of all the variety of neutral esters, in practice, neutral organophosphorus compounds (NPOC) are most often used, organophosphorus acids (FOCs) among organic acids, and quaternary ammonium compounds (QAC) among organic bases [48]. In some cases, the extraction is carried out with mixtures of extractants of different classes, when used, a noticeable increase in the separation coefficients is often observed ("synergistic effect") [70].

To carry out the extraction separation of a multicomponent mixture, extraction cascades are used in practice. Although extraction cascades allow separation with different directions of phase movement (co-current, counter-current), in industry, as a rule, continuous counter-current cascades are used due to their highest efficiency.

In general, the separation technology consists of three main stages - extraction, washing and re-extraction - the implementation of which in a counter-current extraction cascade depends on the characteristics of the mixture to be separated.

In particular, the extraction separation of REE is most often carried out in countercurrent extraction multistage cascades with exchange washing (return of a part of the better extractable component to the cascade), which makes it possible to obtain high concentrations of compounds of the separated components in the products (Figure 24) [69].

Figure 24 - Cascade equipment for the separation of individual REE (Romedmet, RF)

Analysis of the well-known literary sources showed that phosphogypsum is a promising source of REE, including cerium and neodymium, and a promising method for extracting REE from phosphogypsum is a complex waste-free technology [16], which, in addition to obtaining REE, provides the associated production of a wide range of building materials. The REE isolated from phosphogypsum by this technology contains more than 98% of REE oxides and can be used as a feedstock for the production of cerium dioxide and neodymium oxide.

2. Taking into account that cerium is present as the main component in a partially oxidized form in the composition of the selected raw material, it should be separated from other REE at the first stage of separation of the REE. The most acceptable method for this is electrochemical additional oxidation of cerium with subsequent extraction of its oxidized form TBP from a nitrate solution.

Research in this direction should be devoted to the search for promising anode and separating diaphragm materials as an alternative to rather expensive platinized titanium anodes and ceramic diaphragms manufactured by the laborious method of extrusion molding of a porous base, as well as determining the optimal conditions for the extraction separation of the oxidized form of cerium from other REEs.

3. RGD isolated from phosphogypsum contains radioactive impurities, therefore, the process flow diagram for RGC separation should include a decontamination stage. Taking into account the close chemical properties of thorium and cerium (+4), it is necessary to study the behavior of thorium and other radioactive impurities during extraction and determine the ways of their separation from cerium and REE.

The stage of sedimentation of oxalates and carbonates in the REM technology largely determines the yield and quality of the oxides obtained. The Japanese company "Mitsubishi" has developed and patented the following method for the sedimentation of oxalates: an alkali solution is introduced into an aqueous acidic solution containing free hydrochloric (or nitric) acid, ions of rare earth metals and oxalic acid (without sediment), an alkali solution is introduced to neutralize the acid, in this case, a fine-crystalline, well-formed sediment of REM oxalates falls out [].

Powders of basic yttrium, lanthanum, cerium and neodymium carbonates were obtained by the method of homogeneous sedimentation, which were characterized by the following parameters: grain size, grain shape, crystal structure and behavior during thermal decomposition.

The purity of the initial powders of yttrium oxide and carbonates of lanthanum, neodymium and cerium was not less than 99%, other SEMs were about 1%, the content of non-rare earth impurities did not exceed 0.1%. Everything

other reagents were of reactive grade. The initial solutions were obtained by dissolving the corresponding powders in an excess of HNO_3, heated to boiling, and then filtered. The concentration corresponded to 0.4 M (according to the REM cation).

Homogeneous sedimentation was carried out as follows: 50 ml of the initial solution were added to 750 ml of distilled water and to 13 g (in the case of Nd, to 26 g) of urea. The solution was heated to reflux for 1 hour while stirring with a magnetic stirrer. The resulting suspension was centrifuged, washed with water and acetone, and then dried.

The size and shape of the particles of the obtained powders were evaluated using a scanning electron microscope. Additionally, the particle size was measured with a particle analyzer on a powder sample weighing about 0.1 g, dispersed in 250 ml of water. The carbon content was determined by analyzing the absorption of CO_2 released during heat treatment. The nitrate content was determined using an ion-selective electrode and an ion analyzer. The thermal decomposition of the starting powders was analyzed using a thermal analyzer. Each series of experiments used about 30 mg of powder. Powder samples were heated to a temperature of 1000 ° C at a rate of 20 ° C / min in air, and the curves of thermogravimetric analysis and differential thermal analysis were plotted.

Homogeneous sedimentation of V cations and some rare-earth metals from hot aqueous solutions of urea was used to obtain homogeneous powders with the general formula LnONCO3. The studied powders of lanthanum, neodymium and cerium consist of crystalline particles of orthorhombic structure and regular geometric shape with a size of 1-6 microns, while yttrium powders consisted of spherical amorphous particles with a size of 0.4 microns. Powders of Y, La, Nd hydroxycarbonates decomposed in two stages: first to Ln_2O-2CO3, and then to Ln_2O_3, while Ce hydroxycarbonate was directly converted into CeO_2 upon heat treatment in air [27].

Research is being carried out to study the structure and properties (optical, magnetic, electrical, etc.) of oxides and other compounds of rare-earth metals. Particular attention is paid to yttrium oxide. Much work has been done at the University of St. Iowa (USA) to study the influence of the spray drying process on the sintering of yttrium oxide in terms of the quality of the resulting powders.

Spray drying of deposited materials results in the formation of solid spheroidal particles and then larger agglomerates. The resulting powders were sintered for 1 h at a temperature of 1750 ° C to a density of 95% of theoretical. Powders Y2 O3, pre-dried on trays (otherwise processed identically), were poorly sintered (up to 63-80% of theoretical density). Consequently, spray drying of sediments produces a powder that is better amenable to sintering than tray drying. Statistical analysis of the data shows that the main influence is exerted by the flow rate of the air mixture through the nozzle of the dryer (sprayer): the higher the feed rate, the greater the density of the Y2-O3 powders obtained. The electrical conductivity and structural defects of yttrium oxide were studied as a function of the water vapor pressure [28, 29].

The research laboratory of the Japanese company "Hitachi LTD" has studied the epitaxial growth of neodymium oxide films. The cubic phase in such films is formed at a temperature of 400-600 ° C. For the growth of REM oxide films, the method of reactive evaporation was initially used. The experimental material was neodymium oxide, which has only one valency +3 and a low melting point (at a temperature of 1024 ° C). Nd-2O3 films were grown on substrates in an O2 atmosphere at a pressure of 1.4 * 10-2 Pa by evaporation of metal Nd in a tantalum heater boat. After a vacuum of 1 * 10-5 Pa was created in the main furnace chamber with the help of two oil diffusion pumps, O2 was fed into the chamber and its pressure was brought to 1 * 10-3. After some time, the O2 pressure was increased to 1.4 * 10-2 Pa, and the pressure at the end of the boat, where the evaporated metal Nd was located, was maintained at the level of 7 * 10-4 Pa.

In the experiment, we used substrates of Si, CaF2, and quartz glass polished and etched in HF. The temperature of the substrates in the range from room temperature to 700 ° C was measured using a Pt- (Pt + 13% Rh) thermocouple. At a deposition rate of 0.014 to 0.067 nm / s, the film thickness is 1 μm.

Films deposited on various substrates were characterized by X-ray diffraction analysis. The presence of phases was determined by powder diffraction, and the fact of epitaxial growth was checked by a two-crystal X-ray method using a CuK$\mathscr{L}$ radiation source and an Si (III) plate as the first monochromatic crystal.

Epitaxial growth on a Si substrate was unsuccessful due to the oxidation of the substrate surface, while on a CaF2 substrate it was successful, which was confirmed by the two-crystal X-ray method. If it is possible to prevent oxidation of the surface of semiconductor substrates, REM sesquioxides can be considered as promising materials for epitaxial insulating films [30].

