

SCRREEN2

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FACTSHEETS UPDATES BASED ON THE EU FACTSHEETS 2020

HAFNIUM

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HAFNIUM

OVERVIEW

Hafnium (Hf) is a chemical element that was discovered in 1923 and its name is derived from the Latin name for Copenhagen "Hafnia". Hafnium is a hard, ductile metal similar t!o stainless steel in its appearance and chemically very similar to zirconium. For this reason, zirconium is discussed on several occasions in this factsheet. In nature, hafnium is always bound up with zirconium compounds, from which it needs to be extracted using advance metallurgical processing (ALKANE, 2017). Its main commercial sources are zircon and baddeleyite; these are available as by-products from the extraction of titanium minerals (Nielsen & Wilfing, 2010).





Figure 1. Simplified value chain for hafnium in the EU¹

Table 1. Hafnium supply and demand in metric tonnes, 2016-2020 average						
lobal	Global	EU	EU Share	EU Suppliers	Impo	

production	Producers	consumption			reliance
71	France 49%	11.3	16%	France 78%	0%
	USA 44%			Ukraine 16%	
	China 3%			China 3%	
	Russia 3%			Russia 2%	

Prices: The hafnium market is relatively small, highly concentrated and, since hafnium is a by-product of zirconium metal purification, strongly linked to the zirconium market (European Commission, 2020). On the demand side, the developments in hafnium's major application areas, super alloys for aerospace industry and nuclear rods, will have a significant effect on hafnium prices in the future (cf. European Commission, 2020; Mordor Intelligence, 2020). The price volatility of unwrought hafnium in the period 2016-2020 was around 2.1%.

¹ JRC elaboration on multiple sources (see next sections) This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958211







Figure 2. Annual average price of hafnium between 2000 and 2020 (USGS, 2021)².





Primary supply: Hafnium is extracted as by-product from zirconium recovery routes. The world annual hafnium production from zirconium ores was about 71 tonnes in 2016. Due to lack of repeated production

² Values in €/kg are converted from original data in US\$/kg by using the annual average Euro foreign exchange reference rates from the European Central Bank (<u>https://www.ecb.europa.eu/stats/policy_and_exchange_rates/euro_reference_exchange_rates/html/eurofxref-graph-usd.en.html</u>)





data, this value has been used as average for the period 2012-2016 in the calculation for the criticality assessment.

Secondary supply: Given the existence of hafnium as a by-product of titanium and zirconium, it is likely that hafnium waste from production processes is reintroduced in the process. At the validation workshop, experts assessed that there is no information available on recycling of superalloys

Uses: The main global uses of hafnium are as applications as superalloys and for the nuclear industry.



Figure 4: EU uses of hafnium

Substitution: Hafnium can be substituted by other alloy metals, such as magnesium, cobalt, chromium, niobium and tantalum, based on similarity in performance (corrosion resistance, thermal stress) (Bedinger, 2016).

Application	Share	Substitutes	SubShare	Cost	Performance
		Magnesium	10%	Similar or lower costs	Similar
		Niobium	5%	Similar or lower costs	Similar
Superalloys	61%	Tantalum	5%	Similar or lower costs	Similar
		Cobalt	10%	Similar or lower costs	Similar
		Chromium	10%	Similar or lower costs	Similar
Nuclear control rod	11%	Silver	17%	Slightly higher costs (up to 2 times)	Similar
		Cadmium	17%	Similar or lower costs	Similar
		Indium	16%	Similar or lower costs	Similar
Catalyst precursor	7%	Zirconium	30%	Similar or lower costs	Reduced

Table 2. Uses and possible substitutes of hafnium

Other issues: Elemental hafnium is a flammable solid and catches fire spontaneously if exposed to air (ECHA, 2022). The (US Occupational Safety and Health Standards, 2022) subpart Z "Limits for Air Contaminants" sets a limit of 0.5 mg/m³ of air as an 8-hour concentration for hafnium.





