METHODS OF EXTRACTING WOLFRAM FROM TECHNOLOGICAL WASTE OF WOLFRAM CONTAINING ORES

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Annotasia: Extracting tungsten from technogenic waste (lying tailings of processing plants and waste cakes), processing concentrates and extracting useful components from them with subsequent use as secondary raw materials is one of the urgent tasks in the field of deep and complex processing of mineral raw materials. This task has several priorities. Firstly, the metal extracted from secondary raw materials is significantly cheaper than the metal extracted from ore due to a number of technological conversions in processing. Secondly, after removing metals from waste, the latter can be usefully utilized into finished products, creating a waste-free technology.

Keywords: Technogenic waste, waste-free technology, electrostatic separation, mineral raw materials, finely dispersed minerals, scheelite, wolframite, industrial product.

Аннотация: Технологическая переработка вольфрама из техногенных отходов (лежалых хвостов обогатительных фабрик и шламовых отходов), переработка концентратов и извлечение из них ценных компонентов с последующим использованием в качестве вторичного сырья является одной из

актуальных задач в области глубокой и комплексной переработки минерального сырья. Данная задача имеет ряд приоритетных аспектов. Во-первых, металл, извлечённый из вторичного сырья, значительно дешевле металла, получаемого из руды, что обусловлено сокращением числа технологических переделов при переработке. Во-вторых, после извлечения металлов отходы могут быть эффективно использованы для получения готовой продукции, что способствует формированию безотходных технологий.

Ключевые слова: Техногенные отходы, безотходная технология, электростатическая сепарация, минеральное сырьё, тонкодисперсные минералы, шеелит, вольфрамит, промышленная продукция.

Annotatsiya: Texnogen chiqindilardan (boyitish fabrikalarining yotgan dumlari va shlam chiqindilari) volframni ajratib olish, konsentratlarni qayta ishlash va ulardan foydali komponentlarni chiqarib olib, keyinchalik ikkilamchi xomashyo sifatida foydalanish mineral xomashyoni chuqur va kompleks qayta ishlash sohasidagi dolzarb vazifalardan biridir. Ushbu vazifa bir qator ustuvor jihatlarga ega. Birinchidan, ikkilamchi xomashyodan olinadigan metall rudadan olinadigan metallga nisbatan ancha arzon bo‘lib, bu qayta ishlash jarayonida texnologik bosqichlar sonining qisqarishi bilan izohlanadi. Ikkinchidan, metallar ajratib olingandan so‘ng qolgan chiqindilarni tayyor mahsulotlarga samarali yo‘naltirish mumkin bo‘lib, bu chiqindisiz texnologiyalarni shakllantirishga xizmat qiladi.

Kalit so‘zlar: Texnogen chiqindilar, chiqindisiz texnologiya, elektrostatik separatsiya, mineral xomashyo, mayda dispersli minerallar, sheelit, volframit, sanoat mahsuloti.

An important problem in creating a waste-free technology is its organizational and technical principles, where the development of processing methods and equipment selection, the structure of departments, and economic efficiency play an important role. In this regard, there is a positive experience of a number of mining and processing enterprises, both in foreign countries and CIS countries.

Modern mineral extraction technology usually represents a complex of physical and chemical processes. The completeness of subsoil use is largely determined by the first stage of mineral raw material processing - enrichment. Currently, in world practice, modern technologies for enrichment are successfully used, based on the use of even slight differences in the physical, physicochemical, and chemical properties of minerals.[1]

Traditionally, various methods are used in the beneficiation of tungsten ores: gravitational beneficiation, flotation, magnetic and electrostatic separation, and chemical beneficiation methods. The gravitational method ensures satisfactory extraction of tungsten from wolframite ores and remains the main method for their enrichment in world practice to this day. When enriching scheelite ores using the gravity method, the extraction of tungsten does not exceed 70% due to the sheelite's tendency to overmelt, which leads to the formation of fine slimes and significant tungsten losses in the tailings.