The attention of researchers is also attracted by the semiconducting properties of solid solutions of yttrium sulfides and single crystals of samarium sulfide, superconducting properties of molybdates and other REM compounds, photoelectric properties of scandium tantalate and neodymium phosphates.

7 PILOT INDUSTRIAL TESTS

Pilot tests were carried out in accordance with the current technological regulations, the experimental results were confirmed by theoretical and laboratory data.

1. Pilot tests of phosphogypsum processing, which were carried out in the lead plant LLP "Yuzhpolymetal", Shymkent, South Kazakhstan region from November 20 to December 20, 2013. Analytical control of physical and chemical parameters of tests were analyzed in the chemical-technological laboratory of Yuzhpolymetal LLP, analyzes using the ICP MS method were carried out in the regional engineering testing laboratory "Structural and biochemical materials" Auezov. To carry out the tests, the following activities were carried out:

1. Equipped unit for leaching phosphogypsum in sulfuric acid with a propeller stirrer. The unit is equipped with a mobile pH meter.

2. A unit for neutralizing solutions of the uranium industry with ammonia water up to pH - 8.5-9.0, productivity - 2.5 l / h with a propeller stirrer is equipped. The unit is equipped with a mobile pH meter.

3. A filtering unit for dirty and clean cake of concentrates has been installed, filtering area m2 - 0.56, with the following components: pressure gauge, plate for frame press filter - 14 pcs, feed pump, filter cloth.

The leaching process of phosphogypsum was carried out in the following way. Phosphogypsum, in the amount of 10.0 kg and pre-crushed, is placed in the leaching unit. Manganese ore is added to it as an oxidizing agent at the rate of 10 g / kg of phosphogypsum. A leach solution is prepared in the amount of 20 l, the amount of sulfuric acid is calculated at the rate of 20.0 g / l, a mixer with a rotation of 400 rpm is turned on and the leaching process is carried out for 2 hours. After leaching, the solution is immediately filtered on a frame press filter. After filtration, the solution is determined for the quantitative composition of rare earth metals, and the filtration cake is packed for further use in the construction industry. The solution containing rare earth metals is sent for further sedimentation of the amount of rare earth metals. The solution is neutralized with ammonia water at the rate of 17 ml / l of the solution; sediment is sedimented with vigorous stirring. After sedimentation is isolated (about 15-30 minutes), the solution is sent to the filtration department. After filtration, the solution is treated with sulfuric acid and, according to the technology, is sent for re-leaching of phosphogypsum of the next batch, and the sediment containing rare earth metals is sent to a vat for further dissolution. The vat is made of stainless steel with a propeller agitator. Hydrates are dissolved with the addition of sulfuric acid at the rate of 62.5 g / kg of hydrates. In the process of dissolution with vigorous stirring, incomplete dissolution of hydrates is observed, while the pH of the solution is 3.0-3.5. The solution is filtered on a vacuum filter, with separation of aluminum and iron hydrates. The solution contains ions of rare earth metals (hereinafter REM), which are then sedimented by saturated solutions of sodium hydroxide with the release of insoluble sediments of REM hydrates. The solution is filtered, the sediment of rare earth metals is dissolved with sulfuric acid to pH 2.0, while complete dissolution of hydrates is observed. Oxalic acid is added to the solution in dry form, with a ratio of oxalic acid to REM ions of 2: 1. With slight stirring and settling for 2-4 hours, rare earth oxalates are released. The solution is sent for filtration of pure commercial REM. After filtration of REM oxalates according to known technologies, the REM salt undergoes a temperature treatment - 900 oC, where the REM concentrate is obtained. REM concentrate contains lanthanide oxides up to 90.2-93.2%, which corresponds to the commercial qualities of these metals.

The results of pilot tests of hydrometallurgical processing of phosphogypsum to obtain concentrates of rare earth metals are presented in tables 38-39.

Table 38 - Results of pilot tests of primary cleaning from non-ferrous metals

Experience number	Source material - phosphogypsum		MnO2, kg	H2SO4, kg	NH4OH, ml	1 hydrates of rare earth metals			H2SO4, g	NaOH, kg	2 hydrates of rare earth metals		
	Weight, kg	REM amount, g				Kg	REM amount, g	Extraction,%			g	REM amount, g	Extraction,%
1	10,0	10	0,62	0,4	340	1,6	9,0	90	80	0,11	80	8,5	94,4
2	10,0	10,0	0,62	0,4	340	1,9	9,5	95	75	0,12	78	8,4	88,4
3	10,0	10,0	0,62	0,4	340	1,7	9,2	92	78	0,10	81	8,4	91,3

Table 39 - Results of pilot tests for obtaining commercial concentrates of rare-earth metals

REM hydrates, g	H_2SO_4, г	Solution			$H_2C_2O_4$, г	REM oxalates			Calcination		Commercial concentrate of REM			
		pH	Volume, ml	REM amount, g		г	REM amount, g	Extraction,%	T, °C	τ, ч	Output, g	REM amount,%	Through extraction,%	Note
80	5,5	2,0	100	8,5	18,0	11,4	8,40	98,8	900	3	9,15	91,8	94,4	-
78	5,4	2,1	100	8,4	18,0	10,7	8,3	98,8	900	3	9,24	89,8	94,0	-
81	5,5	2,1	105	8,4	18,0	11,0	8,25	98,2	900	3	9,09	90,7	93,8	-

The results of chemical-spectral analyzes on the content of impurities in the concentrate of rare-earth metals are shown in Table 40.

Table 40 - Content of impurities in the combined concentrate of rare earth metals from 3 lots

Chemical composition of REM concentrate	Content, %
Oxides of rare earth metals	90,76
Al	0,4
Fe	0,33
Na	0,5
P_2O_5	<1,5
CaO	<1,13
SiO_2	<0,02
SrO	<0,08
rest	<5,28

The results of pilot tests showed the effect of the feasibility of introducing the developed technology of hydrometallurgical processing of phosphogypsum from the Taraz phosphoric plant to obtain concentrates of rare earth metals.

Pilot testing of lead production sinter dust containing rare metals.

When opening sinter dust with sulfuric acid solutions in the presence of manganese concentrate, solutions were obtained containing, g / dm3: 20-22 cadmium, 0.12-0.24 rhenium, 0.4-0.6 thallium, 5-6.5 zinc, 15-20 sulfuric acid, 10-30 chlorine, 25-30 manganese. Manganese in solutions is in the form of Mn (II) compounds. But, since solutions represent a complex multicomponent system, due to the occurrence of secondary reactions, the likelihood of the formation of Mn (VII) compounds is not excluded.

In the workshop for processing sinter dust of lead production, there are two technological schemes for extracting rhenium from solutions: sorption and extraction. When the content of chloride ions in the solution is up to 10 g / dm3, rhenium is extracted by sorption, above 10 g / dm3 - by extraction. The presence of significant amounts of manganese in productive solutions was the basis for research on the effect of its ions on the extraction of rhenium and cadmium using the technology existing in the shop. The influence of the concentration of manganese and the degree of its oxidation on the sorption of rhenium was studied.

The experiments were carried out on sorption columns with Ambersep 920 U anion exchanger. The volume of the ion exchanger in the column was 0.05 dm3. The solutions were passed at a speed of 1 rpm. The process of sorption of rhenium from these solutions proceeded similarly to its sorption from model solutions without any complications. But the total dynamic exchange capacity (PDOE) of the Ambersep 920 U anionite for rhenium decreased from 6.61% to 3.9%, the amount of the passed solution - from 826 to 220 beats. vol., there is also no capacity before rhenium "breakthrough" into the filtrate (table 41). The reason for the decrease in these parameters is the presence of chloride ions in industrial solutions, which have a depressing effect on the sorption of rhenium.

