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A review of recovery technologies of rare and rare earth metals from wastes generated in titanium and magnesium production

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ABSTRACT
It is acknowledged that titanium and magnesium production wastes pollute the environment, which in the sequence they create an environmental hazard for soils, groundwater and vegetation. Meanwhile, these wastes can be considered secondary resources of rare and rare earth metals. In recent years, the processing of industrial waste has been a new trend for the extraction of rare and rare earth metals, which can partially cover the demand in case of their disposal. This article is devoted to a review of the available literature and articles on the extraction of rare metals from titanium-magnesium production waste using various processing methods. Methods of their utilization are discussed with an emphasis on the extraction of rare and rare earth metals. This review considered waste processing technologies of various pyrometallurgical and hydrometallurgical processes. Technological schemes of various leaching and extraction processes were presented to give a holistic view of waste processing and extraction of rare metals contained in them. In general, the article contains an overview of the works published on the extraction of rare metals, such as REE (rare earth elements), niobium, tantalum and vanadium.

Keywords: titanium wastes, rare metals, niobium, vanadium, scandium, rare earth elements, leaching, chlorination

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Introduction

Rapid industrialization has influenced the demand for rare metals, in particular titanium and titanium-bearing materials. Titanium is used for different branches of the car industry, aerospace, doping, petroleum engineering, and chemical processing. However, during the recovery of titanium-bearing raw materials, there are massive amounts of waste generated. These wastes are sent to special landfills or sludge storage facilities and they pose a significant danger to the environment, polluting soils and natural waters. Because they are released into the atmosphere and acidic industrial wastewater is discharged into water streams. It is widely known that for the recovery of titanium, the Kroll process is commonly used. As a result, various residues, especially such as titanium chloride residues, electrolytes, sludge, and gases, residues are formed consisting of chlorides, and oxychlorides of rare metals [1].

The complex recovery of waste in titanium production has long been considered one of the most pressing issues. The waste contains various valuable components and rare metals. Considering that reserves of rare metals are concentrated in the surface layer of waste, in turn, it affects the fall in the cost of production of rare metals. Niobium, tantalum and scandium oxides with a total content of 0.6-1.5% are found in titanium production waste [2].

It is acknowledged that the Kroll method based on magnesium thermal reduction is used for processing titanium concentrates. Therefore, a large amount of waste is formed. For the process of producing 1 ton of titanium, about 2 tons of chloride waste are formed. In this regard, there is a need to neutralize chloride residues [3]. Various chloride wastes (used electrolytes, melts, sludge) are thrown into waste landfills and are harmful to the environment because they are not used as raw materials. In the production of titanium tetrachloride, titanium-containing slag is used, which contains a significant amount of rare metals-Nb, Ta, Sc, V, Zr, etc. In addition, in large quantities, the additives Fe, K, Na, Ca, Na, and Mg are irretrievably lost. During chlorination, most of these impurities are converted into chlorides and oxychlorides, and due to their physicochemical properties, they are concentrated in individual semi-products and production waste. This leads to high chlorine consumption, additional costs and environmental pollution [[4], [5]].

Sludge and waste are stored in special warehouses and landfills at titanium-magnesium plants. In turn, waste storage is an expensive service, as well as in the event of an increase in the norms of the maximum permissible concentration (MPC) in accumulated waste and the enterprise will face fines and sanctions. [6].

The purpose and objective of the review are to highlight existing technologies for processing wastes that are generated in titanium and magnesium production, as well as the survey of methods of recovery rare and rare earth metals from them.

Recovery of Nb and Ta from titanium wastes. Niobium (Nb) and tantalum (Ta) are rare metals and the qualities of both metals make them critical raw materials. In nature, tantalum and niobium are most often found together. In deposits, as in the earth's crust, the concentration of Nb is usually an order of magnitude higher than Ta. It is worth noting that niobium itself has a high affinity for titanium which in turn it affects the formation of a wide range of niobium minerals with titanium. In addition to this, these two mineral groups (titanoniobates and tantaloniobates) are regarded as economically viable options for niobium recovery. Owing to this fact, titanium raw materials and waste, by-products are considered one of the sources of niobium production [7].

