ANNOTATION

Dissertation work on the topic:
«DEVELOPMENT OF A COMPLEX TECHNOLOGY FOR PROCESSING BLACK SHALE ORES IN KAZAKHSTAN»,
Submitted for application for the degree of philosophy doctor PhD in the specialty 6D070900 – «METALLURGY »
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Assessment of the current state of the scientific or technological problem (task) being solved. Currently, due to the development of fundamental and applied sciences, the consumption of rare refractory and rare earth metals is growing rapidly in the world.

Vanadium is one of the valuable rare metals widely used in various branches of modern production.

The main commercial applications for vanadium are in steel, where its ability to form carbides gives the steel hardness and increased wear resistance. Over 90% of all vanadium produced in the world is spent on steel alloying, the remaining 10% is consumed by non-ferrous metallurgy, chemistry, etc.

In the production of various classes of steels and alloys, vanadium is one of the best alloying elements, a substitute for tungsten, molybdenum, niobium, Nickel and other metals. The specific weight of pure vanadium is 5.96 g/cm^3, the metal is extremely hard, but it can be processed. As a result of the addition of vanadium, steel acquires a uniform structure, elasticity, malleability, abrasion and impact resistance, corrosion resistance, hardness and heat resistance under temperature loads.

Recently, more and more vanadium is consumed to produce titanium-based superalloys used in nuclear, space, aviation, mechanical engineering and shipbuilding. Vanadium alloys and compounds with silicon, titanium, and gallium are used for superconducting magnets. Also a large consumer of vanadium is the chemical industry, which uses vanadium (V) oxide for the manufacture of catalysts that work in toxic environments. Small consumers of vanadium are the glass, textile, and ceramic industries, where vanadium oxides are used as persistent chemical pigments; in agriculture, vanadium is used as a fungicide; in photography and cinematography as a developer; in medicine, vanadium compounds are used for the preparation of medicines.

The use of high-strength vanadium steels for oil and gas pipes, including drill, welded and riveted metal structures, is promising. In addition to steel, vanadium additives improve the properties of many non-ferrous and precious metals. Silver-vanadium alloys are used for the production of backup batteries. Bronze and brass with an addition of 0.5% vanadium are used in the manufacture of complex parts.

According to the source, the market is expected to increase consumption of vanadium redox batteries (VRB). A VRB battery is a type of rechargeable flow – through battery that uses vanadium ions in various oxidation states to store chemical energy.

According to research by Acumen Research and Consulting, the vanadium market is expected to grow by 6.6% over the forecast period 2020 - 2026 and the global vanadium market size is expected to reach us $ 56 billion by 2026.

Vanadium products are produced in 20 countries, and more than 75% of the world's production is produced by developed countries.

Over the past decade, China has become the main producer and main consumer of vanadium in the world. In terms of supply rates, China now accounts for about 58% of the global supply market and at least 30% of global vanadium consumption. During the economic crisis (2009), it maintained and expanded its own raw materials industry by reorienting to the domestic market and increasing imports of other metals. Today, China continues to increase its production of vanadium and plays an increasing role in global production.

Vanadium production in the CIS countries is concentrated in Russia (23%).

Titanomagnetite ores of Kazakhstan are not currently processed. The Ust-Kamenogorsk titanium-magnesium combine produces titanium slags from ilmenite ores of the Satpayevsky Deposit with associated extraction of vanadium (V) oxide. However, all the resulting vanadium product is directed by doping titanium, used in aircraft construction.

Thus, we can conclude that there is a demand for vanadium, and if we trust the forecasts, the demand for the metal will increase every year.

The most important source of vanadium is titanomagnetites containing 0.05-0.8% vanadium and phosphorous ironstones containing 0.03-0.1 % vanadium. Titanomagnetites are common in the United States, Canada, Africa, Australia, and post-Soviet countries.

Vanadium is extracted from titanium-magnetites, slags and residues and then converted to (V_2O_5 and V_2O_3). Most vanadium (V) oxide is converted to ferrovanadium or nitrided vanadium to be used for doping. At all stages of the process of obtaining vanadium-containing materials, it is estimated by the content of vanadium (V) oxide in the raw material. The amount of vanadium (V) oxide is usually quoted as the cost of 1 pound of vanadium (V) oxide 98% or the cost of 1% of vanadium in ferrovanadium or other vanadium ligature.

The increased demand for rare and rare earth metals and their use in various industries require the involvement of new raw materials sources in production. Currently, only ordinary, complex-sulfide ores with the extraction of only basic components are in commercial development.

Kazakhstan is one of the countries in the world where the richest ore deposits of vanadium are located. The conjuncture of metal in raw materials sources is as follows: 1 - shale of the Big Karatau 69.4 %; 2 - titanomagnetites 13.0 %; 3 - oil 12.3 %; 4 – bauxite 4.1 %; 5 - ilmenite 1.2 %.

