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RESOURCE-SAVING AND ENVIRONMENTAL PROTECTION IN NUCLEAR-GRADE ZIRCONIUM AND HAFNIUM PRODUCTION

[1]Mukhachev A.P., [2]Yelatontsev D.O., [1]Shevchenko V.H.

[1]M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine, [2]Dnipro State Technical University

Abstract. The development of efficient and environmentally friendly technological processes for processing zircon concentrate is an urgent problem in the technology of producing reactor-pure zirconium and hafnium used in nuclear power. The review presents the environmental, technical and economic characteristics of zircon decomposition processes using existing industrial technologies and provides data on the environmental safety of each technology. It is shown that current industrial technologies do not meet the criteria of sustainable development and allow emissions of toxic reagents into the environment. New applications of particularly pure zirconium and hafnium compounds which have emerged in recent decades, with impurity content of 10^{-3}–10^{-5}%, require less corrosive reagents than chlorine and fluorine, new resource-saving processes and equipment. Today, technical zirconium oxide with a purity of 98% is the main industrial product of zircon processing, but it allows for losses of hafnium, scandium and silicon. This is equivalent to financial losses of over USD 150 million per year. Based on the analysis of promising halogen-free technologies, a new integrated zircon processing technology is proposed which allows producing scarce hafnium, scandium and silicon compounds along with reactor-pure zirconium and its high-purity chemical compounds. The chemicals consumed in the zircon processing process are utilized in the production of mineral fertilizers, eliminating environmental pollution. The use of the highly efficient refining extraction process in a nitric acid environment using centrifugal extractors with an available tributilphosphate extractant allows us to obtain reactor metals with a purity of 99.95%. The production of high-purity zirconium, hafnium, scandium and silicon oxides meets the demand for non-nuclear products, which expands the volume of integrated zircon processing and meets the growing market demand for new functional materials. The integrated approach to zircon processing can reduce the cost of zircon by producing by-products, recycling consumed reagents and eliminating non-recyclable solid and liquid waste. This will ensure environmental protection even with relatively small volumes of reactor-pure metal production.

Keywords: zircon, zirconium, hafnium, scandium, silicon, resource-saving, nuclear purity.

1. Introduction

According to the energy strategy of Ukraine by 2030, the development of the nuclear power complex is planned, expanding the production of nuclear purity zirconium, increasing the volume of production of its alloys and organizing the production of pipes, rods, sheets for heat-emitting assemblies [1]. When organizing the production of products from domestic raw materials, the question of justifying the economic efficiency and environmental safety of the technology arises. Taking into account the risk of a negative impact of this industry on the state of the objects of the surrounding natural habitat and the health of the population, many countries are developing environmentally safe zircon processing technologies. In recent decades, work on the creation of combined technologies for processing zirconium with the production of tetrachloride, electrolytic powder and sponge has been actively carried out to eliminate the shortcomings of chloride technology [2–4].

Zirconium concentrates contain up to 33% silicon, up to 2% hafnium, up to 0.02% scandium, impurities of titanium, iron and aluminum, as well as products of the uranium and thorium decay (^{226}Ra, ^{40}K). This requires complex processing of zircon in compliance with the norms of environmental legislation regarding the isolation and safe burial of radioactive elements.

A study of research conducted by scientists in the field of traditional zirconium processing shows that there are two main directions of production of zirconium and its compounds:

- with deep separation of zirconium and hafnium;
- without separation of zirconium and hafnium, with the production of dispersed powders of high purity ZrO_2 with natural hafnium content, which is the basis of several promising materials for functional ceramics.

In the first direction, chloride-fluoride technologies of zircon decomposition are used to obtain zirconium with a purity of not more than 99.7–99.8% for atomic energy [5–8].

The second direction involves the decomposition of zircon with alkaline reagents and obtaining materials for non-nuclear usage. This technology remains promising since the volume of non-nuclear applications of zirconium products has reached the volume of reactor zirconium production and continues to increase [9].

The advantage of the first direction is the use of purification of zirconium from hafnium and impurities in a chloride-rhodanide environment as a refining process. The advantage of the second direction is the environmental friendliness of the zircon decomposition. Both directions do not solve the problem of the complex processing of zircon with the disposal of the reagents used.

An alternative to the first two directions is a technology developed in Ukraine that combines both goals – obtaining reactor zirconium with full extraction of valuable components (Hf, Sc, Si) and obtaining nanostructured ZrO_2, with maximum use of the reagents used and as well as other highly pure compounds of zirconium and hafnium (chlorides, fluorides, carbides, borides, nitrides) [10–14]. Due to the solution of the main tasks of zirconium production in one common technology, the volume of profitable products can be increased to the level of competitive cost. The main stages of the new technology were outlined in [10].

The development of atomic energy in the world is accompanied by an increase in the production of zirconium at existing facilities. Currently, the world has created capacities for the production of 7000 tons of zirconium sponge and 140 tons of hafnium sponge per year, but due to the reduction in the pace of development of nuclear energy, they are loaded by approximately 50% [15].