The chemical composition of spent titanium chlorinator melts is presented in Table 1 [8].

According to Table 1, the content of niobium in spent melt of titanium chlorinators (SMTC) is on average 0.025-0.030%, which is a good indicator, given that rare metals are concentrated in a scattered form. Another important feature of niobium is its large smear on titanium and its ability to heterovalent isomorphism. This affects the formation of niobium impurities and the formation of niobium compounds in titanium minerals. This means that the higher the concentration of titanium in raw materials and waste, the higher the niobium impurities [[9], [10]]. The importance of niobium and tantalum lies in their internal properties such as corrosion resistance, conductivity, high electrical capacity and biocompatibility. Both metals have similar chemical and physical properties, which makes them easier to separate and clean. However, their content in the Earth's crust is very low, Nb-0.002%, Ta-0.0002% [11]. Such limited availability requires the processing of secondary raw materials containing Ta and Nb, including titanium-magnesium waste, as well as metal waste and intermediates.

Recovery of pure titanium is a complex and technically difficult process; as crude titanium ore can not be recovered directly from its natural form. Therefore, raw titanium ore is processed by the Kroll method. As a result, titanium tetrachloride is formed, which in turn is used for obtaining titanium dioxide (TiO_2) pigment and titanium sponge. The titanium tetrachloride ($TiCl_4$) contains substantial amounts of niobium, tantalum and scandium due to accompanying elements in titanium ore [12]. These rare metals can not be recovered by traditional methods because the slurry contains $TiCl_4$.

Xiang et al. [13] developed a process flow sheet (figure 1) for recovering niobium concentrate from

$TiCl_4$ slurry residue by evaporation and acid leaching (HCl). According to their research, titanium tetrachloride ($TiCl_4$), niobium concentrate and solution of aluminium chloride ($AlCl_3$) were recovered separately. The authors first evaporated the slurry at 200°C for 60 minutes. As a result, around 98% of titanium was recovered from the slurry. Then, they leached the residue with HCl (concentration -2.1 mol/l, L/S ratio of 6:1, T-80°C, t-60 minutes) and washed it with an ammonia solution (2 mol/l, L/S ratio of 4:1 ml/g, t-30 minutes, at room temperature). Their results after filtration indicated that Nb concentrate content with Nb-53,40% and Ta-5,57% was obtained.

In other studies, the authors investigated the recovery of niobium from chloride residues generated from the chlorination of titanium slags [[14], [15]]. In order to recover two-stage leaching process was suggested. The technological scheme of two-stage leaching is shown in Figure 2 [15]. For the first stage of leaching, water is used, whereas 4.0 M of HCl (Hydrochloric acid) is used in the second stage. The leaching process was carried out at 25°C, with an S:L ratio of 1:4 and a mixing speed of 400 rpm. Cation exchange sorbents such as Purolite-C104 and KU-2-8H were used for the sorption of niobium from the leaching process solution. After the leaching process with water, the pulp was sent to the filtration process to separate the pregnant leach solution and the niobium-rich cake. Then, the leaching solution was sent to the processes of obtaining scandium and carnallite. When using Purolite-C104 ion exchange resin, the sorption efficiency of niobium from solution with the concentration of 2 g/l was around 71.0 % (0.071 g/g) in 3.5 hours. Meanwhile, in terms of KU-2-8 H ion exchange resin, this indicator was about 89.0 % (0.089 g/g).

Table 1 - Chemical composition of spent titanium chlorinator melt [8].