MARKET ANALYSIS, TRADE AND PRICES

GLOBAL MARKET

Table 3. Hafnium supply and demand in metric tonnes, 2016-2020 average

Global production	Global Producers	EU consumption	EU Share	EU Suppliers	Import reliance
71	France 49% USA 44% China 3% Russia 3%	11.3	16%	France 78% Ukraine 16% China 3% Russia 3%	0%

Hafnium is a by-product of a certain part of zirconium production. Hafnium is obtained during zirconium metal purification, which is a process step for the use of zirconium in the nuclear industry (European Commission, 2020). As there are no other current alternatives to produce hafnium, the zirconium demand for the nuclear industry drives the hafnium production. The two largest producers are France and the United States accounting for almost 90% of the global hafnium production in 2019 (ARC, 2021). Furthermore, China and India presented some low-volume production of hafnium that is consumed locally (ARC, 2021; European Commission, 2020).

EU TRADE

For this assessment, hafnium is evaluated at the processing stage.

Table 4. Relevant Eurostat CN trade codes for hafnium				
Processing/refining				
CN trade code title				
81129210	Unwrought hafnium "celtium";			
	hafnium powders; hafnium waste			
	and scrap (excl. ash and residues			
	containing hafnium)			

Figure 5 and **Erreur ! Source du renvoi introuvable.** show the EU trade in hafnium at processing stage between 2000 and 2021. With respect to the product group 'unwrought hafnium, hafnium powders, hafnium waste and scrap', the EU was a net exporter in each year of the period (numbers in parentheses indicate the years associated with the quantities): EU imports varied from 0.8 t (2004) to 24.6 t (2017); EU exports ranged between 6.1 t (2020) and 58.8 t (2006).







Figure 5. EU-trade flows for the category 'unwrought hafnium, hafnium powders, hafnium waste and scrap', from 2000 to 2021 (based on Eurostat, 2021)

Figure 6 presents the average EU imports of hafnium at processing stage, by country, for the period 2000-2021. For 'unwrought hafnium, hafnium powders, hafnium waste and scrap', Ukraine was the main EU supplier with 31% of EU's imports. United States, United Kingdom, Canada and Russia followed with 22%, 22%, 7% and 7%, respectively. United States and China were the main contributors to EU imports in the category 'articles of hafnium and germanium (n.e.s.)'; they covered 31% and 24% of total EU imports in this category, respectively. China has gained importance as an EU supplier in this category since the mid-2010s.



Figure 6. EU imports for the category 'unwrought hafnium, hafnium powders, hafnium waste and scrap', by country, between 2000 and 2021 (based on Eurostat, 2021).





PRICE AND PRICE VOLATILITY

Data on global hafnium trade and prices is available to a very limited extent. The hafnium market is relatively small, highly concentrated and, since hafnium is a by-product of zirconium metal purification, strongly linked to the zirconium market (European Commission, 2020). In the past, there have been reports relating these hafnium-market characteristics to (potential risks of) hafnium-price peaks, e.g., price peaks due to insufficient supply / decreasing stock piles / vulnerability of the market to relatively small changes in demand/supply (Reuters, 2014) or due to declining zirconium demand for nuclear rods (and, thus, declining zirconium production and hafnium supply) in the aftermath of the Fukushima nuclear disaster (Albrecht, 2015; European Commission, 2020).

On the demand side, the developments in hafnium's major application areas, super alloys for aerospace industry and nuclear rods, will have a significant effect on hafnium prices in future (cf. European Commission, 2020; Mordor Intelligence, 2020). The price volatility of unwrought hafnium in the period 2016-2020 (as measured by the standard deviation of the data points depicted in Figure 7) was around 2.1%. The maximum year-on-year price change in the period 2015-2020 was the price decrease by 26% between 2015 and 2016.



Figure 7. Annual average price of unwrought hafnium between 2000 and 2020, in US\$/kg and €/kg (based on USGS, 2021)³. Dash lines indicate average prices for 2000-2020.

³ Values in €/kg are converted from original data in US\$/kg by using the annual average Euro foreign exchange reference rates from the European Central Bank (<u>https://www.ecb.europa.eu/stats/policy_and_exchange_rates/euro_reference_exchange_rates/html/eurof_xref-graph-usd.en.html</u>)

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OUTLOOK FOR SUPPLY AND DEMAND

In 2020, global zirconium production slightly decreased, which in turns a reduction of hafnium production during the same period. This was because some factories had to stop their production due to the COVID-19 pandemic (Mordor Intelligence, 2021; USGS, 2021). However, the global market of hafnium is expected to increase a compound annual growth rate (CAGR) of 7% between 2021 and 2026 (Mordor Intelligence, 2021). In this period, the hafnium production will be driven by the demand in aerospace, submarines and semiconductors industries (Mordor Intelligence, 2021). For nuclear control rods, demand is expected to increase by 4%; a 3% increase is expected for all other applications (European Commission, 2020).