The quality of reactor zirconium obtained according to the chloride scheme remains low, at the level of 99.7% with increased content of O, N, Fe, Cr, Ni and C. The level of impurities determined the need for complex alloying of zirconium to obtain alloys of the "Zirkaloy-2", "Zirkaloy-4" and "Zirlo" brands.

The use of hafnium as an absorber rod in transport reactors of the US Navy has been known since 1954. There is no information about its use in commercial nuclear reactors. Hafnium could ensure the safety and efficiency of the nuclear power plant by finer regulation of the speed of the nuclear fission reaction of ^{235}U and eliminating the need to bury spent absorber rods [16]. The complete extraction and use of hafnium from zircon can reduce the cost of zirconium by 10–15%.

The development of new alternative energy branches of industry, heat-resistant coatings, functional materials and structural ceramics required purer zirconium compounds to obtain stabilized zirconium oxides and nanostructured zirconium dioxide [17]. The latter is widely used in the production of functional ceramics of fuel cells [18] and oxygen sensors [19], as well as in dentistry and traumatology [20].

To obtain high-purity zirconium oxide with impurity content of less than $1 \cdot 10^{-5}$%, the method of obtaining zirconium oxychloride by dissolving alkaline cake in hydrochloric acid with subsequent evaporation of the salt is used [21]. The difference in the solubility of impurity chlorides and zirconium oxychlorides makes it possible to leave the impurities in the mother solution and obtain pure ZrO_2 by calcining the oxychloride at 800°C. Chlorine turns into hydrochloric acid and returns to the cycle.

The use of nitric acid for the decomposition of the alkaline cake of zirconium in industrial practice is unknown since the problem of separating zirconium from silicon is rather difficult. At the same time, the appearance of new centrifugal extractors makes it possible to effectively separate zirconium and hafnium and obtain highly pure oxynitrates [22].

Thus, the growth in the production of nuclear-purity zirconium compounds has not solved the problem of extracting hafnium and scandium. At the same time, silicon oxide moves into the class of secondary resources with low price and quality. Alkaline methods of decomposing zircon made it possible to obtain a nitric acid solution of zirconium and hafnium with a low silicon content [23]. This made it possible to solve the problem of emulsification during the extraction separation of zirconium and hafnium. The purity of oxynitrates ensured the production of zirconium alloys with a purity of 99.95%.

The purpose of this work is to substantiate the complex processing of zirconium concentrate without the use of halogens but with the extraction of all valuable components in the form of commercial products and the minimum specific energy consumption based on modern high-performance equipment and energy-saving processes.

2. Theoretical part

ENVIRONMENTAL ASSESSMENT OF CURRENT INDUSTRIAL TECHNOLOGIES FOR THE PRODUCTION OF NUCLEAR ZIRCONIUM

Current zirconium processing technologies with the separation of zirconium and hafnium have been known for over 60 years and have not become more environmentally friendly since then. They allow the formation of non-recyclable chloride waste that requires safe burial, for example, in underground horizons at a depth of up to 1 km. The technology of decomposing zircon with aggressive toxic chlorine gas leads to the appearance of solid chlorine waste containing radionuclides transferred from zircon [24]. Their burial must follow radiation safety standards.

To obtain reactor-grade zirconium, two types of zirconium are mainly used – Australian and Ukrainian. The first contains more radioactive elements and is processed only by chloride technology. The second is cleaner, as it contains these elements at the level of 0.3 Bq/g [25].

Ukrainian zircon is processed using fluoride technology by sintering with K_2SiF_6 in the Russian Federation. At the same time, SiO_2 is a by-product and is not recycled, just like hafnium concentrate, which is stockpiled due to the lack of sales market.

The gaseous chloride method of decomposing zircon [26] leads to the transition of chlorine into the solution, as a result of which liquid chlorine waste appears. The re-extraction of zirconium after the extraction separation of zirconium and hafnium with sulfuric acid leads to the formation of basic zirconium sulfate, from which zirconium oxide is obtained by calcining at 900 °C. Sulfate ion turns into waste – low-quality gypsum, which should be buried.

Zircon processing by sintering with K_2SiF_6 is more environmentally friendly than the chloride method because SiO_2 is an inert material. At the same time, electrolysis of K_2ZrF_6 produces anode gas containing chlorine and freons, which have a destructive effect on the Earth's ozone layer. Chlorine turns into calcium chloride in the process of cleaning with lime and goes to burial in underground horizons and freons are released into the atmosphere uncontrollably [27].

Processing of cathode precipitate using an ammonium carbonate solution leads to the formation of a calcium chloride solution, which is also not processed. Replacing $(NH_4)_2CO_3$ with K_2CO_3 creates closed cycles for KCl and reduces the formation of chloride wastes.

The known industrial technologies of the halogen-free processing of zircon by alkalis to obtain non-nuclear zirconium oxide exclude harmful gas emissions [28]. Silicon oxide is used as an inert material. However, these technologies do not solve the issue of extracting hafnium and scandium from zircon.

To obtain ZrO_2 with a purity of 99.9%, the refining process of extraction separation of zirconium and hafnium in a nitric acid medium with the use of a tributilphosphate (TBP) extractant can be used. This method has been studied quite well, but it has not received industrial use due to the lack of the full cycle tests of the KTC-110 alloy in VVER-1000 reactors [29].