Therefore, the main and massive raw material source of vanadium in Kazakhstan is the black shale ores of the Big Karatau.

In connection with the above assessment of the current state of the scientific problem being solved is timely and relevant.

The basis and initial data for development of themes.

Kazakhstan's leading position in terms of raw material reserves of vanadium, uranium, molybdenum and rare earth elements is generally recognized. Kazakhstan's Competitive advantage in the world market of rare and rare earth elements is that it has its own raw materials and successful experience of its own enterprises.

The black shales of Big Karatau are characterized by a high content of vanadium, uranium, molybdenum and rare earth metals. Large volumes allow us to consider them as industrial sources of vanadium, uranium, molybdenum and rare earth metals.

The developed technology for processing black shale ores will allow the production of vanadium (V) oxide, uranium, molybdenum, rare earth metals and carbon concentrate, which have a steady demand on the market.

The huge resources of black shale and the lack of acceptable technologies for their processing were the basis for the need to perform this research work.

Substantiation of the need for this research work.

The need to perform this research work is due to the fact that today there are no technologies that allow complex, cost-effective and sufficiently complete involvement in the processing of black shale deposits.

Most technological schemes for processing black shale ores: heap leaching, high-temperature roasting, low-temperature sulfatization have reached the limit of their technical and economic capabilities.

Information about the metrological support of the dissertation. The work was performed using a complex of physical and chemical methods of research and analysis: x-ray diffraction, thermal, IR spectroscopy, atomic emission spectrometry; the results of technological research.

Metrological support was used in the course of scientific research:

- Testing analytical center at AO "Leading Research Institute of Chemical Technology", accredited for technical competence in the center of expertise and certification - certificate of accreditation №ROSS RU.0001.511072 (Russian Federation, Moscow);
- Laboratory of physical and analytical methods of RSE «National center for complex processing of mineral raw materials of the Republic of Kazakhstan» accredited for technical competence in the National center for expertise and certification – Certificate №35/16 on the assessment of the state of measurements in the laboratory (issued on 07.07.2016, valid until 07.07.2019).

Relevance and novelty of the dissertation topic.

The total resources of valuable metals in black shale of Big Karatau are estimated according to the data as follows: V_2O_5-3200 thousand tons, U-130 thousand tons, Mo-200 thousand tons, REM-630 thousand tons.

Currently, Karatau black shale ores are not processed due to the lack of technology that allows them to be integrated, cost-effective and fully involved in processing.

The involvement of this raw material in production will allow to meet the domestic needs of the country in vanadium and other components. Therefore, the problem of developing a technology that makes it possible to comprehensively, cost-effectively and with sufficient completeness involve black shale deposits in processing is relevant.

The introduction and replication of such technology within the national borders will allow to involve unique deposits in industrial development - Balasauskandyk, Kurumsak, Zhebagly and avoid the constant search for concentrates abroad. Industrial implementation of the technology will contribute to the organization of a new sub-sector, namely, metallurgy of rare and rare earth metals.

The novelty of the topic is the development of a complex technology for processing black shale with the extraction of vanadium, uranium, molybdenum and rare earth metals, by opening the ore using an atmospheric autoclave method.

Scientific novelty of the results obtained:

- it is shown for the first time that in addition to the known anthraxolite and carbonate carbon in the structure of black shales, there is a third phase of carbon in the form of heterogeneously-catalytically embedded CO_2;
- for the first time, an atmospheric autoclave method for opening black shale ore was developed, which includes atmospheric leaching followed by autoclave leaching without adding oxidants and converting vanadium, uranium, molybdenum and rare earth metals into a solution;
- it is shown for the first time that high recovery of vanadium-94%, uranium-98%, molybdenum-85%, and rare-earth metals-80% was obtained during sulfuric acid autoclave leaching of black shale ores without the use of oxidants under optimal technological conditions: sulfuric acid concentration-140-150 g/dm^3; process temperature-150 °C; autoclave pressure-1.0-1.1 MPa; leaching duration-2 hours; S:L ratio = 1- 0.8;
- for the first time, proposed plausible mechanisms of oxidation of compounds of vanadium in lower oxidation States, confirmed by thermodynamic studies indicating that at temperatures of 140-160 ° C and a pressure of 1,0-1,1 MPa in the environment of H_2SO_4 observed oxidation couples V^{2+}/V^{3+} to V^{3+}/V^{4+} in the first, oxidation of vanadium occurs under the influence of the atomic oxygen formed upon the decomposition of sulphuric anhydride; according to the second, the technical result is achieved both by obtaining a part of the active reagents-iron (+III), vanadium (+IV), and sulfuric acid during the destruction of sulfide minerals that are part of the initial ore, while the decisive role of hydrated forms of iron (+III) as oxidants is noted.

The purpose of the research is to develop a complex technology for processing black shale ores from the Balasauskandyk deposit to produce vanadium (V) oxide, -REM,- uranium, - molybdenum-containing industrial products and carbon concentrate.