Table 41 - Data on the sorption of rhenium from solutions containing manganese on the ion exchanger Ambersep 920 U

Skipped solutions, specific volume	Re content in solution, mg / dm3	Filtrate		DOE (swollen ion exchanger)	
		Re content			
		mg / dm3	% ref.	%	kg / t
80	140,0	42,28	10,2	1,7296	17,296
90	230,0	87,40	38,0	2,0148	20,148
100	230,0	93,15	40,5	2,2884	22,884
ПО	230,0	138,70	60,3	2,4710	24,710
120	230,0	157,80	68,8	2,6154	26,154
130	267,0	186,40	68,8	2,7766	27,766
140	267,0	184,20	69,0	2,9422	29,422
150	267,0	209,00	78,3	3,0582	30,582
160	267,0	213,60	80,0	3,1650	31,650
170	258,0	206,40	80,0	3,3382	33,382
180	258,0	193,50	75,0	3,3982	33,982
190	258,0	204,60	79,3	3,5050	35,050
200	258,0;	215,90	83,7	3,5892	35,892
210	258,0	213,10	82,6	3,6670	36,670
220	258,0	225,00	87,2	3,7450	37,450
240	258,0	221,00	85,7	3,8080	38,080
260	258,0	221,10	85,7	3,8860	38,860

However, the obtained indicators - PDOE, the amount of the passed solution before rhenium "breakthrough" into the filtrate and complete saturation of the ion exchanger with rhenium do not differ from the production indicators, i.e. in the absence of manganese in solutions.

Thus, it was revealed that in the processes of sorption of rhenium from sulfuric acid solutions containing Mn (VII), redox reactions occur. This is evidenced by the formation of deposits of various manganese oxides, the composition of which is roughly established using IR spectroscopic and crystal-optical methods of analysis. Primary, secondary amino groups (Ambersep 920 U) probably act as reducing agents. In the anion exchanger Ambersep 920 U, along with grains containing quaternary ammonium bases (which are not reducing agents), there are also grains that probably contain primary, secondary amines, which are reducing Mn (VII).

Desorption of the rhenium-rich anionite was carried out with ammonium nitrate 250 g / dm3 dissolved in sulfuric acid 20 g / dm3 at a phase ratio S: L = 1: 4 received 200.0 ml of eluate with a rhenium content of 4.0 g / dm3. Then the solution was neutralized with ammonium water to pH 7. On cooling, the rhenium-containing salt sedimented from the eluent, which was processed in accordance with the current regulations for the production of rare metals. The residual concentration in the solution was less than 0.03 g / dm3.

According to the results of the tests carried out at the installation for the production of rhenium-containing salts from sinter dust of lead production by the hydrometallurgical method, 8.0 g of significantly pure ammonium perrhenate with a rhenium content of 69.2% was obtained. The resulting product complies with GOST 31411-2009 suitable for further production of pure rhenium.

3. Pilot industrial tests of the processing of solutions of the uranium industry were carried out at the lead plant LLP "Yuzhpolymetal", Shymkent, South Kazakhstan region from November 20 to December 20, 2013. Analytical control of physical and chemical parameters of tests were analyzed in the chemical-technological laboratory of Yuzhpolymetal LLP, analyzes using the ICP MS method were carried out in the regional engineering testing laboratory "Structural and biochemical materials" Auezov. To carry out the tests, the following activities were carried out:

1. A unit for neutralizing solutions of the uranium industry with ammonia water up to pH -8.5-9.0 was equipped, productivity - 2.5 l / h with a propeller stirrer. The unit is equipped with a mobile pH meter.

2. A filtration unit for dirty and clean cake of concentrates was installed, filtration area m2 - 0.56, with the following components: pressure gauge, plate for frame press filter - 14 pcs, feed pump, filter cloth.

The process of neutralizing solutions of the uranium industry is carried out in the following way. Solutions of uranium sorption mother liquors in the amount of 50.0 l are poured into the neutralization unit, the mixer is turned on with a rotation of 400 rpm. A mobile pH meter is installed, and a neutralizing reagent, ammonia water, is added at a rate of 17 ml / l of solution. The neutralizing unit is located under the ventilation chamber. After neutralization, the solution is immediately filtered on a frame press filter. After filtration, the solution is determined for the quantitative composition of rare earth metals, and the filtration sediment is sent to a vat for further dissolution. The vat is made of stainless steel with a propeller agitator. The hydrates are dissolved with the addition of sulfuric acid and the initial solution at a S: L ratio of 2: 1. In the process of dissolution with vigorous stirring, incomplete dissolution of hydrates is observed, while the pH of the solution is 3.0-3.5. The solution is filtered on a vacuum filter, with separation of aluminum and iron hydrates. The solution contains ions of rare earth metals, which are then sedimented by saturated solutions of sodium hydroxide with the release of insoluble sediments of REM hydrates. The solution is filtered, the sediment of rare earth metals is dissolved with sulfuric acid to pH 2.0, while complete dissolution of hydrates is observed. Oxalic acid is added to the solution in dry form, with a ratio of oxalic acid to REM ions of 2: 1. With slight stirring and settling for 2-4 hours, rare earth oxalates are released. The solution is sent for filtration of pure commercial REM. After filtration of REM oxalates according to known technologies, the REM salt undergoes a temperature treatment - 900 oC, where the REM concentrate is obtained. REM concentrate contains lanthanide oxides up to 90.2-91.2%, which corresponds to the commercial qualities of these metals.

The results of experimental-industrial tests of hydrometallurgical processing of solutions of the uranium industry of the PV-19 deposit with obtaining concentrates of rare earth metals are presented in tables 42-43.

Table 42 - Results of pilot tests of primary cleaning from non-ferrous metals

Experience №	Initial solution		NH_4OH, l	1 hydrates of rare earth metals			H_2SO_4, kg	NaOH, kg	2 hydrates of rare earth metals		
	Volume, l	REM amount, g		kg	REM amount, g	Extraction,%			kg	REM amount, g	Extraction,%
1	50,0	1,5	0,850	4,0	1,5	100	0,180	0,250	0,2	1,40	93,3
2	50,0	1,5	0,840	3,9	1,5	100	0,175	0,256	0,25	1,45	96,6
3	50,0	1,5	0,845	4,0	1,5	100	0,178	0250	0,24	1,40	93,3

Table 43 - Results of pilot tests for obtaining commercial concentrates of rare earth metals

REM hydrates, g	H_2SO_4, g	Solution			$H_2C_2O_4$, g	REM oxalates			Calcination		Commercial concentrate of REM			
		pH	Volume, ml	REM amount, g		g	REM amount, g	Extraction,%	T, °C	τ, h	Output, g	REM amount, %	Through extractio ,%	Note
200	15,5	2,0	210	1,40	3,0	1,6	1,40	100	900	3	1,52	92,1	96,6	-
250	16,0	2,1	210	1,45	3,0	1,7	1,45	100	900	3	1,55	93,5	98,3	-
240	15,5	2,1	215	1,40	3,0	1,6	1,40	100	900	3	1,58	88,6	96,6	-

The results of chemical-spectral analyzes for the content of impurities in the concentrate of rare-earth metals are shown in Table 44.

Table 44 - Content of impurities in the combined concentrate of rare earth metals from 3 lots

Chemical composition of REM concentrate	Content, %
Oxides of rare earth metals	91,8
Al	0,5
Fe	0,5
Na	0,5
P_2O_5	<0,80
CaO	<0,88
SiO_2	<0,002
SrO	<0,008
rest	<2,55

The results of pilot tests showed the effect of the feasibility of introducing the developed technology of hydrometallurgical processing of solutions of the uranium industry of the PV-19 deposit to obtain concentrates of rare earth metals. Based on the pilot tests carried out, a technological scheme for processing solutions of the uranium industry was developed, which is shown in Figure 25.