Composition	Content, %	Composition	Content, %	Composition	Content, %
TiO_2	1-2	$MgCl_2$	6-12	$MgCl_2$	4.5-5,0
SiO_2	4-7	$CaCl_2$	3-4,5	Cr_{total}	0.8-1.55
C	3-6	$FeCl_2$	10-12	Nb_2O_5	0.025-0.030
Sc_2O_3	0.01-0.03	$FeCl_3$	1-3	Ta_2O_5	0.005-0.006
$AlCl_3$	5-6	KCl	22-47	Cl^-	45-50
V_2O_5	0.01-0.45	NaCl	14-18		

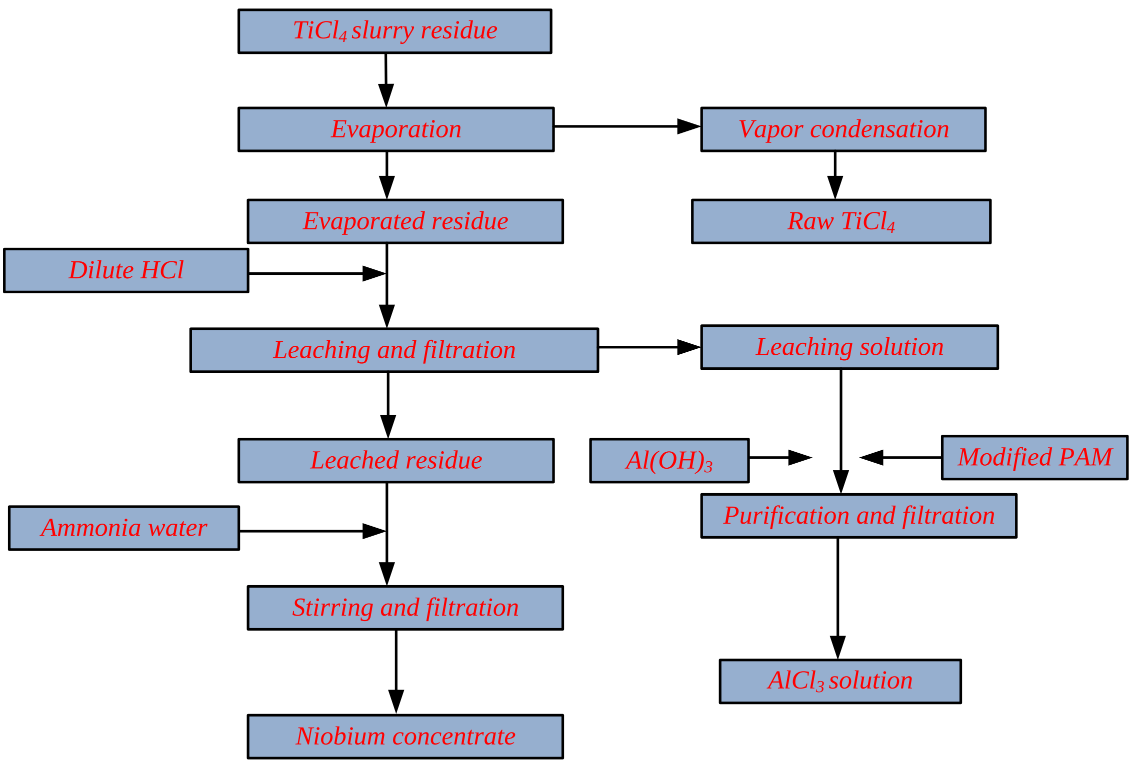

Figure 1 - Technological flow sheet of metal recovery from $TiCl_4$ slurry residue [13].