DEMAND

GLOBAL AND EU DEMAND AND CONSUMPTION

The annual apparent consumption of hafnium in the EU was 11.3 tonnes in 2016.

For the production data, there is no official publication. Literature and EU data consider a production of 35 tonnes since 2012.

However, small commodity markets like the hafnium market tend to be very volatile, thus the validity of the consumption figure for the whole period is uncertain. For example, the US imports increased within the abovementioned period from 24 tonnes per year to 180 tonnes per year (Bedinger, 2016). The figures imply that the hafnium consumption in the US exceeded the EU figure by far in 2016.



Figure 8. Hafnium (CN 81129210 Unwrought hafnium, powders waste and scrap) processing stage apparent EU consumption. Production data from Eurostat Prodcom (2021) is available only for 2019-2020. Import and export data from Eurostat Comext (2021) for is available for 2002-2020. Consumption is calculated in hafnium content (EU production+import-export).





Hafnium processing stage EU consumption is presented by HS code CN 81129210 Unwrought hafnium, powders waste and scrap. Import and export data is extracted from Eurostat Comext (2021). Production data of gallium is extracted from Eurostat Prodcom (2021) using PRCCODE 24453062 Unwrought hafnium "celtium"; hafnium powders.

Based on Eurostat Comext (2021) and EU prodcution average import reliance of hafnium at processing stage is 0 % on the period.

GLOBAL AND EU USES AND END-USES

The main global uses of hafnium are as applications, as superalloys and within the nuclear industry.

Figure 9 shows the breakdown of estimated use globally (the percentage use splits are mirrored within a JRC study on Hafnium and nine other newly 'critical materials' 2021, categorised as 'finished products used in the EU). No further data updates were suggested with SCRREEN Expert and Validation workshops in 2021 and 2022.



Figure 9. Global end uses of hafnium in 2016 (ALKANE, 2017)

Relevant industry sectors are described using the NACE sector codes (Eurostat, 2022). The calculation of economic importance is based on the use of the NACE 2-digit codes and the value added at factor cost for the identified sectors (ERREUR ! SOURCE DU RENVOI INTROUVABLE.). The value-added data uses 2019 Eurostat figures.





Table 5. Hafnium applications, 2-digit NACE sectors, associated 4-digit NACE sectors, and value added per sector (Eurostat, 2022)

Applications	2-digit nace sector	Value added of sector (m€) 2019	4-digit nace sector
superalloys	C24 - manufacture of basic metals	63,700	24.45 other non-ferrous metal production
plasma cutting tips	c25 - manufacture of fabricated metal products, except machinery and equipment	186,073	25.73 manufacture of dyes and pigments
nuclear control rod	c25 - manufacture of fabricated metal products, except machinery and equipment	186,073	25.45 manufacture of other tanks, reservoirs and containers of metal
catalyst precursor	c20 - manufacture of chemicals and chemical products	117,150*	20.13 manufacture of bodies (coachwork) for motor vehicles; manufacture of trailers
oxide for optical	c26 - manufacture of computer, electronic and optical products	84,074*	
semiconductors	c26 - manufacture of computer, electronic and optical products	84,074* * data to 2014 only	26.6 manufacture of engines and turbines







APPLICATIONS OF HAFNIUM

The major applications for hafnium are described below. Other uses of hafnium are as refractory ceramic materials, microchips and nozzles for plasma arc cutting.

SUPERALLOYS

The major application for hafnium is as an alloy addition in polycrystalline nickel-based super alloys (for example, MAR-M 247 alloy contains 1.5% hafnium).

These alloys are used in the aerospace industry both in turbine blades and vanes, and in industrial gas turbines.

The super-alloy industry requires the purest form of hafnium, crystal bars, with low zirconium content. Demand and supply for this form of hafnium is approximately equal, making the sector volatile.

NUCLEAR

Hafnium is used in nuclear control rods due to its high thermal neutron absorption cross section (Bedinger, 2016).

Hafnium (and zirconium) is used in nuclear reactors and nuclear submarines and must in a pure form to work effectively. This leads to the production of hafnium-free zirconium and, as a result, hafnium as a by-product.