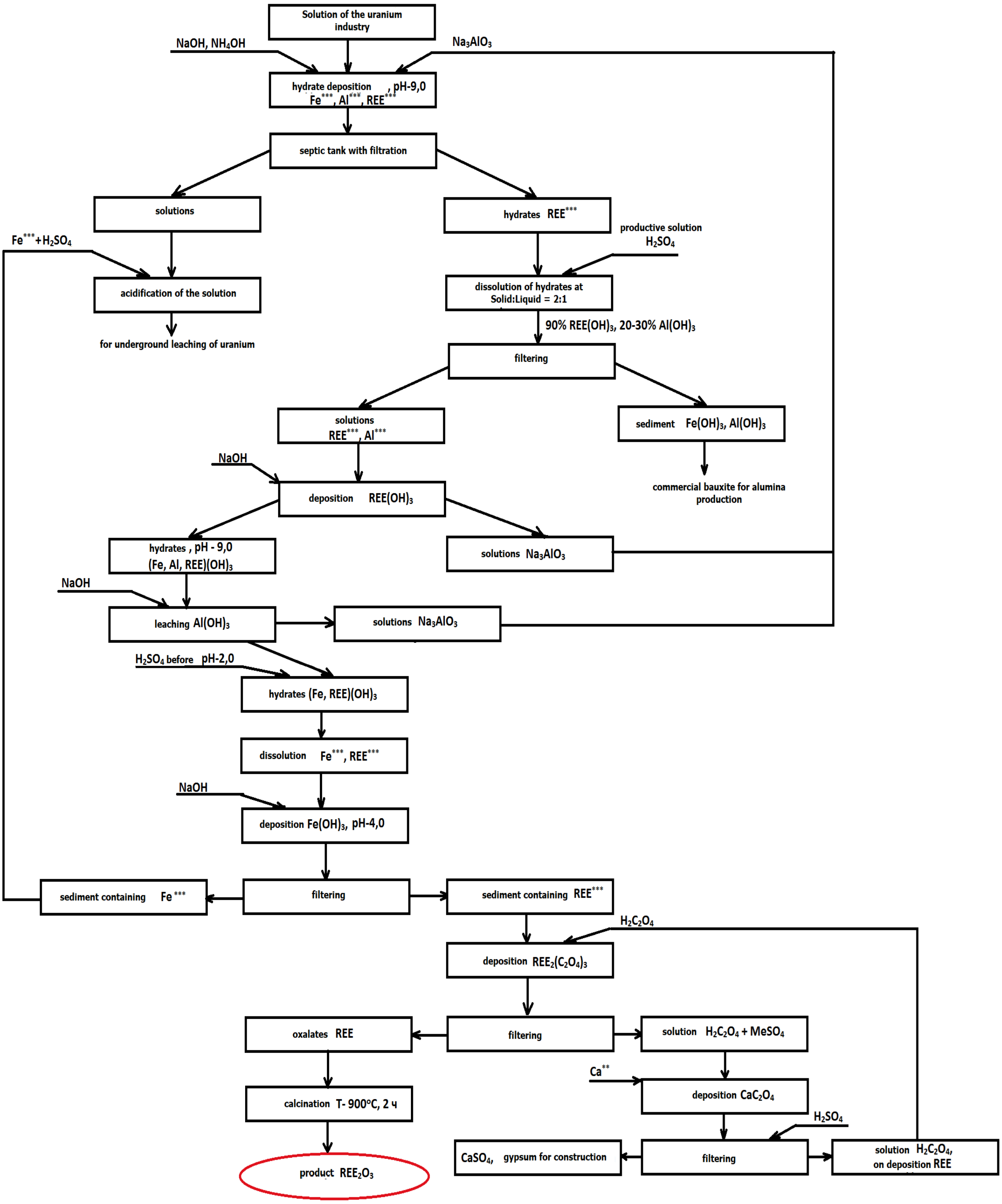
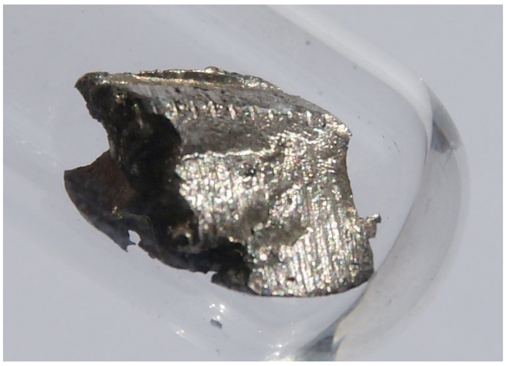


Figure 25 – Technological scheme for the processing of solutions of the uranium industry

8 MAIN CHARACTERISTICS OF INDIVIDUAL REE AND THEIR FIELDS OF APPLICATION

Lanthanum – shiny metal of silvery-white color, the content in the earth's crust is about 2.9 · 10−3% by weight, in seawater - about 2.9 · 10−6 mg / l. The main industrial minerals of lanthanum are monazite, bastnesite, apatite and loparite. Lanthanum is concentrated along with cerium, praseodymium and neodymium. In its pure state, it is malleable and malleable. Weakly paramagnetic. The crystal structure is close-packed type of the closest hexagonal packing. Prices for lanthanum metal with a purity of 99-99.9 are about $ 2-4 per gram. Lenses for video cameras and photo cameras are made from it; catalysts for cleaning exhaust gases in the production of xylene, polybutadiene rubber, some types of polyethylene; phosphors for light sources and X-ray technology, heat-resistant protective coatings, high-temperature nickel-based alloys, ceramic capacitors, piezoelectric elements, resistors (LaB_6), thermistors, thermionic emitters, heating elements, optical modulators, cathodoluminophores for cathode ray tubes. Promising areas of use are hydrogen power engineering ($LaNi_5$), MHD generators, fuel cells. High-temperature superconductivity at 40 ° K was discovered in lanthanum-strontium-copper ceramics. Lanthanum is a moderately toxic substance.

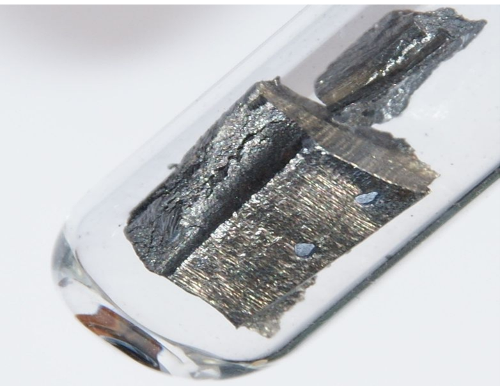
Cerium is a silvery-white ductile and malleable metal, easily forged and machined at room temperature, the content in the earth's crust is 70 g / t, in the water of the oceans -5.2 10-6 mg / l. It is used for glass polishing and discoloration, glaze damping, in the manufacture of polishing materials for integrated circuits, alloying of high-strength cast iron, iron and nickel-cobalt heat-resistant alloys; catalysts for the synthesis of ammonia, filters-neutralizers of vehicle exhaust gases, flue gas cleaning, solid electrolytes, optical lenses, magnets. in Japan, a technology is being developed for the manufacture of cerium titanate fibers, which is considered as a substitute for the more traditional silicon carbide. Has a toxic effect on fish and lower aquatic organisms. Has the ability to bioaccumulate.



Praseodymium - silver-yellow metal, density 6.475 g / cm³, melting point 932 0C. Praseodymium is a soft, malleable and workable metal, the content of praseodymium in the earth's crust is 9 g / t, in the water of the oceans - 2.6 · 10−6 mg / l; staining of ceramics and swelling, damping of glaze, catalysts, ceramic capacitors, incandescent coals. PrCo5 magnets successfully replace Sm-Co magnets in some areas of application. Seiko Epson (Japan) has developed Pr-Fe-B magnets with copper additions, which, having the same magnetic force as neodymium, have higher strength and less tendency to corrosion.