Thus, the current technologies of zircon processing to obtain reactor zirconium allow the loss of reagents of accompanying valuable elements and must be brought into line with the principles of sustainable economic development, to ensure comprehensive waste-free processing of raw materials and reagents. This should reduce the cost of production to make it more competitive and complying with the environmental certificate.

TECHNICAL AND ECONOMIC ASSESSMENT OF CHLORINE TECHNOLOGY

The chlorine technology of zircon processing was created based on the experience of obtaining titanium sponge by the chlorination method, therefore it took over all its inherent environmental and economic disadvantages. Reactor-grade zirconium technology began to develop in the 1960s and the demand for reactor zirconium increased significantly in the following decades. Today, it reaches up to 4000 tons of zirconium per year [15].

Relatively small volumes of production of zirconium and hafnium did not create environmental problems, since the costs of liquid and solid chloride waste burial were small and practically did not affect the price of zirconium. Chloride effluents are similar to seawater, so they were not considered hazardous to the environment. Excessive production of chlorine during the production of NaOH by electrolysis made chlorine a non-deficient reagent, but due to toxicity, it is necessary to transfer it to a safer state. At the same time, the toxic properties of chlorine and its aggressiveness to materials at high temperatures require more expensive technical solutions for sealing technological equipment and preventing its corrosion, during which zirconium is inevitably contaminated [30].

At present, the chloride-magnesium thermal technological scheme for the production of metal zirconium is the major one in the USA, UK and France. The decomposition of zircon is carried out with chlorine at temperatures of 900–1100 °C. The conversion of aggressive chlorine into less toxic soluble compounds, such as NH_4Cl and $CaCl_2$, solves the problem of its safe burial but requires excluding the territories from economic turnover. Chlorine is almost completely removed from production and is not regenerated [31].

Chlorine technology uses six high-temperature processes in the temperature range of 600–1000 °C. These operations include the chlorination of zirconium, purification of zirconium from impurities in the melt, calcination of basic sulfate, chlorination of zirconium and hafnium oxides, the distillation of chlorides and vacuum separation of magnesium chloride. In addition, the reduction of zirconium chloride requires high-purity magnesium obtained by electrolysis of magnesium chloride. This leads to an increase in capital costs and the cost of zirconium.

Let's estimate the loss of chlorine at the stage of primary chlorination, which is described by the equations:

$$ZrSiO_4 + 4Cl_2 + 4C \rightarrow ZrCl_4 + SiCl_4 + 4CO\uparrow \quad (1)$$

$$ZrCl_4 + H_2O \rightarrow ZrOCl_2 + 2HCl \quad (2)$$

$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O \quad (3)$$

According to the stoichiometry, chlorine consumption is 3.15 tons per 1 ton of zirconium in the raw material. At the production of zirconium products in the volume of 1500 tons/year, chlorine consumption will be up to 5000 tons. To neutralize this amount of chlorine, up to 4000 tons of calcium oxide is required. So the specific cost for lost reagents rises to 1 USD per 1 kg of zirconium.

The technical and ecological analysis of the technology is carried out based on the optimal volume of production and the required quality of the product. The monopolization of the market of reactor zirconium in the world allows it to maintain production volumes at existing capacities and stabilize the production price [32].

The quality of the zirconium sponge obtained by the Kroll method is not high enough in terms of nuclear properties, although it meets ASTM requirements. The purity standard of reactor zirconium is iodide metal, which is much more expensive than the sponge. The negative effect of impurities is compensated by alloying the sponge with nickel, chromium, iron and tin, which complicates the technology of obtaining products capable of withstanding the standard period of operation in the active zone of the nuclear power reactor [33].

Alloying leads to an increase in the price of the processing metal turnovers, the volume of which can reach 20–30% of the production output. The composition of alloys such as "Zirkaloy-2", "Zirkaloy-4" and "Zirlo" cannot provide a degree of nuclear fuel burnup of more than 50 MW per 1 kg of uranium per day and a service life of more than 4 years [34]. Available limits of nuclear fuel operation parameters determine the degree of nuclear fuel burnout of 70 MW per 1 kg of uranium per day and a service life of 5–7 years.

Currently, the price of a tube made of zirconium alloys remains at the level of 200 USD per 1 kg and it determines the cost share of zirconium products in the heat-emitting assemblies at the level of no more than 5% [15].

TECHNICAL AND ECONOMIC ASSESSMENT OF FLUORIDE ELECTROLYSIS TECHNOLOGY

The second industrial method of obtaining reactor-grade zirconium became possible after the creation of the process of electrolytic production of zirconium powder from the $KCl\text{-}KF\text{-}K_2ZrF_6$ melt in a hermetic electrolyzer with a capacity of 10 kA [35]. The use of K_2ZrF_6 for electrolysis required the development of a new zircon decomposition process using K_2SiF_6 in a KCl melt. It is realized in a drum furnace according to the reaction:

$$Zr(Hf)SiO_4 + K_2SiF_6 \rightarrow K_2Zr(Hf)F_6 + SiO_2 \qquad (4)$$

The joint production of K_2ZrF_6 and K_2HfF_6 allows their separation in the process of fractional crystallization with an extraction degree of 50–70% of zirconium, depending on the content of hafnium. The method is resource-saving, as it allows for the loss of reagents and by-products (hafnium, silicon oxides and scandium are not recovered).