SUBSTITUTION

Application	Share	Substitutes	SubShare	Cost	Performance
		Magnesium	10%	Similar or lower costs	Similar
		Niobium	5%	Similar or lower costs	Similar
Superalloys	61%	Tantalum	5%	Similar or lower costs	Similar
		Cobalt	10%	Similar or lower costs	Similar
		Chromium	10%	Similar or lower costs	Similar
Nuclear control rod	11%	Silver	17%	Slightly higher costs (up to 2 times)	Similar
		Cadmium	17%	Similar or lower costs	Similar
		Indium	16%	Similar or lower costs	Similar
Catalyst precursor	7%	Zirconium	30%	Similar or lower costs	Reduced

Table 6. Uses and possible substitutes of hafnium

SUPERALLOYS

Hafnium can be substituted by other alloy metals, such as magnesium, cobalt, chromium, niobium and tantalum, based on a kind of similarity in performance (corrosion resistance, thermal stress) (Bedinger, 2016).

In certain superalloys, zirconium can be used interchangeably with hafnium (USGS, 2022).





NUCLEAR

A well-established option within nuclear powerplants is to substitute hafnium with silver-cadmium-indium control rods (Graves, 1962; USGS, 2022).

Niobium (columbium), stainless steel, and tantalum provide limited substitution in nuclear applications (USGS, 2022).

OTHERS

Chromite and olivine can be used instead of zircon for some foundry applications (USGS, 2022).

Zirconium can substitute hafnium in catalyst precursor applications. Titanium and synthetic materials may substitute in some chemical processing plant applications (USGS, 2018).

Dolomite and spinel refractories can also substitute for zircon in certain high-temperature applications.

SUPPLY

EU SUPPLY CHAIN

France and USA are the major hafnium producing countries with combined share of more than 85% globally in 2019. India and China present a low-volume domestic hafnium production but are not exporting (industryarc.com). France is the world major producer of hafnium, and the only one in the EU, with 35 tonnes of annual production in 2016. Cezus (the French nuclear group Areva) dominates hafnium market in Europe (mcgroup, 2022). In France, hafnium is produced from zirconium dioxide, a semi-processed material produced from zircon sand. Given the substantial domestic supply and the limited consumption, there is no import reliance of the EU. Figure 1 presents the EU sourcing data for hafnium. (AlLKANE, 2017; Eurostat, 2019).

Supply of hafnium is heavily dependent on the nuclear industry and its demand for pure zirconium. Hafnium is used in nuclear reactors because it is an excellent absorber of neutrons. Hafnium is put in the fuel rods themselves to absorb excess neutrons and prevent a chain reaction that would cause an explosion.

Production of zirconium requires the separation of the two metals, to allow the extraction of hafnium as byproduct. This implies a dependence of hafnium supply on the zirconium market, in particular the zirconium used in nuclear control rods.

Given the geographical concentration of hafnium production, it is remarkable that export restrictions with possible effect on hafnium are widely recorded by OECD (2016). This phenomenon can be explained by the trade code applied for the analysis. The related 6-digit CN product group (code 8112 92), contains also niobium, gallium, indium, vanadium and germanium. Most of the countries applying these exports restrictions are no relevant EU sources for hafnium in the period 2012-2016. Russia with almost 0.9 tonnes per year has applied an export tax rate of 6.5%.

Recently, hafnium global and European prices continue to rise, mainly caused by the fact that supply is not very flexible, replacement supply not available and demand high and increasing (argusmedia, 2021).





SUPPLY FROM PRIMARY MATERIALS

GEOLOGY, RESOURCES AND RESERVES OF HAFNIUM

GEOLOGICAL OCCURRENCE

The presence of hafnium in the earth's crust is somewhat rare, with 5.3 ppm upper crustal abundance (Rudnick & Gao, 2003).

Hafnium occurs in most types of magmatic and sedimentary rocks as well as in sediments, but usually in very low concentrations. Hafnium is not present in nature in its elemental form. The only mineral known with hafnium as major constituent is hafnon ((Hf,Zr)SiO₄). Hafnon occurs in tantalum-bearing granite pegmatites in the Zambézia district of Mozambique, and hafnian zircon has been identified in a niobium-tantalum-rich granitic complex in China (Wang et al., 1996).