Neodymium - the metal is silvery-white in color with a golden hue, the neodymium content in the earth's crust (according to various sources) is 25-37 g / t, in the water of the oceans - 9.2 10-6 mg / l. color television (CT), ceramic capacitors, glass coloring, glaze damping, catalysts, lasers, computer displays, magnesium alloys. More recently, the industrial Nd-Fe-B magnetic specific magnetic energy is 4-10 times stronger than conventional types of magnets. They change for car engines and industrial equipment, audiovisual equipment, NMR tomographs. The new magnetic device (APS undulator), which generates radiation, the intensity of which is 10,000 times higher than achieved so far, uses 244 Nd-Fe-B magnets. Very important fields of application of neodymium are: alloying of special structural alloys and steels (modification of high-quality steels), neodymium in the form of an additive of 1.5% increases the strength of pure titanium by one and a half times and therefore serves for its alloying; production of powerful permanent magnets (neodymium-yttrium-cobalt, neodymium-iron-boron). Neodymium compounds are used in agriculture (seed treatment to accelerate germination and yield). Alloying with neodymium significantly increases the strength of thermoelectric materials based on bismuth and antimony tellurides and selenides and increases the thermo-EMF of these materials. There is an indication that doping thermoelectric alloys of the bismuth-tellurium-cesium system with neodymium also increases their strength, thermo-emf and time stability.

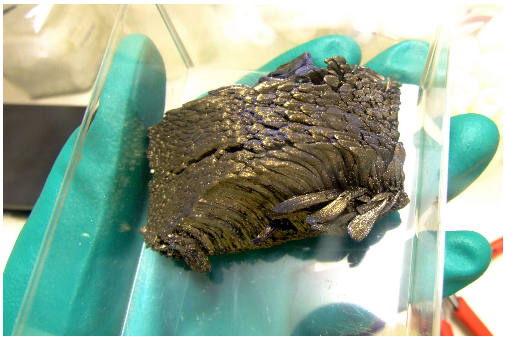
Prices for neodymium with a purity of 99-99.9% in 2011 were about 110 US dollars per 1 kilogram, depending on the production technology used and the country of origin, as well as on the final form of the finished product and its area of application and use. In 2014, the price of 99% pure neodymium was approximately US $ 70 per kg.



Samarium – a silvery metal, the content of samarium in the earth's crust is 8 g / t, in the water of the oceans - 1.7 · 10−6 mg / l is the main component of one of the strongest and most stable high temperature permanent magnets, which made it possible to create fundamentally new electric motors. 1982 to 1990 Sm consumption in Japan increased 5 times. In 1987, 720 t of Sm-Co magnets were produced there. Despite the high cost and scarcity of raw materials, according to forecasts, Sm-Co magnets will not be completely replaced, at least in the military and ARKT. Other areas of application of samarium are ceramic capacitors, lasers, catalysts. Samarium oxide has a very high refractoriness, resistance to active metal melts and a high melting point (2270 ° C). Therefore, it is used as a good refractory material. Samarium and strontium manganates have a gigantic magnetocaloric effect and can be used to design magnetic refrigerators. The biological role of samarium is poorly understood. It is known to stimulate metabolism. The toxicity of samarium and its compounds, like that of other rare earth elements, is low.

Europium - silver-white metal, in its pure form - soft dark brown metal. It is part of the phosphor for central heating, X-ray phosphors, control rods in nuclear reactors. Eu_2O_3 cermets have begun to be used in fast breeder reactors. Europium ions are used to generate laser radiation in the visible region of the spectrum with a wavelength of 0.61 μm (orange rays), therefore, europium oxide is used to create solid-state and less common liquid lasers. Europium is an indispensable component of phosphors used in cathode-ray and plasma color screens. Euro banknotes are protected from counterfeiting by Europium-based phosphors. Europium cations are used in medical diagnostics as fluorescent probes. Radioactive isotopes of europium are used in the treatment of some forms of cancer.

In 2014, the price of metallic europium EBM-1 ranged from 800 to 2000 US dollars per kg, and of europium oxide with a purity of 99.9% - about 500 dollars per kg. Europium belongs to low-toxic elements.



Gadolinium - soft viscous metal of silvery-white color, gadolinium clarke in the earth's crust (according to Taylor) - 8 g / t, content in ocean water - 2.4×10^{-6} mg / l. It is a part of storage devices (ZU) on cylindrical magnetic domains, high-power lasers, optical glasses, microwave devices, X-ray technology, fiber optics, an additive to nuclear fuel, magnetostrictive devices, magneto-optical plates, permanent magnets. The coating of gadolinium-containing paint provides protection against radioactive radiation. New and rapidly growing applications for gadolinium are cryogenic magnetic refrigerators and heat pumps. Gadolinium-148, which undergoes alpha decay (half-life of 93 years), is a safe yet extremely powerful heat source for radioisotope thermoelectric generators.

Gadolinium is an inhibitor of mechanosensitive ion channels, reversibly blocks them in micromolar concentrations. It can also block some other ion channels.

Prices for metallic gadolinium with a purity of 99.9% at the end of 2014 amounted to USD 132.5 per kg.

Terbium – soft viscous metal of silvery-white color, terbium clarke in the earth's crust (according to Taylor) - 4.3 g / t. phosphors for central heating, high-performance fluorescent lamps, X-ray technology, optical discs for video players, magnetostrictive devices. Terbium-iron alloy - the best magnetostrictive material of modern technology (especially its single crystal) - is used for the production of powerful drives for small displacements (for example, adaptive optics of large reflector telescopes), sound sources of enormous power, and ultra-powerful ultrasonic emitters. In addition, a number of terbium compounds also exhibit giant magnetostriction, and in this respect, terbium titanate and, in particular, its single crystal are of particular interest. Complex compounds of terbium (along with europium and samarium) are used in OLED devices. This is due to good luminescence characteristics: high luminescence intensity and low spectral line half-width.

According to existing data, terbium has no biological role. Like other lanthanides, terbium compounds should have below average toxicity.

China is the main supplier of rare earth elements. The pricing policy, which he correctly pursued, led to a sharp rise in prices (5-10 times) in 2010-2011. The price for one kilogram of metallic terbium reached $ 4,400, in 2016 the price dropped to $ 1,000 per kilogram. The price of terbium, like other rare earth elements, is highly dependent on the degree of purification.

In 2013, 1 gram of 99.9% pure terbium could be bought for 64 euros. In Russia in 2014-2016 for a metal ingot weighing 2 grams and 99.9% purity they asked for 150 euros.

Dysprosium - metal with a luster of silver, clarke of dysprosium in the earth's crust (according to Taylor) 5 g / t, the content of oceans in the water is 2.9 · 10−6. Dysprosium is an excellent alloying component of zinc alloys. The addition of dysprosium to zirconium dramatically improves its manufacturability (but increases the thermal neutron capture cross section). Thus, zirconium doped with dysprosium is easily amenable to pressure treatment (pressing of rods). The dysprosium-iron alloy, in polycrystalline and especially in monocrystalline form, is used as a powerful magnetostrictive material. Dysprosium ions have long been used in medical lasers (wavelength - 2.36 microns). Dysprosium oxide is used in the production of heavy duty magnets.

Prices for metal dysprosium in ingots with a purity of 99-99.9% in 2008 amounted to 180-250 dollars per 1 kg. In 2014, 10 grams of 99.9% pure dysprosium could be purchased for 114 euros.

Does not play a biological role. Dysprosium metal dust irritates the lungs.