During the electrolysis, gaseous chlorine and freons nos. 11, 12, 13 and 14 are released but not processed [36]. The specific losses of reagents per 1 ton of zirconium powder: chlorine – 0.6 t, fluorine – 0.3 t. Their disposal is still not ensured, which increases the cost of the powder and harms the environment.

The electrolytic method of obtaining zirconium and other rare metals has long attracted the attention of scientists [37], however, the low corrosion resistance of equipment in a chloride-fluoride melt did not allow for obtaining clean products and ensuring the continuous operation of electrolyzers. In the first stage, an open process was implemented with garnisage protection of the bath and chlorine removal when the anode gas was diluted 2000 times. The metallic zirconium contained impurities of nitrogen and oxygen, which required expensive iodide refining.

The development of a hermetic 10 kA industrial electrolyzer made it possible to eliminate the contact of zirconium with air and obtain a clean and plastic metal, which became the basis for obtaining new functional alloys of zirconium with niobium.

Today, this technology provides up to 20% of the world's volume of zirconium production.

With a hafnium content of 0.05% in zirconia, the fluoride technology did not allow obtaining zirconium by more than 50%. After the appearance of new areas of application of hafnium (aircraft engine turbines, military affairs), the industrial processing of 6% hafnium concentrate to obtain metallic hafnium of nuclear purity, with full utilization of reagents in the production of fertilizers, began. This significantly improved the environmental characteristics of zirconium production and increased the degree of use of reagents, reducing electricity consumption. The process can be described by reactions:

$$K_2Zr(Hf)F_6 + 4KOH \rightarrow Zr(Hf)(OH)_4 + 6KF \quad (5)$$

$$2KF + H_2SO_4 \rightarrow K_2SO_4 + HF\uparrow \quad (6)$$

The new technology made it possible to carry out industrial tests of the extraction separation technology of zirconium and hafnium on centrifugal extractors and obtain zirconium and hafnium compounds of high purity. The electrolysis from the melt of the KCl-ZrF_4 electrolyte showed a higher efficiency than the standard KCl-K_2ZrF_6 electrolyte, both in terms of product purity and the performance of electrolyzers [38].

However, pure metal could not be obtained in the process of electrolysis, as the zirconium powder was in the solidified electrolyte in the form of a cathode precipitate. Processing of the precipitate by the carbonate method, as well as the process of vacuum separation of the sponge, solved the task of cleaning the metal from electrolyte salts but required special fire safety measures due to the pyrophoricity of the zirconium powder.

Replacing ammonium carbonate with potassium carbonate made it possible to create a closed cycle for potassium chloride and eliminate its losses. The process of washing the powder has become almost wasteless.

The process of electrolysis of zirconium was undesirable due to the formation of chlorine and freons at the anode as a result of the discharge of potassium chloride. Capturing chlorine with a 20% NaOH solution made it possible to obtain a solution of sodium hypochlorite and laundry bleach for sanitary needs. This made it possible to reduce the cost of zirconium powder by more than 20% [10].

At the same time, the technology did not solve the problem of processing and disposal of freons. The output of freons is up to 1000 kg per 1 ton of zirconium powder, which led to fluorine losses in the amount of more than USD 300000 per year. Refining of freons made it possible to reduce the cost of the powder by USD 0.6 per 1 kg.

A new resource-saving technological scheme for zircon processing, which combines fractional crystallization and extraction with the production of ZrF_4 and K_2ZrF_6 in a ratio of 1:2, is shown in Fig. 1.