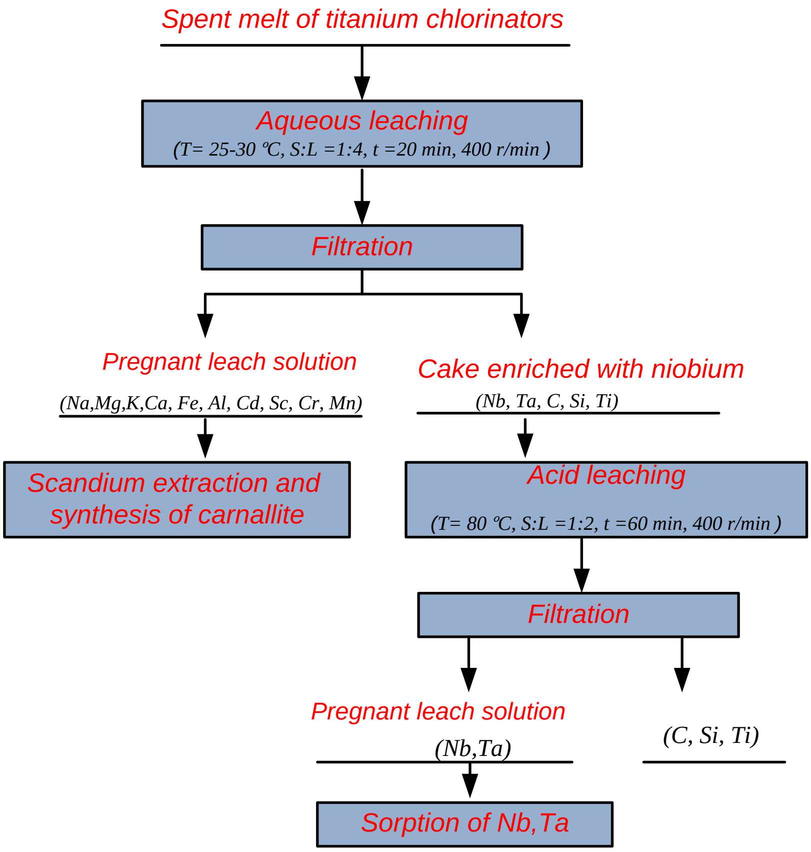

Figure 2 - Flow sheet of the two-stage leaching process [15].

Recovery of V from titanium wastes. Ilmenite ore commonly contains titanium, iron, and vanadium. Most of the vanadium passes into titanium slag, during the reduction melting of ilmenite concentrate. Throughout, the chlorination of titanium slag, about 70% of vanadium is concentrated in technical $TiCl_4$ mainly in the form of $VOCl_3$ and partially VCl_4. The presence of vanadium in titanium sponge significantly deteriorates the quality of titanium [[16], [17]].

Purification of titanium tetrachloride from impurities is a key stage in the production of titanium sponges. Because $TiCl_4$ contains a significant amount of impurities in the dissolved state and in the form of a fine mechanical suspension. For example, $SiCl_4$, $VOCl_3$, VCl_4, CCl_4, $SOCl_2$ and other chloride solutions are mixed with $TiCl_4$ in all ratios. As a result, it leads to the form of a continuous series of solutions that is a hindrance to further processing Titanium tetrachloride is purified from impurities in various ways, such as sedimentation, filtration, rectification, and distillation [18].

These wastes as a form of pulp represent a mixture of $TiCl_4$, $TiCl_3$, and $AlCl_3$. When mixing pulps of lower chlorides with titanium tetrachloride titanium trichloride interacts with vanadium oxytrichloride and converts it into an insoluble form of $VOCl_2$. The precipitate containing $VOCl_2$ is sent to the extraction of vanadium [[19], [20]].

Sidorenko et al. proposed (figure 3) [21] vanadium recovery by the method of liming aluminium vanadium cake with further processing of lime cake. The authors suggested washing lime cake with water. After that, the compounds of vanadium, aluminium and titanium passed into the dechlorinated cake and the chloride ions and the main part of calcium into the solution. The dechlorinated cake is easier to treat during oxidative roasting without adding special additives. The optimal temperature for roasting was between 700-750°C. After roasting, the cinder was leached by soda between 70-80°C. Hence, vanadium pentoxide is converted into the soluble form of $NaVO_3$. Whereas, insoluble compounds formed the cake that contained aluminium and titanium.