The object of research is the black shale ores of Big Karatau, the Balasauskandyk Deposit.

The subject of research is the structural structure of black shales, physical and chemical studies of phase transformations during atmospheric autoclave leaching and sorption separation of vanadium from uranium, molybdenum and rare earth metals, and impurities.

Research objectives, their place in the performance of research work in general:

- to study the structural component of black shale ore;

- research and develop atmospheric autoclave technology for sulfuric acid leaching of vanadium, uranium, molybdenum, and REM from black shale ores without adding an oxidizer;
- scientific substantiation of the mechanism of autoclave opening of black shale ores;
- develop a technology for efficient sorption separation of vanadium from uranium, molybdenum, rare earth metals and other impurities;
- propose a technological scheme for complex processing of black shale ores to produce vanadium (V) oxide, -REM, - uranium, -molybdenum-containing industrial products and carbon concentrate;
- perform an economic assessment of the developed technology for complex processing of black shale ores.

The tasks presented above and solved in this dissertation work are logically related to each other and are directed at achieving the set research goal.

Methodological base. The main methods of research and analysis used in the performance of the dissertation work include:
- x-ray diffractometric analysis of the initial sample and the obtained products on an automated DRON-3 diffractometer;
- x-ray spectral microanalysis on an electron probe microanalyzer of the Superprobe 733 brand of the Japanese company Joel;
- thermal analysis on the Q-1500D derivatograph;
- chemical analysis of samples using an atomic emission spectrometer (VARIANAA 240SS) and the author personally using standard methods;
- IR spectroscopic analysis on a two-beam infrared spectrophotometer UR-20 in the region of 400-3600 cm^{-1},
- microscopic studies on the Inca Energy energy dispersion spectrometer of the English company «Oxford Instruments»;
- calculation of thermodynamic characteristics of reactions performed using the Outokumpu HSC Chemistry thermodynamic calculation program version 5:1.

The following standard laboratory equipment was used:
- laboratory autoclave of the company Part instrument (USA);
- thermostat (water);
- a mechanical stirrer with adjustable number of revolutions;
- vacuum pump;
- drying cabinet;
- the reactor volume of 2 dm^3;
- contact thermometer up to 100 ^0C;
- fridge;
- rotameter;
- the control of air flow.

All measurement and research results were obtained using instruments and measuring instruments that have passed state metrological verification.

Provisions for protection:
- research results on the structural structure of the original black shales, which allowed us to establish the presence of heterogeneously-catalytically embedded CO_2;

- the developed atmospheric-autoclave method for opening black shale ore without the supply of an oxidizer, which allowed to achieve a high degree of extraction of vanadium, uranium, molybdenum and rare earth metals into the solution;

- mechanism of oxidation of lower vanadium oxides, allowing 140-160 ºC and a pressure of 1,0-1,1 MPa in the H_2SO_4 medium mechanism of oxidation of the pair V^{2+}/V^{3+} to V^{3+}/V^{4+};

- results of research on sorption separation technology that allowed efficient separation of vanadium from related metals to produce uranium-molybdenum-containing industrial products and REM concentrate;

- technological scheme of the developed technology for processing black-shale ores of Balasauskandyk, which provides complex processing of black-shale ores to produce vanadium (V) oxide, -REM, - uranium, -molybdenum-containing industrial products and carbon concentrate with a high degree of purity.

- technical and economic assessment of the developed technology for complex processing of black shale ores with a calculated payback period.

Practical significance of the results. On the basis of the findings of the structural components of black shale ores, atmospheric-pressure oxidation, mechanism of oxidation of the compounds of vanadium in lower oxidation by atomic oxygen, studies on the sorption separation of vanadium from uranium, molybdenum, rare earth metals - developed a complex technology of processing of black shale ore deposit Balasubranyam receiving of vanadium oxide (V), -REE, - uranium-molybdenum middlings and concentrate carbon.

The technology has passed the stage of integrated laboratory tests at JSC "VNIIHT», which confirmed the possibility of extracting vanadium, uranium, molybdenum and rare earth metals with a high degree of recovery.

Testing the work. The main provisions of the dissertation work are reported:

- at the international scientific and practical conference « Mining Sciences in the industrial and innovative development of the country», Almaty, 2015;

- at the international conference «Scientific and technical support of mining production», Almaty, 2016.

12 publications were published on the topic of the dissertation, including:

- 3 articles in the journals Metallurgist (Web of Science database if (2017) -0.144 (36% - percentile) and Research journal of Pharmaceutical,Biological and Chemical Sciences (Scopus SJR database 0.19);

- 4 articles in journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan.;

- 1 report in the materials of international conferences abroad;

- 4 reports in the materials of international conferences in Kazakhstan.

Structure and scope of the dissertation. The dissertation consists of an introduction, 6 chapters, conclusion, and 1 appendix. The work is presented on 116 pages of typewritten text, contains 45 tables and 34 figures. The list of sources used includes 100 items.