The occurrence of hafnium is attended by zirconium, which is about 25 times more abundant in Earth's crust (132 ppm). Commonly these two elements are combined in solid solution with each other. The two major sources of zirconium and hafnium are zircon ($ZrSiO_4$) and baddeleyite (ZrO_2), in which hafnium is normally present 1.5-3.0 wt%.

The world's largest primary deposits of zirconium and hafnium are associated with alkaline igneous rocks, and, in one locality on the Kola Peninsula of Murmanskaya Oblast, Russia, baddeleyite is recovered as a byproduct of apatite and magnetite mining. Another rare hafnium-bearing mineral is eudialyte (Na₁₅Ca₆Fe₃Zr₃ Si₂₆O₇₃(OH)₄Cl₂) which is locally abundant in alkaline and peralkaline magmatic rocks such as nephelinites and syenites (Jones III et al. 2017). Eudialyte-bearing rocks have been identified in alkalic intrusive complexes worldwide (Marks at al.; 2011; Sjöqvist et al., 2013) e.g. the Lovozero Massif in the Kola Peninsula, Russia, hosts nearly monomineralic eudialyte ores that contain 10 % ZrO2 (Kogarko, 1990; Mikhailova et al., 2020). Another known eudialyte -rich ore is Norra Kärr in southern Sweden (Sjöqvist et al. 2013; Gates et al., 2013).

Otherwise, there are few primary igneous deposits of zirconium- and hafnium-bearing minerals with economic value at present. The main economic ore deposits worldwide are heavy-mineral sands (the so-called placers) produced by the weathering and erosion of preexisting rocks and the concentration of zircon and other economically important heavy minerals (Jones III et al. 2017). As a result, all hafnium produced comes from zirconium ores. Therefore, hafnium production depends exclusively on zirconium extraction and refining and total Hf output is assumed to be small. During the processing of these ores, hafnium is processed as by-product (Zr-Hf ratio is about 50:1). Globally, there exist today three predominant ore types that are relevant zirconium and hafnium sources: heavy mineral sands (HMS), carbonatites and to a minor degree peralkaline intrusions.

Global resources and reserves: The world's largest primary deposits of hafnium are associated with alkaline igneous rocks e.g. the Kovdor deposit (baddeleyite) and the Lovozero complex (eudyalite) in the Kola Peninsula, Russia (Kogarko, 1990). The most economic hafnium deposits are placers, sedimentary formations with heavy-mineral enrichment as a result of weathering and transport processes.





Global resources of hafnium are estimated at 1 million t Hf content. Hafnium is exclusively produced as a byproduct of zirconium metal. Production of Hf-free zirconium is the main source for Hf. In 2016, around 28 kt of hafnium contained in zirconium ores were extracted. It is important to note that only a minor fraction (< 1%) of the hafnium contained in zirconium ores extracted is recovered and enters the value chain for hafnium. The main fraction is considered as lost (as impurities in zircon and zirconium products) (Matoz et al., 2021).

Country	Zirconium Reserves (tonnes)	Percentage of total (%)
Australia	51,000,000	65
South Africa	14,000,000	18
Other countries	7,200,000	9
India	3,400,000	4
Mozambique	1,100,000	1
China	500,000	1
United States	500,000	1
Indonesia	N/A	N/A
World total (rounded)	78,000,000	100

Table 7. Global reserves of zircon reserves in year 2016 (Data from Bedinger, 2016)

Data on hafnium supply, demand and reserves are not recorded; the figures available are generally estimates (European Commission, 2014). Deposits of heavy metals sands, which are commercially recoverable, are found in China, Malaysia, Thailand, India, Sri Lanka, Australia, South Africa, Madagascar, and the United States. For example, in Virginia (USA), hafnium and zirconium were mined primarily from the deposits of heavy mineral sands in Hanover, Dinwiddie and Greensville counties. Several historic prospects for zirconium and possibly hafnium have been reported near the town of Ashland in the Hanover County. Although local sandstone contains approximately 33 % zircon by weight, the area was not industrially mined. Heavy mineral sands were mined in Dinwiddie and Greensville counties. (https://energy.virginia.gov/geology/Hafnium.shtml).

World reserves for hafnium are, with some exceptions, not recorded, but can be estimated from those of zirconium. Table 1 shows the estimated world reserves of zircon (Bedinger, 2016). USGS estimates world resources of hafnium associated with those of zircon and baddeleyite as exceeding 1,000,000 tonnes. In Greenland, hafnium resources (mainly Skaergaard intrusion) estimate is 1,100,000 t (Eilu et al., 2021).