The concentration of the soda solution fluctuated in the range of 33-100 g/dm^3, and the leaching time was between 1-4 hours. According to the authors, evidence leaching proceeded better in denser pulps. The highest degree of vanadium extraction was observed at a solution concentration

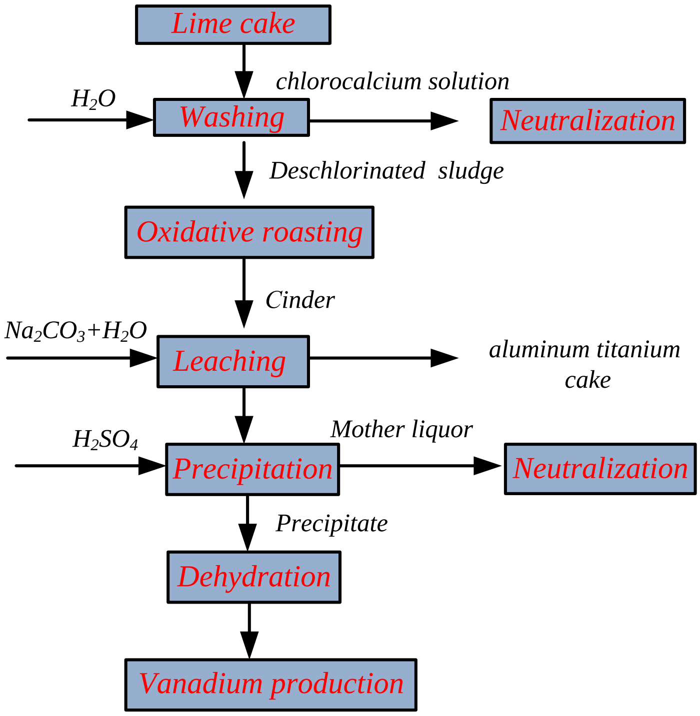

Figure 3 - Technological flow sheet for recovery vanadium from lime cake [21].

of 50 g/dm^3. An increase in the leaching time at this concentration led to an increase in the degree of extraction of vanadium from 90 to 96.5%.

Recovery of REEs from titanium wastes. Rare earth elements (REEs) are a group of 17 elements, including scandium (Sc), yttrium (Y) and 15 lanthanides [22]. REEs are almost not mined from primary ore deposits, because of their economic feasibility and effectiveness. Owing to this, the urgent demand has prompted many organizations to evaluate alternative sources of REE [[23], [24]].

As elucidated above, Sc is a less abundant element and it is a related group of REE. According to the latest works, scandium recovery from secondary sources has been accelerated from different by-products (tailings, waste acids, and solid residues, residue streams) in the production of other metals including REE, titanium, aluminium, iron ore, and uranium [[25], [26], [27], [28], [29], [30]].

Scandium is the solid residue generated in Titanium dioxide (TiO_2) production [31]. Titanium-bearing ores contain high content of scandium and are the most important resource for their extraction [[32], [33]]. For instance, in China, the ilmenite ores on average contain 0.002-0.004 Scandium oxide (Sc_2O_3) [34]. Scandium resources are accessible in the form of liquid wastes of TiO_2 pigment production, and industrial production volume is estimated to be 8.4 million tons around the world [35].

One of the resources of scandium is hydrolyzed sulfuric acid, which is generated in the production of titanium dioxide [[36], [37]]. The authors studied the separation and recovery of Sc and Ti from the hydrolyzed sulfuric acid waste of titanium dioxide [32] by using the solvent extraction method. This method is based on using a mixed solution of Na_3PO_4 and H_2O_2 to selectively scrub titanium over scandium from the loaded organic solution bearing scandium and titanium. Then, NaOH solution (4 mol/l) is added to strip scandium from the scrubbed solution. Authors, scandium stripping was 93% and after elaboration results, the final product of scandium was 83,9%.