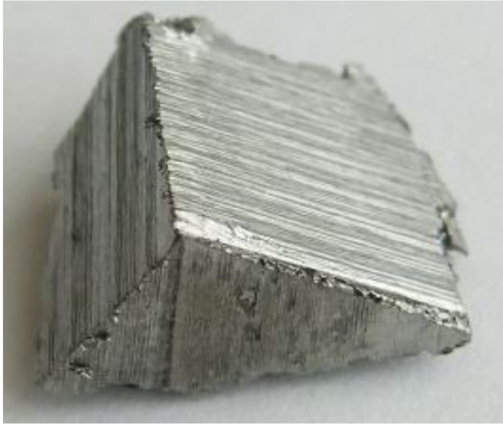
Holmium **-** relatively soft, malleable, lustrous silvery metal, the content of holmium in the earth's crust is 1.3 · 10−4% by weight, in seawater 2.2 · 10−7%. Ultra-high-purity holmium is used to make pole pieces for superconducting magnets for producing super-strong magnetic fields. In this respect, the holmium-erbium alloy plays an important role. The thermoEMF of holmium monotelluride is 40 μV / K. pigments, lasers, ferrite bubble chargers, phosphors, magnetic flux capacitors of strong magnetic fields, catalytic filters at thermal power plants. A new type of superconducting ceramics with holmium, developed in Japan, is distinguished by its stability and the ability to obtain a higher critical current density in comparison with yttrium.

Prices for holmium oxide with a purity of 99-99.99% in 2006 were about 120-191 dollars per 1 kg. It does not have a biological role, but it stimulates the exchange of substances.

Erbium - soft malleable silvery metal, erbium clarke in the earth's crust (according to Taylor) - 3.3 g / t, the content in the water of the oceans - 2.4 · 10−6. Density 4.77; melt 15220C, bp 2863 oC. It oxidizes in air, forming a pink oxide Er2O3. One of the most important directions in the use of erbium is its use in the form of oxide (sometimes borate) in nuclear technology. For example, a mixture of erbium oxide and uranium oxide can dramatically improve the operation of RBMK reactors, improving their energy distribution, technical and economic parameters, and, which is especially important, the safety of the reactors. For example, the addition of erbium oxide to uranium oxide as a burnable neutron absorber allows at the initial stage to “isolate” part of the uranium from participation in the reaction, “releasing” it later. This makes it possible to put more nuclear fuel into the reactor without prejudice to violate its nuclear safety, to increase its operating life before reloading new fuel, to level the power release regimes with a constant decrease in the amount of uranium fuel.

Erbium oxide single crystals are used as high-performance laser materials.

Erbium oxide is added to the silica melt in the production of ultra-long-range optical fibers (ELE - erbium-doped fiber). When constructing ultra-long optical paths, the problem of intermediate signal regeneration arises due to its natural attenuation during propagation in a quartz filament. If the route passes through “difficult” sections (for example, under water), the placement of “converting” regeneration stations (ie those that convert a weak optical signal into an electrical one, amplify it and convert it back into laser radiation) becomes technically a very difficult task due to the need to provide such stations with power. Erbium-doped optical fiber has the ability to absorb light at one wavelength and emit it at another wavelength. An external semiconductor laser sends 980 or 1480 nm infrared light into the fiber, exciting erbium atoms. When an optical signal with a wavelength of 1530 to 1620 nm enters the fiber, the excited erbium atoms emit light at the same wavelength as the input signal.



Thulium - is an easily processed silver-white metal, its content in the earth's crust is 2.7 · 10−5 wt. %, in seawater - 10-7 mg / liter. Along with other rare earth elements, thulium is present in minerals such as xenotime, euxenite, monazite, loparite and some others. The thulium-170 isotope is used for the manufacture of portable X-ray units for medical purposes, as well as in metal defectoscopy. More recently, it has been proposed as a fuel in radioisotope energy sources. Thulium ions are used to generate infrared radiation with a wavelength of 1.91 microns. In addition, vapors of metallic thulium are used to excite laser radiation with a tunable wavelength (frequency). Thulium does not play any biological role, although it is known to stimulate metabolism. Soluble thulium salts are low-toxic, but insoluble compounds are non-toxic. The element is practically not assimilated by plants and, therefore, cannot enter the food chain. The average thulium content in plants is about 1 mg per tonne of dry weight. The price of metal thulium with a purity of> 99.9% is approximately $ 2.2 thousand per 1 kg, the price of thulium oxide with a purity of 99.9% is $ 1.1 thousand per 1 kg.

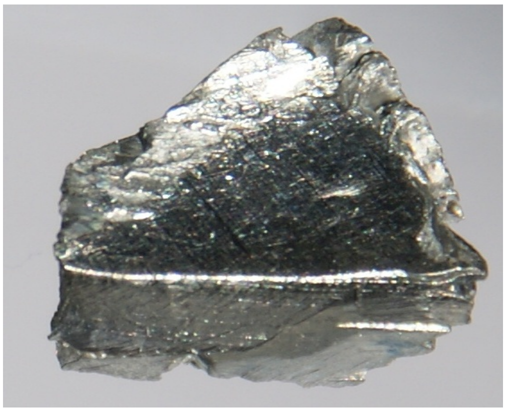
Ytterbium - light gray metal, ytterbium clarke in the earth's crust (according to Taylor) 0.33 g / t, the content of oceans in the water is 2 · 10−6. Prices for metallic ytterbium with a purity of 99-99.9% in 2006 amounted to 260-420 dollars per 1 kg. Ytterbium ions are used to generate laser radiation in the near infrared range, with a radiation wavelength of 1.06 ÷ 1.07 microns, and in the form of ytterbium oxide are used to produce high-power fiber lasers. Monocrystalline alloy barium fluoride - ytterbium fluoride doped with holmium ions is used as a powerful and technologically advanced laser material. Ytterbium under irradiation with neutrons in a nuclear reactor is partially converted into the isotope hafnium-

178 - 178m2Hf. There are proposals to use this isomer as an energy accumulator, although these projects are only at the research stage. Ytterbium oxide is used as a dielectric in the production of silicon MIS structures.

The content in the human body is not known exactly, but is small: in the blood 0.0047 mg / l, in the bone tissue 0.07 × 10-4%, in the muscle tissue 0.02 × 10-4%. Does not play a biological role, has low toxicity. Stimulant. Suspected of being carcinogenic. Daily requirement: 0.016 mg.

Lutetium - silver-white metal, easy to machine. It is the heaviest element among lanthanides in terms of both atomic weight and density (9.8404 g / cm³). The melting point of lutetium (1663 ° C) is the highest of all rare earth elements. Due to the effect of lanthanide compression among all lanthanides, lutetium has the smallest atomic and ionic radii. It is used to generate lutetium ion laser radiation. Content in the earth's crust is - 0.00008% by weight. Content in seawater - is 0.0000012 mg / l. The main industrial minerals are xenotime, euxenite, bastnesite. Lutetium scandate, lutetium gallate, lutetium aluminate, doped with holmium and thulium, generate radiation with a wavelength of 2.69 microns, and neodymium ions - 1.06 microns, and are excellent materials for the production of powerful lasers for military use and for medicine. Lutetium oxide finds a small volume application in nuclear technology as a neutron absorber and also as an activation detector. Cerium-doped monocrystalline lutetium silicate (LSO) is a very good scintillator and, as such, is used for particle detection in nuclear physics, elementary particle physics, and nuclear medicine (in particular, in positron emission tomography). In recent years, considerable interest in lutetium is due, for example, to the fact that when a number of heat-resistant materials and alloys on a chromium-nickel base are doped with lutetium, their service life sharply increases.

The price of metallic lutetium with a purity of> 99.9% is 3.5-5.5 thousand dollars per 1 kg. Lutetium is the most expensive of the rare earth metals due to the difficulty of separating it from a mixture of rare earth elements and its limited use. Soluble salts are of low toxicity.



Yttrium - light silver rare earth metal, chemical analogue of lanthanum. Earth clarke 26 g / t, content in seawater 0.0003 mg / l. phosphors for DH and fluorescent lamps, optical glasses, garnets and ferrites for electronic and microwave devices, artificial diamonds, steel for nuclear reactors, magnesium and nickel-cobalt superheat alloys, ceramic and plasma-sprayed protective coatings, heating elements, oxygen sensors, microwave devices. Yttrium oxide is introduced as a stabilizing additive - from 3 to 10 and even up to 20%. The addition of an insignificant amount of Y2O3 (0.001-0.1%) increases the electrical conductivity of aluminum alloys by 50%. Yttrium is investigated in structural materials for thermonuclear reactors; moreover, it is easily machinable. Yttrium with a purity of 99-99.9% costs an average of 115-185 US dollars per 1 kg.