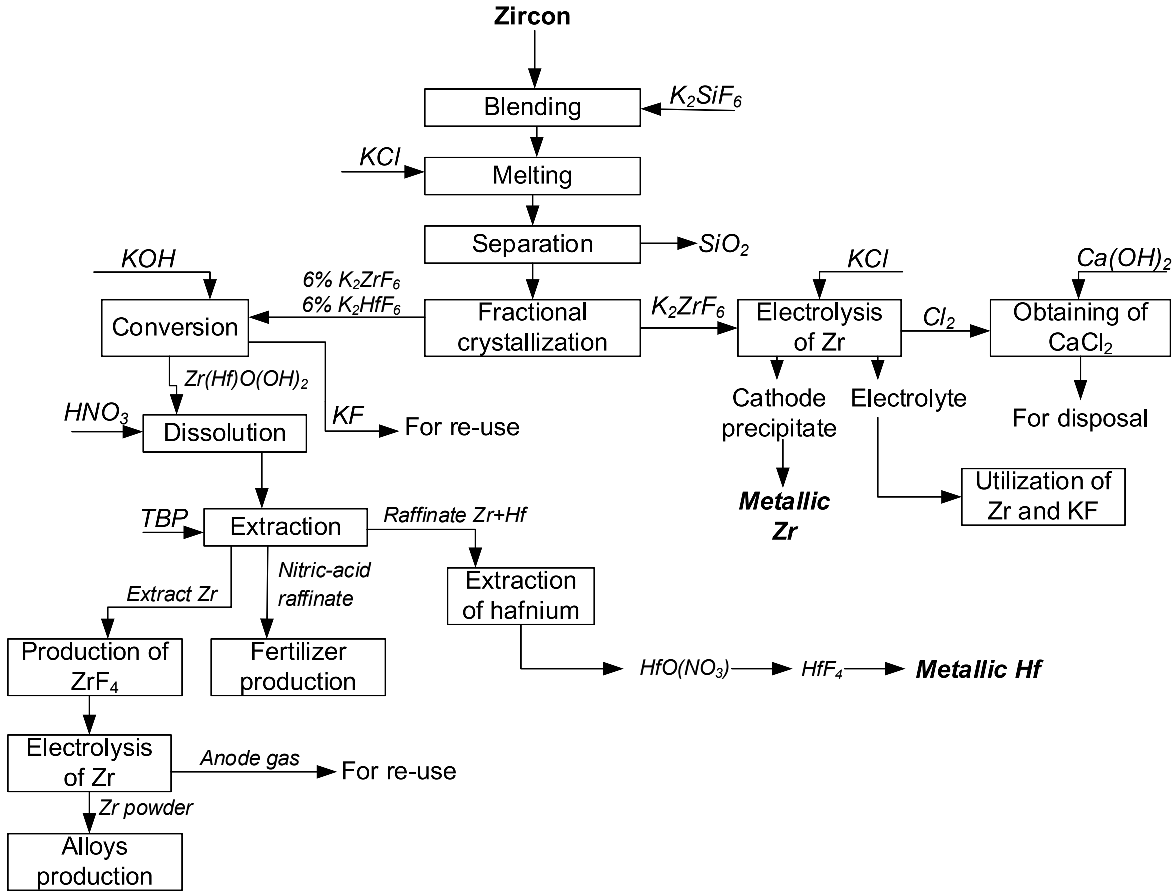

Figure 1 – Flow-chart of zircon processing by fluoride technology

Feeding the 10kA electrolyzer with the ZrF_4 and K_2ZrF_6 partially improves production technological indicators and reduces reagent losses. At the same time, losses of part of the reagents and raw materials remained and the volumes of sewage for burial, although reduced, still required disposal.

ENVIRONMENTAL ASSESSMENT OF HALOGEN-FREE TECHNOLOGY

The halogen-free zircon processing technology was developed in the USA to obtain technical-grade ZrO_2 for the production of refractories [39]. Chalk or soda (NaOH, Na_2CO_3) was used as reagents. Hafnium, silicon and scandium were not obtained as commercial products.

To create a modern sustainable production of zirconium and hafnium in Ukraine, the alkaline method of decomposing zircon is the most promising. To ensure the sustainable development of zirconium and hafnium production, the following tasks must be solved:

- ensure maximum extraction of zirconium and hafnium;
- convert SiO_2 into a commercial product;
- return reagents to the technological cycle, preventing their loss;
- ensure the required purity of zirconium and hafnium in the content of metal impurities at the level of 10^{-3}–10^{-5}% and nitrogen and carbon – less than 0.005%;
- extract the valuable and scarce scandium;

- improve the process of electrolysis of zirconium by complex processing of cathode and anode products.

The choice of technology of processing zircon with soda with heat leaching with nitric acid is determined by the availability of domestic production of soda and sodium nitrate. The main strategic task of the production of reactor-grade zirconium is the creation of a waste-free, complex industrial technology with the production of not only by-products based on hafnium, scandium and silicon but also a wide range of particularly pure zirconium compounds in the form of oxynitrate, carbonate, oxychloride and acetate. This will allow increasing the volume of zircon processing to the most profitable level without negative impact on the environment. The release of sodium nitrate from the used reagents makes it possible to exclude the formation of industrial effluents.

The earlier environmental analysis [2] of the industrial technology for the production of reactor zirconium did not take into account the factors of resource-saving. However, the analysis quite convincingly showed the ecological advantages of the new Ukrainian technology.

The concentration of radioactive elements during the enrichment of raw materials gradually increases and, in the final operations, it may exceed radiation safety standards. During zircon enrichment, they accumulate in the heaviest fraction – hafnium hydroxide. This requires the organization of environmental control and a separate hafnium processing scheme.

The development of energy-saving technological equipment and corrosion-resistant materials made it possible to ensure the maximum permissible limit for all harmful substances. The elimination of toxic reagents made it possible to significantly improve production safety and reduce the specific consumption of reagents and energy.

In technological operations, such aggressive reagents as hydrofluoric acid and hydrogen fluoride are used, which require the protection of workplaces and personnel. The technical level of fluoroplastic equipment prevents the leakage of toxic reagents into the environment. The achieved global level of freon production technology allows the use of known processes for their capture from the anode gas in order to prevent uncontrolled emission into the atmosphere.