Currently, the main method for enriching scheelite ores, especially fine-grained and low-grade ones, is flotation. In this case, soda, liquid glass, tannin serve as medium regulators and depressants, oleic acid, sodium oleate, and liquid soap as collectors; pine oil, terpineol, technical cresol, and other reagents serve as foaming agents. Flotation is carried out in an alkaline environment at a pH of 9-10. Adding copper and iron sulfate salts to liquid glass contributes to the depression of calcite, fluorite, and apatite. Sometimes, a combined method for enriching scheelite ores is used, combining flotation and gravitational enrichment with chemical treatment. However, in practice, the extraction of tungsten into standard concentrates does not exceed 72%, a significant amount is lost with tailings. The tailings of processing plants are stored in special warehouses and are technogenic production waste. For example, 12 million tons of enrichment tailings containing 0.066% tungsten trioxide have accumulated in the TMO warehouse of the Ingichka Production Association.[2]

In industry, several methods of processing tungsten concentrates are used. The choice of one or another method depends on the type of raw material (tungsten or scheelite concentrate), production scale, and technical requirements for the purity of tungsten trioxide. In each technological scheme for processing tungsten concentrates, the following stages can be distinguished: decomposition of the concentrate; obtaining technical tungsten acid; purification of the technical acid from impurities and obtaining the necessary commercial product. Production schemes for processing tungsten concentrates are divided into two groups depending on the adopted opening method: sintering or alloying with soda and acid decomposition. In all cases where alkaline reagents are used for decomposition, aqueous solutions of sodium tungstate are obtained, from which volframic acid or other tungsten compounds are subsequently precipitated.

In world practice, one of the main sources for obtaining tungsten is scheelite concentrates. To extract tungsten from them, they mainly use the autogenous soda leaching method developed by Soviet scientists led by Professor I.N. Maslenitsky. The advantage of this method is that it can be used for processing high-grade concentrates, as well as intermediate products and waste from enrichment. The extraction of tungsten from scheelite during autoclave-soda leaching is about 98%, with a portion remaining in the solid residue.[3]

The geological and ecological study of tailings ponds encompasses a wide range of issues related to geology, design and construction, economics, and the technology of their formation. The common solution is to describe and model the processes of formation and interaction of tailings ponds (their constituent elements) with the environment in order to find optimal engineering solutions that have minimal impact on the ecosystem. The choice of such decisions is important both in the regulatory and environmental aspects.

Technological waste from ore beneficiation poses an increased ecological hazard due to its negative impact on the air basin, surface and groundwater, and soil cover across vast territories. However, using them as additional sources of ore-mineral raw materials will significantly reduce the scale of disruption of the geological environment in the region.

Similarly, the storage of ore beneficiation waste and the formation of tailings storage facilities for TMO processing have a negative impact on the environment in several areas: violation and withdrawal of land from economic use; pollution of water sources and disruption of the water balance in the areas where they are created; pollution of the atmosphere and adjacent tailings storage areas with dust particles.

Continuous improvement of mineral raw material processing technology, application of more progressive methods and techniques, and selection of optimal technological schemes allow for the economically justified isolation of profitable waste from previously unpromising waste for processing. In addition, technogenic waste occupies vast areas of land, including well-cultivated arable land, urban areas, and irrigated pastures, altering the natural landscape and forming unique relief forms.

Existing methods for extracting tungsten from technogenic waste from the beneficiation of tungsten-containing ores into the scheme usually include the following:

-separation into large and small fractions;

-screw separation followed by obtaining a fine fraction of the tungsten-containing intermediate product;

-release of sulfide-containing material and secondary waste.

In a screw separator, the obtained tungsten-containing intermediate product is purified to obtain a crude tungsten-containing concentrate. On concentrating tables, the tungsten-containing concentrate is separated to obtain a tungsten concentrate, which is then subjected to flotation to obtain a high-grade conditional tungsten concentrate and a sulfide-containing product. Further, to obtain secondary waste and a tungsten-containing intermediate product, the tailings of the screw separator and concentrating table are combined and subjected to classification of tungsten-containing ore beneficiation tailings, and the condensed product is subjected to beneficiation in a screw separator.