EU RESOURCES AND RESERVES

Hafnium reserves in the EU are estimated at 6800 t Hf content. Hafnium is is produced in France as a byproduct of zirconium metal manufacture EU (Matoz et al., 2021). Known resources in Northern Europe are Sweden 6,781 t and potential resource in Finland at Sokli. In Norway and Sweden, all zirconium-rich mineral resources present a potential resource for hafnium (Eilu et al. 2021).

The single hafnium reserve in the EU reported is Norra Kärr in Gränna, Sweden. Norra Kärr is a rare earths deposit, which contains beside REEs also zirconium, hafnium, uranium and thorium. The main hafnium-hosting mineral is eudialyte (Na₁₅Ca₆ Fe₃ Zr₃ Si₂₆O₇₃(OH)₄ Cl₂) (GBM, 2015).





At the Minerals4EU website, no data is available on resources and reserves for hafnium in Europe (Minerals4EU, 2019).

Table 6. Reserve data for the EO					
Country	Reporting code	Quantity	Unit	Grade	Code Resource
					Τνρε
Sweden	CIM Guidelines	23,571	ktonnes	0.0286%	Probable

Table 8. Reserve data for the EU

WORLD AND EU MINE PRODUCTION

World primary hafnium production data are not available, mainly because of the close association with the nuclear industry. Quantitative estimates of hafnium reserves are not available and the time of the report preparation.

Hafnium is extracted as by-product from zirconium recovery routes. The world annual hafnium production from zirconium ores was about 71 tonnes in 2016. Due to lack of repeated production data, this value has been used as average for the period 2012-2016 in the calculation for the criticality assessment.

Heavy mineral sands mining projects are in progress in China, Australia, and Siberia (USGS, 2020). The U.S. maintains a supply of hafnium in the National Defense Stockpile, and is a net exporter. In the United States, hafnium is mined in Florida and Georgia. In Virginia, hafnium and zirconium are primarily from the mineral zircon sourced from deposits of heavy mineral sands in Hanover, Dinwiddie and Greensville counties. (https://energy.virginia.gov/geology/Hafnium.shtml). In the US, in 2021, hafnium metal was produced from zirconium chemical intermediates by one producer in Oregon and one in Utah (USGS 2022).

OUTLOOK FOR SUPPLY

The primary production of hafnium is directly related to the zirconium production. There is a number of heavy mineral sands projects in development that could produce zircon containing hafnium. Strandlines Resources is developing the Fungoni project in Tanzania and the Coburn project in Western Australia. Base Resources is planning to increase its production levels by expanding exploitation at Kwale mine and developing the Torliara project in Madagascar. Savannah Resources and consortium partner Rio Tinto are continuing to advance the Mutamba project in Mozambique. Finally, Alkane Resources' Dubbo Project could potentially process a fine-grained micro-porphyritic trachyte that contains an unusual hydrous zirconium silicate, which could provide a source of zirconium (edisongroup, 2019).

SUPPLY FROM SECONDARY MATERIALS/RECYCLING

POST-CONSUMER RECYCLING (OLD SCRAP)

According to the results of the recent Material System Analysis on Hafnium116, the EoLRIR (End-of-Life Recycling Input Rate) is calculated to 0% (see Table 3) (European Commission, under publication). Currently, there is little information available on hafnium recycling. Recycling of superalloys containing hafnium would





translate into hafnium recycling, however, experts assessed at the validation workshop that there is no information available on such recycling. It is likely that currently little to no post-use EOL recycling of hafnium is being carried out, given its contamination in the nuclear industry and the low percentage content in superalloys. UNEP reports that the end-of-life recycling rate is lower than 1% (UNEP, 2011). There are no indications that this has changed since then. Hafnium metal recycling is considered insignificant in the United States (Bedinger, 2016).