Permanent magnets (Sm, Nd), for which consumption growth in Japan amounts to tens of% per year, ceramic capacitors (La, Ce, Nd), three-band phosphors (Y, Eu , La, Ce, Tb), catalysts for cleaning exhaust gases of cars (La, Ce), polishing materials for integral circuits (Ce), ceramics for cutting tools and oxygen sensors (Y).

Consumption forecast.

Based on the development trends in the demand for rare earth metals up to 1983, the US Mining Bureau predicted the most probable consumption of TR2O3, in 2000 58 thousand tons (minimum - 29, maximum - 92), including 34 thousand tons in the USA. tons with an average annual growth rate of 2.6 and 3.1%, respectively. However, over the past 5 years, fundamental changes have taken place in the structure and scale of consumption of rare-earth metals, which have led to a decrease in demand for the amount of oxides by almost half.

Prospects for growth in the consumption of individual REM are estimated quite high (annual growth - up to 15%), although the quantitative forecast can hardly be any reliable now. This opinion of many economists abroad is confirmed by recent ad hoc research by one of the leading marketing companies - Roskill Information Service Ltd. (London). The optimistic forecast is explained, first of all, by the fact that in many countries of the world new areas of application of rare earth metals are being developed very intensively, special companies have been created and government programs are in place to search for areas of application of cerium rare earth metals in order to prevent their overproduction and rise in price. scarce metals. The prospects for the industrial consumption of yttrium-containing high-temperature superconductors (HTSC) are unclear, although a forecast of a possible increase in demand for yttrium for the next 10 years to 14 thousand tons has already been published in Japan. Roskill's Information Services, Ltd. published a more moderate forecast of consumption - 5600 tons of Y2O3 in 2000. In Japan, France, the USA, commercial production of superconducting products - wires, rods, tapes, children's toys - has already been established, experimental samples of integrated circuits have been made. In Germany, samples of wire more than 1 km long were made.

High growth rates of demand are predicted for neodymium (1987 - 800 tons; 1992 - 1350 tons; 2000 - 5350 tons) and samarium in the production of permanent magnets; europium and yttrium in the production of phosphors for color television in connection with the trend towards an increase in screens; gadolinium - in the production of magnetic refrigerators, nuclear fuel, materials for protection from radiation; terbium - in the production of phosphors and magneto-optical devices. However, on the basis of the available discoveries, overproduction is foreseen for these yttrium lanthanides, as well as for lanthanum, praseodymium and, to a lesser extent, cerium. In all likelihood, the problem of unbalanced demand for individual REMs in relation to raw materials and production will remain one of the most acute for them for a long time to come.

In the PRC, successful studies are being carried out on the use of REMs as fertilizers in agriculture. An experiment conducted in Hunan province for three years showed that wheat yields increased by 5-8% with improved quality due to higher protein and lysine content. The possibility of increasing the yield of rice, peanuts, soybeans, tea, tobacco, watermelons was noted; increase in fruit size, sugar content, earlier ripening in the absence of toxicity. REM consumption amounted to 450 tons per 530 thousand hectares. A joint company is organized to carry out similar experiments in Australia.

The provision of the world economy with reserves of rare earth metals at the current level of production and consumption exceeds 100 years, both for the world as a whole and for individual producing countries, however, the threat of a shortage of certain metals remains relevant, due to the disproportions between their content in the developed raw materials and unevenly developing demand. For example, in recent years, there has been a periodical shortage of samarium, in connection with which prices have significantly increased.

Export. The main exporters of concentrates are Australia, which exports all produced monazite concentrate, the USA and China (bastnesite concentrate). In 1990, exports from Australia amounted to 14.1 thousand tons of concentrate, of which 90% was exported to France, 5% to the United States, and the rest to other countries.

In India and Brazil, the export of monazite concentrates is prohibited due to their radioactivity. The export item is mainly chloride smelting. In 1986, India exported to Japan 750 tons of chlorides, 200 kg of yttrium oxide, 136 tons of other products; in the USA - 1 thousand tons of chlorides (in 1985 - 2 thousand tons).

The main exporters of high-purity RH products are the French company Rhone-Poulenc and the American company Molycorp. Inc.

The PRC plays an increasing role in the world export of various types of raw materials and products. 1978-1995 receipts from exports increased by 50% per year, in 1987 6.5 thousand tons of rare earth products were exported (25% more than in 1986) in the amount of 61.6 million dollars. China supplies the world market with concentrates, chloride, intermediate products, including Sm-Gd-Eu concentrate. Eu concentrate, oxides and metals. In April 1987, the PRC government made a decision to introduce significant changes in the export procedure; minimum price levels and a limit on the export of ores for raw materials containing europium, yttrium, samarium were established; the right to export REM ores was granted to three export-import corporations; the creation of a commission to determine the lower price limit is planned. Restrictions do not apply to bastnesite ores of the Bayan-Obo deposit. Since 1990, the PRC has been the world's largest exporter.

Import. The main importers of rare earth concentrates are France and Japan. France imports monazite concentrates from Australia, Japan - various types of raw materials and intermediate products from China, bastnezite from the USA, chlorides from India and Brazil. The USA imports monazite concentrates (96% from Australia), xenotime from Malaysia and various finished products. High-purity individual compounds and metals are imported mainly by the countries of Western Europe, the USA, and Japan.

Japan has recently significantly increased its imports of rare earth metals, preferring to purchase not raw materials, but semi-finished products and high-purity compounds. In some years, imports in value terms increased by 40-50%, and over ten years by 4 times. In 1987, it amounted to $ 100 million, including 34% each from France and China, 17% from the United States, and the rest from India, Brazil, Taiwan, etc. Purchases of some individual oxides increased especially: from 1983 to 1986 biennium lantana - 1.7; cerium - 7.7; neodymium - 3.6; samarium - 2.6; europium - 1.2; gadolinium - 3.7; terbium - 5.3; yttrium - 4.1 times (Table 8).

Prices are highly dependent on the purity of the products and the size of the supply. Reference prices in the USA for a number of elements are published by the American Metal Market newspaper, but prices for all REMs are only by Research Chemicals. Until recently, prices for oxides and metals have remained fairly stable.

CONCLUSION

Based on the conducted analyses of scientific and patent literature, the technogenic deposits of rare and rare-earth metals of Kazakhstan were revealed. In technogenic mineral formations of enterprises of mining production of the Republic of Kazakhstan, there are reserves of valuable components, commensurate with the reserves of natural mineral deposits, and they can and should be considered and used as technogenic mineral deposits. The highest losses, respectively, and resources, of underexploited valuable components in the dumps of field development, are very significant - in tailings, the lowest - in the slag of metallurgical processing. Available in Kazakhstan technogenic mineral formations of mining production at their annual output of one billion tons are used for the needs of no more than 6-7 %. Wide use of them in economic turnover will allow increasing resource saving on a huge scale due to saving of operational capital costs of exploration, extraction and processing of mineral raw materials.

Wastes of chemical-metallurgical industry, namely, wastes of phosphorus industry (phosphoslam, phosphogypsum), waste cakes and dust of lead production, overburden rocks of coal deposits, ash dumps and slags of thermal power plants, waste pulps of the tailings dump of the polymetallic plant of JSC "Achpolimetall", uranium solutions of underground leaching (sorption mother liquor) were considered. Based on the physico-chemical analyses performed, the composition of the presented samples revealed a low content of rare and rare-earth metals. The highest content of rare metals is found in lead dust and uranium solutions. Therefore, due to the intensification of the leaching process, the redox parameters of some rare metals in the Pourbaix diagrams were considered, which determined the use of an oxidizer for rhenium, cadmium, etc. Based on the phase composition, the ionic state of the rare earth metals (where all are in higher oxidation states) was established and oxidation of the rare earth metals was not necessary. Therefore, manganese oxidizer can be used in several other many rare earth metals where the range of oxidation degrees is wide.