Further extraction of tungsten from the residual waste is carried out as follows. Gravitational enrichment tails are first finely ground and then degreased in a classifier, and the resulting materials are separated in hydraulic classifiers. After classification, the resulting classes are enriched separately on concentration tables. Then, the coarse-grained tailings are returned to the grinding cycle, and the fine-grained tailings are thickened and re-enriched on concentrating tables to obtain the finished concentrate. After this, the intermediate product, which enters the final grinding stage, and the tailings are sent for flotation. The concentrate of the main flotation is subjected to single purification. The initial material contains from 0.3 to 0.5% WO_3; the extraction of tungsten reaches up to 96%, with about 72% of tungsten extracted by flotation. At the same time, the tungsten content in the flotation concentrate does not exceed 10-12% WO_3.

This technological scheme of gravity enrichment for processing technogenic waste has several disadvantages - high load at the initial stage of the process on the enrichment operation on concentration tables, multi-operation nature, and low quality of the resulting concentrate.

For the processing of tungsten-containing slags, their flotation is used, in particular, tungstate in the PRC and at the Canadian "Mount Plysad" factory, and at some "Yokberg" (Sweden) and "Mittersil" (Austria) factories, flotation has been completely replaced by gravitational enrichment. However, this technology has not found widespread application in global practice.[4,5]

Screw separators are widely used in practice to enrich tungsten-containing ores, waste, and sludge.

At the Canadian "Clymax Molybdenum" factory, by extracting molybdenum from molybdenite flotation tailings, volfram concentrate is also obtained along the way. Tungsten-containing tailings are divided into two parts - dump slags and cassiterite concentrate using screw separation. The sludge discharge is directed to the dump tailings, and the fraction in the form of sand is directed for the flotation separation of pyrite concentrate containing 55% sulfides (S) and its subsequent discharge into the dump tailings. Using screw separation and cones, the chamber product is cleaned to obtain pyrite-containing tailings and wolframite-cassiterite concentrate, and then they are processed on concentrating tables. As a result, wolframite-cassiterite concentrate and tailings are obtained. The raw concentrate, after dehydration, is sent for purification. After magnetic separation and flotation of phosphates (the flotation removal of monazite from it) to remove iron, the concentrate is dried. The resulting dry concentrate is classified and, after the first stage, separated using stepwise magnetic separation into concentrate with a WO_3 content of 65% and after the second stage, concentrate with a WO_3 68%. In addition, a tin (cassiterite) concentrate containing 35% tin is obtained, which is a non-magnetic product.[4]

The disadvantages of this method are the complexity and multistage nature of this method, as well as its high energy intensity.

A method for processing scheelite-containing tailings using an improved separation process to remove harmful materials and process ore minerals is also known. The method includes, for the purpose of removing various foreign materials, the stages of homogenizing mixing of scheelite-containing waste, introducing pulp into the reactor, and "filtering" the pulp. In addition, subsequent separation of the pulp by screw separation, condensation, and dehydration of non-metallic minerals to obtain a cake occur. After this, the cake is dried and the dry cake is crushed using a hammer crusher operating in a closed-loop sieve, the crushed minerals are separated using a "micron" separator into fine and coarse grain fractions (granules), and the coarse-grained fraction is magnetically separated to obtain magnetic minerals and a non-magnetic fraction containing scheelite. The multi-operation nature and the use of energy-intensive wet cake drying are the main disadvantages of this method.

A method of additional extraction of tungsten has been applied to the tailings of the Ingichka mine.

The method consists of the following operations:

- pulp preparation and its subsequent deslamation in a hydrocyclone, i.e., removal of the class - 0.052 mm;

- separation of the sludge-free pulp in a cone separator;

- two-stage purification of the cone separator concentrate to obtain a concentrate containing 20.6% $_{WO3,}$ with an average extraction of 29.06% $_{WO3}$ on concentrating tables.

The main disadvantages of this method are the low quality of the resulting concentrate and the low extraction of WO_3.

The technology for extracting tungsten from old stale tailings includes the following operations:

- operation for obtaining crude tungsten concentrate,

- the operation of obtaining the intermediate product,

- operation for obtaining gold-bearing products and secondary waste.

These operations are carried out using gravitational wet enrichment methods and subsequent refinement of the obtained crude concentrate and intermediate product using gravitational (centrifugal) enrichment and magnetic separation to obtain a conditional tungsten concentrate containing 63% $_{WO3,}$ with 50% $_{WO3}$ extraction.[5]

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