MSA Flow Value	(t)
B.1.1 Production of primary material as main product in EU sent to processing in EU	n/a
B.1.2 Production of primary material as by product in EU sent to processing in EU	n/a
C.1.3 Imports to EU of primary material	n/a
C.1.4 Imports to EU of secondary material	n/a
D.1.3 Imports to EU of processed material	4.9
E.1.6 Products at end of life in EU collected for treatment	4.6
F.1.1 Exports from EU of manufactured products at end-of-life	n/a
F.1.2 Imports to EU of manufactured products at end-of-life	n/a
G.1.1 Production of secondary material from post-consumer functional recycling in EU	
sent to processing in EU	n/a
G.1.2 Production of secondary material from post-consumer functional recycling in EU	
sent to manufacture in EU	n/a

Table 9. Material flows relevant to the EoL-RIR of Hafnium, average 2012-2016 (EC 2019)

INDUSTRIAL RECYCLING (NEW SCRAP)

Given the existence of hafnium as a by-product of titanium and zirconium, it is likely that hafnium waste from production processes is reintroduced in the process. At the validation workshop experts assessed that there is no information available on recycling of superalloys.

PROCESSING OF HAFNIUM

Hafnium is typically found in zirconium ores with zirconium to hafnium ratios of approximately 50:1. As the demand for zirconium is larger than for hafnium, and due to the ratio between hafnium and zirconium prices, hafnium is always retrieved as a by-product of the zirconium processing. Hafnium is extracted from hafnium bearing zirconium ores using predominantly Kroll process which is based on chlorination of zircon under high temperature to produce a mixed zirconium/hafnium tetrachloride (Rosenberg & Sharif 2016).

After crushing, milling and roasting the ore, the material is leached and undergoes a solvent extraction. From this solution, zirconium and hafnium are extracted, and potentially niobium is recovered. After precipitation, the resulting oxide is chlorinated in the presence of coke at high temperature to hafnium tetrachloride and reduced to sponge by magnesium. Hafnium sponge is vacuum-melted into ingots and hafnium metal can be further refined by electron beam melting zonerefining, molten salt electrorefining and Hydrogen plasma arc melting (Rosenberg & Sharif 2016; Alkane 2017).





The separation of the pair zirconium and hafnium is difficult due to the similarity of their chemical properties such as atomic radius, ionic radius and electronegativity. Several methods have been applied to separate this ionic pair. Such methods include fractional crystallization, ion exchange, fractional distillation, thermal diffusion, solvent extraction and electrochemical separation (Felipe et al., 2013).

The recovery of hafnium takes place during the refinement of zirconium where nuclear-grade pure zirconium is required. Without a nuclear industry, it is likely that no hafnium would be recovered because its low concentration in zirconium metal would otherwise make its recovery too expensive.

The global hafnium production is geographically highly concentrated. Most of the global production of hafnium (i.e. refining of zirconium) is done in France and the United States, whereas the production of high purity zirconium for nuclear applications is dominating. For about 2008 and 2012, respectively, AREVA, the only French producer, reported a production of 50 tonnes per year, however, the representativity of this value could not be assessed and the reference year remained unclear, thus it was not considered in the criticality assessment (AREVA, 2008). Since 2012, the French production is estimated at 35 tonnes per year. The global refined hafnium production is shown in Figure 11



Figure 11. Global refined hafnium production on 2016-2020 (EU data)

Beside a very high concentration of supplier countries, there is also a clear concentration on few hafnium producers (companies and plants), thus the global supply chain is vulnerable accordingly. Relevant producers were Areva (France), ATI Wah Chang (U.S.) and Revert-Recycled (U.S.), together making up more than 90% of the global supply.





OTHER CONSIDERATIONS

HEALTH AND SAFETY ISSUES RELATED TO THE HAFNIUM OR SPECIFIC/RELEVANT COMPOUDS AT ANY STAGE OF THE LIFE CYCLE

Elemental hafnium is a flammable solid and catches fire spontaneously if exposed to air (ECHA, 2022). The (US Occupational Safety and Health Standards, 2022) subpart Z "Limits for Air Contaminants" sets a limit of 0.5 mg/m³ of air as an 8-hour concentration for hafnium.

ENVIRONMENTAL ISSUES

No data was found on this aspect.

NORMATIVE REQUIREMENTS RELATED TO MINING, PRODUCTION, USE AND PROCESSING OF THE HAFNIUM

The Environmental Protection Agency (EPA) promulgated the Nonferrous Metals Manufacturing (NFMM) Effluent Guidelines and Standards (40 CFR Part 421) initially in 1974-1976, and added subcategories and revised the regulations in 1980-1990 pursuant to Clean Water Act amendments and litigation. The regulations cover wastewater discharges from a wide range of metal manufacturing facilities. The NFMM Effluent Guidelines and Standards are incorporated into NPDES permits for direct dischargers and permits or other control mechanisms for indirect dischargers (see Pre-treatment Program). Among the 31 facilities listed under the Guidelines, letter O refers to primary zirconium and hafnium. (EPA, 2021).