The physical and chemical properties of manganese concentrate, phosphogypsum and lead dust were determined.

Rare metals in uranium solutions will be considered in the 4-5 stage of this project, so it was analyzed for chemical composition. At this time the physical and chemical properties of solutions for the extraction of rare and rare-earth metals from them are being studied. Dust from lead production was analyzed for elemental and phase composition, after which leaching processes of rare and rare-earth metals were carried out. Optimal leaching parameters were determined: temperature regime, solid to liquid ratio, the concentration of leaching solution, and consumption of oxidizer - manganese dioxide. Experimentally established optimal mode of the process of leaching agglomerates together with manganese concentrate with sulfuric acid solutions: manganese concentrate consumption - 15% of dust weight, sulfuric acid concentration - 1.0 mol/dm^3, L: S = 3:1, temperature - 80 ° C, leaching duration - 1 hour. Under these conditions, 91.0%

rhenium, 90.0% cadmium, 92% zinc and 96% manganese are extracted into the solution.

In the section of physical and chemical analysis of raw materials the proper level of development of mass spectrometry is presented, which allows creating conditions and pushing to development of knowledge-intensive production, development and creation of new equipment, technologies, etc. The innovative way of development, to which Kazakhstan is currently committed, is probably more suitable than any other for achieving this goal and, in turn, needs it - a developed mass spectrometric infrastructure. According to this, a methodology for determining solid and liquid samples of rare earth and other rare metals was developed.

The largest contribution to the total REM content is made by La (13% - 18%)' Ce (38% - 44%) and Nd (18% - 19%)' amounting in total to 81% of the total REM content. These proportions are maintained for all investigated uranium deposits' which allows talking about the similarity of their trace element compositions as applied to rare earth metals.

Akdala, Kendala and PV-19 are the most attractive in terms of by-product extraction of rhenium and REM.

The method of extracting REM by preliminary selective deposition of iron at pH = 3.8 and then co-sedimentation of REM and aluminum at pH = 9.5 was investigated. When the pH of the solution was raised to 3.8, iron was sedimented to traces, while the aluminum content in the solution decreased by half. When the pH of the solution was increased to 9.5, aluminum was completely sedimented, the REM content in the solution decreased by 90-97% and a collective concentrate containing 2.5-3.5% of the REM sum was obtained.

Laboratory studies on REM extraction from the spent solution of PV-19 deposit were carried out. Content of the amount of REM in the initial solution was 30 mg/dm^3, iron content was 0.33-1.0 g/dm^3 (330-1000 mg/dm^3), aluminum content was 0.6 g/dm^3 (600 mg/dm^3). When studying the method of REM extraction by co-sedimentation of REM and iron by hydrolytic method by neutralizing the solution to pH=9 a collective concentrate containing 1.5-2.5 % of the REM amount was obtained.

Studies were carried out on the purification of the main component from impurities of metals - iron and aluminum. The primary concentrate of the amount of REM can be obtained with a maximum extraction of 93-99% in the hydroxide sediment by preliminary separation of iron hydroxide at pH 4.0 and co-sedimentation of REM hydroxide with aluminum hydroxide at pH = 7. At a higher pH value of the solution, there is the sedimentation of magnesium hydroxide. This is not desirable because it will, firstly, dilute the primary concentrate with magnesium hydroxide; secondly, it will be difficult to dissolve $Al(OH)_3$ in NaOH solution due to the presence of $Mg(OH)_2$ and the formation of $Mg(AlO_2)_2$. A richer REM concentrate can be obtained by redeposition as oxalates or hydrates from the nitric acid solution. Two variants of the technological scheme for obtaining rare earth metals have been suggested and investigated.

Option 1: When neutralizing the initial solution with ammonia it is necessary to carry out neutralization so that there was minimal co-sedimentation with aluminum hydroxide. During neutralization in the pH range of 3.5-5.0, determine the concentration of aluminum and the amount of rare earth metals. Reach maximum sedimentation of $Al(OH)_3$ - 90 % and minimum sedimentation of $Ln(OH)_3$ - 10 % after separation of hydrate cakes $Fe(OH)_3$, $Al(OH)_3$ from a solution, then extract all lanthanides. To do this, use sedimentation of lanthanide phosphates by addition of Na_3PO_4 or bring pH=7.5 to the beginning of $Fe(OH)_2$ sedimentation by addition of alkali containing aluminum. Sediment $Al(OH)_3*Ln(OH)_3$ or $AlPO_4*LnPO_4$ treated with NaOH solution - 10%, obtaining the primary rare earth concentrate, which is dissolved in H_2SO_4 and sediment with oxalic acid all $Ln_2(C_2O_4)_3$, not containing foreign impurities.

Option 2. Solutions of the uranium industry are stirred in vats with ammonia water with continuous supply and solution output, calculated by necessary parameters for further running of the process. Mixing is carried out by an air pump. Ammonia water as per GOST 9-92, 10/21,5/31,5 is added gradually at a rate of 10,0 $l/min/m^3$ of the solution up to pH 5,0. The solution is sent for filtration. The hydrated iron cake is sent to the tailings. The clarified solution is delivered into a vat for stirring with ammonia to pH = 7.5, at which time up to 99% of the amount of REM in the form of hydroxides is sedimented. The slurry-like product is sent to the filtration department. The sediment is dissolved with sulfuric acid in an amount of 7 l/m^3 of sediment. The obtained solution has pH=2.0-2.5 and is heated in the process of dissolution. Then, with rapid cooling, alumokalium alum is planted. The solution after sedimentation of alumokalium alum is mixed with the calculated amount of ammonia (12 l/m^3) or sodium hydroxide (10 kg/m^3) - to obtain hydrate forms, ammonium oxalate (20 kg/m^3) - to obtain oxalates of rare-earth metals, or sodium sulfate (6 kg/m^3) - to obtain double sulfates of rare-earth metals. The obtained salts of rare-earth metals - oxalates, hydrates, double sulfates - are then processed according to the known method of thermal decomposition of salts to obtain lanthanide oxides.

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Қожа Ахмет Ясауи атындағы Халықаралық қазақ-түрік университеті
2021-2022 оқу жылындағы кезектен тыс Сенат мәжілісінің

№2 ХАТТАМАСЫНАН ҮЗІНДІ

Түркістан қаласы **15 қараша 2021 жыл**

Сағат – 15:00 Дүйсенбі

Онлайн

Қатысқандар: сенат мүшелері, «Жоғары оқу орнының үздік оқытушысы – 2021» конкурсының үміткерлері, «Жастар саясаты» департаментінің директоры міндетін атқарушы Даркембай Аружан және студенттік ректор, Халықаралық қатынастар мамандығының 3-курс студенті Мустафа Санжар Ышин

Күн тәртібінде:

2. Әртүрлі мәселелер:

2.4. Университет ОПҚ-ның дайындаған монографияларды бекітіп баспаға ұсыну туралы *(Баяндамашы: Сенат хатшысы Куралбаева Алия Ахметкаримовна)*

Ашық дауыс беру нәтижесінде **СЕНАТ ҚАУЛЫ ЕТЕДІ:**

2.4. Жаратылыстану ғылымдары факультеті Биология кафедрасының қауымдастырылған профессоры, техн.ғ.к. И.О.Аймбетованың ағылшын тіліндегі «Промышленные отходы химико-металлургических производств, содержащие редкие и редкоземельные металлы: способы получения первичных концентратов» (Industrial waste of chemical-metallurgical industries containing rare and rare earth metals: methods for obtaining primary concentrates) (74,44% түпнұсқалылық) атты монографиясы бекітіліп, баспаға ұсынылсын.

Сенат төрайымы **Ж.Темірбекова**

Сенат хатшысы **А.Куралбаева**

Aimbetova Indira Orazgalievna

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