E. Mikeli et al. studied [38] the absorption process of scandium by ion-exchange resins from acidic iron chloride solution ($FeCl_2$) that generated th titanium industry. The authors used two types of exchange resins VP OC 1026 and TP 260 respectively. Among them, VP OC 1026 was more suitable for Scandium extraction and column capacity was 1.46 mg/ml in the experimental conditions. This study also demonstrated the presence of Zr, V, and Ti in the initial solution as they coextracted both resins tests. These metals have more capacity values in the loaded resins,

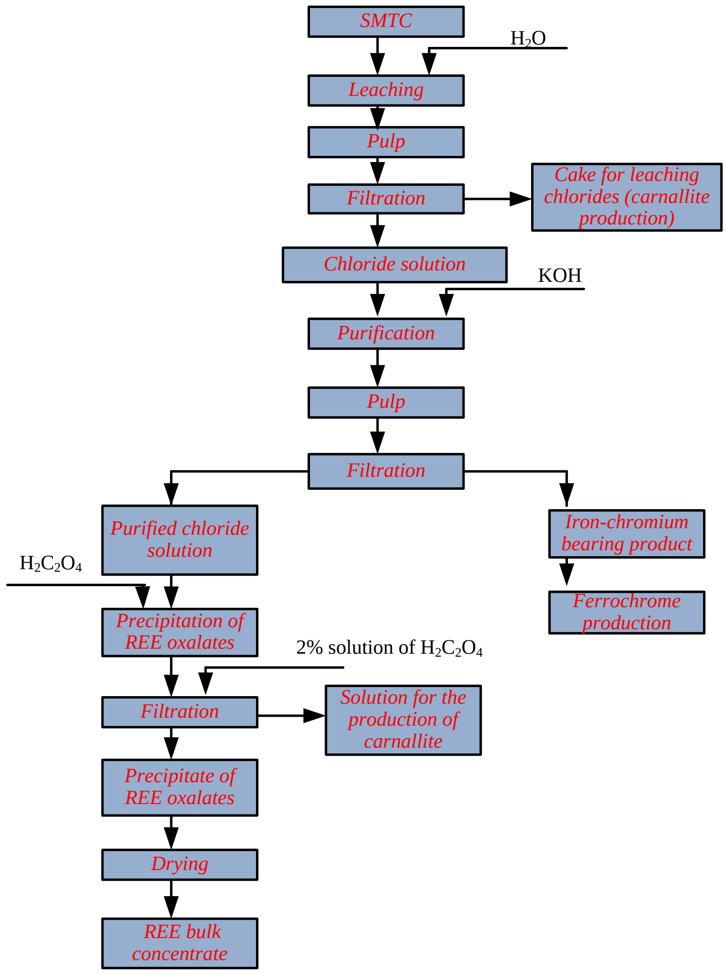

Figure 4 - Technological flow sheet of recovery concentrate of REE from spent melt of titanium chlorinators (SMTC) [40].

however, particularly in VP OC 1026, an improvement in Sc concentration was better than the other metals. It demonstrated that VP OC 1026 resin showed a higher affinity for Sc.

From the commercial perspective, the composition of the rare earth elements in the spent melt of titanium chlorinators (SMTC) is attractive, as the proportion of dysprosium is 57%, neodymium 8%, and cerium is 13% [[39], [40]]. The authors of this work [41] studied the recovery of REE concentrate from SMTC. Thus, the authors proposed technological flow sheet recovery of REE concentrate from SMTC (figure 4). The results of chemical analysis showed that the content of REE oxalates was 96.0%, while the overall content of the main impurities such as barium and iron oxalates accounted for 3.1%. The recovery of rare-earth elements from REE from SMTC into the bulk concentrate reached 66% [42].