In the process of electrolysis, a number of freons is formed, which should be divided into individual uses. This requires capital expenditures, but they pay off with the release of commercial products. Without solving this problem, the electrolysis process will remain environmentally harmful. Of particular practical interest is the production of fluoroplastic-4 (Teflon) powder from freons [40].

The analysis of the technological factors of uranium fluoride production showed that the calcium-thermal method allows obtaining ingots of the Zr-1%Nb alloy and ensures compliance with all environmental requirements for environmental protection. The use of nitric acid, caustic and soda ash as chemical reagents allows the exclusion of sulfuric and hydrochloric acids and the obtaining of fertilizer – sodium nitrate from nitric acid and alkaline solutions. This method was developed and tested in the new Ukrainian technology for obtaining reactor-grade alloys of zirconium with niobium [41].

The implementation of the technology became possible due to the creation of less toxic reagents, high-performance equipment and closed technological cycles with concomitant production of fertilizers, excluding the loss of raw materials and reagents and the generation of environmentally harmful waste. This made it possible to obtain an environmental certificate and opened up the opportunity to sell zirconium products on the world market. Based on the obtained data, an improved zircon processing technology was proposed (Fig. 2).

The use of zirconium and hafnium tetrafluorides allowed sublimation purification in the process of calcium-thermal melting to obtain zirconium ingots [42]. The process is described by the equations:

$$ZrF_4 + Al + Nb + Ca \rightarrow ZrNbAl + CaF_2 \quad (7)$$

$$HfF_4 + Al + Fe + Ca \rightarrow HfFeAl + CaF_2 \quad (8)$$

Calcium-thermal melting replaces the time-resource-consuming operation of processing the cathode product of electrolysis to obtain zirconium and hafnium powders and eliminates the vacuum-arc melting of powder into ingots. In the process of calcium-thermal melting, unlike electrolysis, no dangerous gas emissions are formed. At the first stages of the development of reactor-grade zirconium production, the choice of electrolytic technology was explained by the availability of cheap raw materials (K_2ZrF_6) based on fluorine, which was extracted simultaneously with the production of phosphoric fertilizers, as well as by the possibility of unhindered burial of chloride effluents and gas emissions.

TECHNICAL AND ECONOMIC ASSESSMENT OF HALOGEN-FREE TECHNOLOGY

Technologies for obtaining dispersed and nanostructured zirconium powders without separation of zirconium and hafnium began to develop in recent decades. This results in the loss of scarce metals, which limits their production. There is a need to develop a fundamentally new, more advanced resource-saving technology for obtaining high-purity compounds of zirconium, hafnium, silicon and scandium and recycling used reagents in the production of related products.

The raffinate from the extraction contains scandium, which can be eliminated in the form of Sc_2O_3 in the amount of 0.4 kg/t of zirconium. Silicon oxide from soda solution is precipitated with carbon dioxide to obtain "white soot" brand BS-100 worth up to USD 1.5 per 1 kg.

With a ratio of zircon:soda = 1:3.5, the specific yield of Na_2CO_3 and $NaNO_3$ per 1 t of zirconium is 7.0 t and 11.2 t, respectively. An extraction raffinate with a nitric acid content of 450 g/l is used to neutralize soda. In the process of decomposition of zircon, sodium forms two salts: sodium zirconate and sodium silicate. The majority of sodium is returned to the process, thus, in the first stages, soda and nitric acid are utilized almost completely.