SOCIO-ECONOMIC AND ETHICAL ISSUES

ECONOMIC IMPORTANCE OF RAW MATERIAL FOR EXPORTING COUNTRIES

No relevant data found on this aspect.

SOCIAL AND ETHICAL ASPECTS

Horgan et al. (2022) apply the Emerging Materials Risk Analysis (EMRA) to thin films of hafnia (HfO₂) with the goal of determining the most sustainable route for its mining, processing, use and disposal. The study takes into consideration impacts across environmental, health, and societal parameters, which are all assessed through a literature review. The findings show that societal impacts are related to land-ownership conflicts and supply chain-related disputes. Specifically, the extraction of hafnium is linked to "disputes over site use due to competing political, religious or heritage claim", while the beneficiation and processing phases are linked to "material supply concerns (low recyclability, materials' export requirements)". No references are reported on societal impacts during the use phase of hafnia thin films, while its disposal is related to "unregulated electronic waste recycling processes [which] could impact health of those working at or near the site".





RESEARCH AND DEVELOPMENT TRENDS

RESEARCH AND DEVELOPMENT TRENDS FOR LOW-CARBON AND GREEN TECHNOLOGIES

No data available on this aspect.

OTHER RESEARCH AND DEVELOPMENT TRENDS

 HANSOME project⁴, Hafnium oxide-based nanocomposite scintillators for fast timing detection (2020-2022)

Although hafnium was discovered in 1923, it had not received a lot of attention until now. In the last few years, nanoparticles of hafnium dioxide, also known as hafnia, are bringing hafnium into the limelight thanks to their scintillating "personalities." Scintillators convert the kinetic energy in ionising radiation into detectable light. They are used as ionising radiation detectors in particle research and medical diagnosis. Nanoparticles of hafnia may overcome many of the limits of conventional inorganic solid scintillators because their luminescence properties can be tailored in many ways. The EU-funded HANSOME project aims to significantly augment their response times while stopping the ionising radiation, boosting their value in numerous fields.

• A theoretical study of the atomic layer deposition of HfO2 on Si(1 0 0) surfaces using tetrakis (ethyl methylamino) hafnium and water⁵, (Ba Tai et al. 2022)

The atomic layer deposition (ALD) of hafnium oxide (HfO2) thin film has attracted considerable attention owing to its crucial role in downscaling semiconductor devices. This study theoretically investigatew the reaction mechanisms during the ALD of HfO2 thin film (HfO2–ALD) on silicon (Si) surface using tetrakis(ethylmethylamino) hafnium (TEMAH) and water.

• Stripping of hafnium and zirconium from chelating ion-exchange resin⁶, (Kolon et al. 2022)

Separation of hafnium from zirconium on Diphonix[®] resin is very successful. However, the chemical affinity of these elements to the Diphonix[®] resin is very strong. Therefore, the aim of the present study was to develop a method that would permit the desorption of these metals and the regeneration of the resin. For this purpose, solutions of various ligands such as citrate, oxalate, EDTA, tiron, and carbonate were examined. The lowest weight distribution coefficients of hafnium and zirconium on Diphonix[®] resin were obtained using a 0.25 M ammonium oxalate solution. Its use gave satisfying results with a very good level of the metals recovery in dynamic studies. Due to difficulties in the processing of the obtained zirconium(IV) (hafnium(IV)) oxalate into zirconium(IV) (hafnium(IV)) sulfate, some modification of the stripping method was proposed. The elution of the studied elements by ammonium oxalate solution was preceded by elution with 2 M sulfuric acid. It

⁴ <u>https://cordis.europa.eu/project/id/101003405</u>

⁵ <u>https://www.sciencedirect.com/science/article/abs/pii/S0169433222032305</u>

⁶ https://www.sciencedirect.com/science/article/pii/S0277538722003758

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958211





permitted the removal of 70% of the adsorbed zirconium(IV) as a sulfate solution, ready for returning into the Zr and Hf ion-exchange separation process.

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