Conclusion

Rare metals are widely used in many strategic industry objects. Rare metals are generally found in ores of other metals as concomitant elements and recovered from their slurries and residues. Different metallurgical processes of niobium, vanadium and REEs recovery from titanium and magnesium production, such as spent titanium chloride wastes, titanium dioxide wastes, tailings, and residues are reviewed. Specifically, niobium and tantalum are mainly concentrated in the spent melt of titanium chlorinators (SMTC), sludge, whereas, scandium also is concentrated in SMTC. When it comes to vanadium, it is mainly concentrated in aluminium vanadium cake. Considering, the rare metals and rare earth elements distribution and content, titanium industry residues might be prospective rare metal resources. According to the literature survey, hydrometallurgical methods such as ion exchange, solvent extraction, and leaching are now applicable for the recovery of rare metals from wastes, slurries, and residues, but most of them have not found their method for effective application in the industry. In summary, despite the aforementioned challenges requiring further research, the recovery of rare metals from titanium waste continues to show significant prospects for the foreseeable future.

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Титан және магний өндірісінің қалдықтарын қайта өңдеу арқылы сирек және сирек жер металдарын алу технологияларына шолу

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ТҮЙІНДЕМЕ
Титан және магний өндірісінің қалдықтары қоршаған ортаны ластап, экологиялық қауіп тудыратыны белгілі. Бұның салдарынан, топырақ, жер асты сулары мен өсімдіктер зардап шегеді. Сонымен қатар, бұл қалдықтарды сирек кездесетін және сирек жер элементтерінің (СЖЭ) қайталама ресурстары ретінде қарастыруға болады. Соңғы жылдары техногендік өнеркәсіптік қалдықтарды қайта өңдеу сирек кездесетін және сирек жер элементтерін (СЖЭ) алудың жаңа тенденциясы болып табылады. Бұл мақала әртүрлі өңдеу әдістерін қолдана отырып, титан және магний өндірісінің қалдықтарынан сирек металдарды алу туралы әдебиеттер мен мақалаларға шолу жасауға арналған. Мақалада сирек және сирек кездесетін элементтерді (СЖЭ) алуға баса назар аудара отырып, оларды кәдеге жарату жолдары талқыланады. Жоғарыда келтірілген қайта өңдеу технологиялары әртүрлі пирометаллургиялық және гидрометаллургиялық процестерді қамтиды. Қалдықтарды қайта өңдеу және құрамындағы сирек металдарды алу туралы тұтас түсінік беру үшін әртүрлі шаймалау, сорбция және экстракция процестерінің технологиялық сызбалары ұсынылды. Тұтастай алғанда, мақалада СЖЭ, ниобий, тантал және ванадий сияқты сирек металдарды алу жұмыстарына шолу көрсетілген.

Түйін сөздер: титан қалдықтары, сирек металдар, ниобий, ванадий, сирек жер металдар, шаймалау, хлорлау

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Обзор по технологиям переработки отходов титаномагниевого производства и извлечению редких и редкоземельных металлов

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АННОТАЦИЯ
Известно, что отходы титаномагниевого производства загрязняют окружающую природную среду, создавая экологическую опасность: страдают почвы, и грунтовые воды и растительность. В то же время эти отходы могут быть рассмотрены в качестве вторичных ресурсов редких и редкоземельных металлов. Последние годы переработка техногенных промышленных отходов является новой тенденцией для извлечения редких и редкоземельных металлов, которые могут частично покрыть спрос в случае их утилизации. Данная статья посвящена обзору имеющих литературы и статей по извлечению редких металлов из отходов титаномагниевого производства с использованием различных способов переработки. Обсуждаются способы их утилизации с акцентом на извлечение редких и редкоземельных металлов. Приведенные технологии переработки отходов включают различные пирометаллургические и гидрометаллургические процессы. Были представлены технологические схемы различных процессов выщелачивания и извлечения, чтобы дать целостное представление о переработке отходов и извлечении содержашихся в них редких металлов. В целом, в статье содержится обзор опубликованных работ по извлечению редких металлов, таких как РЗЭ, ниобий, тантал и ванадий.
Ключевые слова: титановые отходы, редкие металлы, ниобий, ванадий, редкоземельные элементы , выщелачивание, хлорирование

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