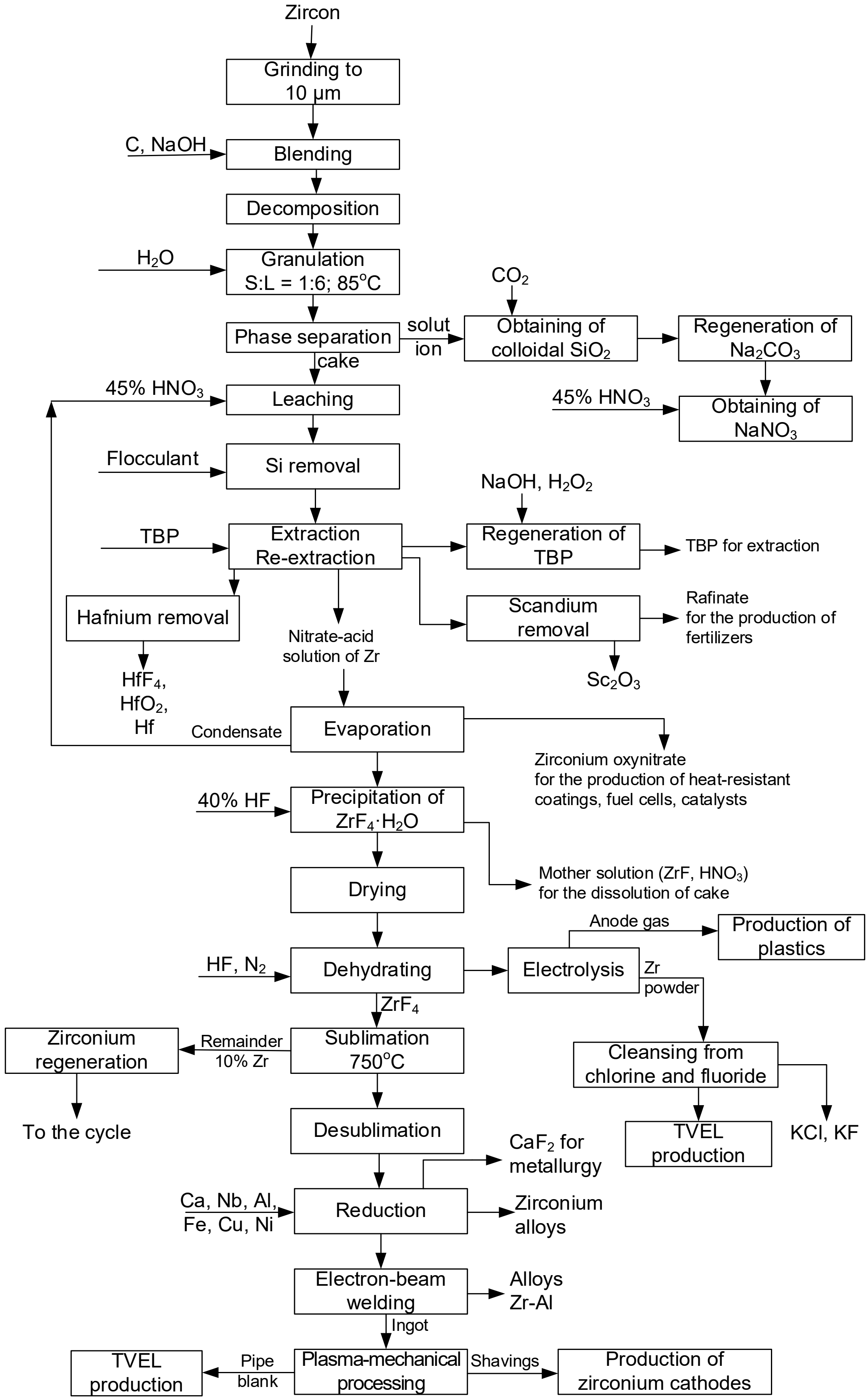

Figure 2 – Flow-chart for obtaining nuclear-grade zirconium products under Ukrainian resource-saving technology

The extraction from the nitric acid environment is resource-saving, as it is a raw material for fertilizers. The TBP extractant is completely regenerated and retains its properties for the selective transfer of zirconium and hafnium from the aqueous phase to the organic phase and back. Impurities of iron, aluminum and titanium turn into inert compounds in the amount of up to 3% of the weight of zirconium. Zirconium oxynitrate is converted to zirconium tetrafluoride with HF.

The use of ZrF_4 instead of K_2ZrF_6 in the electrolysis process provides a significant saving of energy resources (about 30%) [43]. To obtain K_2ZrF_6, expensive potassium carbonate and hydrofluoric acid are required in the amount of 0.234 t and 0.195 t per 1 t of zirconium, respectively. Deposition occurs according to the reaction:

$$ZrO_2(NO_3)_2 + 3K_2CO_3 + 6HF + 4HNO_3 \rightarrow \\ \rightarrow K_2ZrF_6 + 6KNO_3 + 3CO_2\uparrow + 5H_2O \quad (9)$$

at pH 4, therefore, additional consumption of K_2CO_3 is required for acid neutralization in the amount of 3 t per 1 t of zirconium. These costs increase the price of zirconium by USD 1.2 /kg and require capital expenditures for the creation of co-production of fertilizers.

Zirconium tetrafluoride after sublimation can be used for calcium-thermal recovery of zirconium alloys in the form of an ingot, which eliminates the processing of the cathode precipitate, cleaning the anode gas, sintering the powder and forming electrodes for vacuum-arc melting. A comparison of the cost of zirconium alloys with niobium obtained by the methods of electrolysis, powder metallurgy, calcium-thermal and vacuum-arc melting shows their equivalence in the pipe blank [44].

The optimal technology depends on the fulfillment of environmental requirements, but also on the economic conditions of obtaining competitive products on the market. At the same time, the improvement of equipment for electrolysis processes by recycling cathode precipitate and capturing chlorine without the formation of liquid chloride effluents will make electrolysis technology less expensive and more eco-friendly.

Thus, improving the quality of the starting compound (ZrF_4) for obtaining zirconium by electrolysis excludes losses of reagents and harmful emissions into the environment, ensuring the fulfillment of resource-saving criteria.

SUSTAINABILITY CRITERIA FOR THE INDUSTRIAL IMPLEMENTATION OF ZIRCON PROCESSING TECHNOLOGY

The main criteria for the efficiency of zirconium production are the quality of metallic zirconium, which must be increased to 99.95% while reducing the content of impurities critical for radiation resistance (C, N, F, Cl).

Resource-saving technology must take into account the following criteria:

1. Reagents for decomposing zircon should not be scarce, expensive, or corrosive.
2. A specific consumption rate of reagents and technological modes must ensure the maximum extraction of all valuable components.
3. All effluents and solid wastes must be completely utilized.

4. Gaseous emissions of harmful substances must not exceed the maximum permissible level.

5. Reagents must be regenerated to obtain commercial products.

6. Chemical and metallurgical turnovers containing zirconium and hafnium compounds must be recycled in a closed cycle.

All these criteria are met by the complex technology of zirconium processing (Fig. 2) with the use of alkaline reagents and their utilization in the production of fertilizers and the production of new types of high-tech products based on zirconium, hafnium, scandium and silicon.

3. Conclusions

1. The technical and economic analysis of industrial technologies for zircon processing to produce reactor zirconium and hafnium shows that they do not meet the principles of sustainable development and resource conservation.

2. Chloride and fluoride technologies for zircon decomposition generate waste that requires disposal, as well as irreversible losses of reagents that reduce the economic performance of the production.

3. The low quality of hafnium produced by chloride technology requires an expensive iodide refining process, which increases the cost of the metal.

4. Existing technologies do not allow producing high-purity zirconium and hafnium oxides for knowledge-intensive non-nuclear industries.

5. The quality of reactor zirconium produced by current technologies does not exceed 99.8%, which limits the lifetime of nuclear fuel to 4 years.

6. Halogen-free methods of zircon processing are limited to the production of technical zirconium dioxide and do not provide for comprehensive processing of raw materials and utilization of reagents.

7. The use of alkaline methods of zircon decomposition with extraction separation of zirconium, hafnium and scandium in a nitric acid environment allows for their complete extraction with the conversion of all valuable elements into highly soluble chemical compounds and utilization of reagents in fertilizer production.

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About authors

Mukhachev Anatolii Petrovych, Candidate of Physics and Mathematics (Ph.D.), Senior Researcher in Department of Vibratory Transporting Systems and Complexes, M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (IGTM of the NAS of Ukraine), Dnipro, Ukraine, map45@ukr.net

Yelatontsev Dmytro Oleksandrovych, Candidate of Technical Sciences (Ph.D.), Associate Professor in Department of Chemical Technology of Inorganic Substances, Dnipro State Technical University under the Ministry of Education and Science of Ukraine (DSTU of MES of Ukraine), Kamianske, Ukraine, ya.nah2015@yandex.com

Shevchenko Volodymyr Heorhiiovych, Doctor of Technical Sciences (D. Sc), Professor, Scientific Secretary of the Institute, M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (IGTM of the NAS of Ukraine), Dnipro, Ukraine, vgshevchenko@ua.fm

ПИТАННЯ РЕСУРСОЗБЕРЕЖЕННЯ ТА ОХОРОНИ НАВКОЛИШНЬОГО СЕРЕДОВИЩА У ВИРОБНИЦТВІ ЯДЕРНО-ЧИСТИХ ЦИРКОНІЮ ТА ГАФНІЮ

Мухачев А.П., Єлатонцев Д.О., Шевченко В.Г.

Анотація. Розробка ефективних і екологічно чистих технологічних процесів переробки цирконового концентрату є актуальною проблемою у технології отримання цирконію і гафнію реакторної чистоти, які застосовуються в ядерній енергетиці. В огляді представлено екологічну та техніко-економічну характеристику процесів розкладання циркону за діючими промисловими технологіями, наведено дані щодо екологічної безпеки кожної технології. Показано, що сучасні промислові технології не відповідають критеріям сталого розвитку, допускають викиди токсичних реагентів у довкілля. Нові області застосування особливо чистих сполук цирконію і гафнію, що з'явилися в останні десятиліття, з вмістом домішок на рівні 10^{-3}–10^{-5}% вимагають менш корозійно-активних ніж хлор і фтор реагентів, нових ресурсозберігаючих процесів та обладнання. На сьогоднішній день технічний оксид цирконію чистотою 98% є основною промисловою продукцією переробки циркону, але вона допускає втрати гафнію, скандію та кремнію. Це еквівалентно фінансовим втратам на суму понад 150 млн дол. США на рік. На основі аналізу перспективних безгалогенних технологій запропоновано нову комплексну технологію переробки циркону, яка дозволяє отримувати поряд з цирконієм реакторної чистоти та його високочистими хімічними сполуками, ще й дефіцитні сполуки гафнію, скандію та кремнію. Витрачені у процесі переробки циркону хімічні реагенти утилізуються у виробництві мінеральних добрив, усуваючи забруднення довкілля. Застосування високоефективного афінажного процесу екстракції в азотнокислому середовищі на відцентрових екстракторах з доступним екстрагентом ТБФ дозволяє отримати реакторні метали чистотою 99,95%. Виробництво високочистих оксидів цирконію, гафнію, скандію і кремнію задовольняє попит на продукцію неядерного призначення, що розширює обсяги комплексної переробки циркону і задовольняє зростаючі потреби ринку нових функціональних матеріалів. Комплексний підхід до переробки циркону може знизити собівартість цирконію за рахунок випуску супутньої продукції, утилізації витрачених реагентів і ліквідації неперероблюваних твердих і рідких відходів. Це забезпечить захист навколишнього середовища навіть при відносно невеликих обсягах виробництва металу реакторної чистоти.

Ключові слова: циркон, цирконій, гафній, скандій, кремній, ресурсозбереження, ядерна чистота.