SCRREEN2

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FACTSHEETS UPDATES **BASED ON THE EU FACTSHEETS 2020**

ZIRCONIUM

AUTHOR(S):

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ZIRCONIUM

OVERVIEW

Zirconium (chemical symbol Zr) is a metal recovered from zircon (zirconium silicate, $ZrSiO_4$) and baddeleyite (zirconium oxide, ZrO_2), which are extracted from mineral sands and alkaline complexes, respectively. Approximately 75% of zirconium ore is directly used as zircon, while the remaining is transformed in zirconium oxide and other chemicals, including zirconium metal.

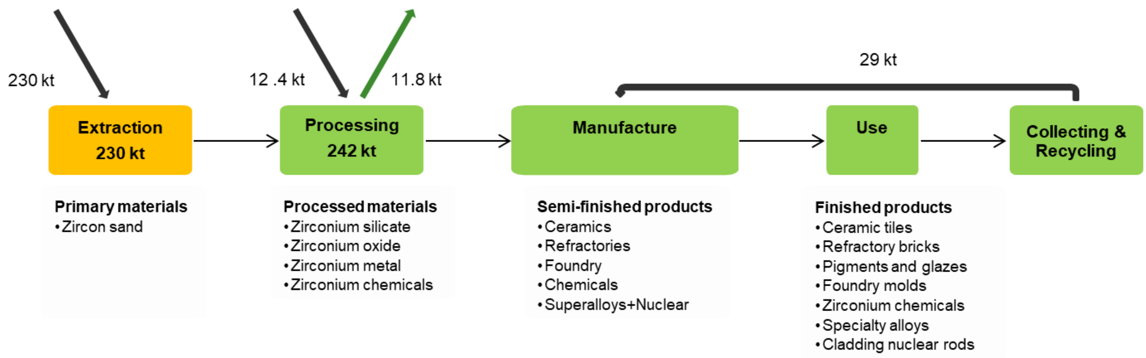

Figure 1. Simplified value chain for zirconium in the EU[1]

Table 1. Zircon supply and demand in metric tonnes, ZrO2 content, 2016-2020 average

Global production	Global Producers	EU consumption	EU Share	EU Suppliers	Import reliance
927000	Australia 34% South Africa 23% Mozambique 11% China 9%	149000	16%	South Africa 42% Australia 32% Mozambique 10% Senegal 9%	83%

Prices: Together with the COVID-19 situation, price trend up to 2021 suggests that zirconium dioxide prices will slightly decrease for 2022(DERA, 2021a). The price volatility of zirconium dioxide was 5% between June 2020 and May 2021 (DERA, 2021b). This shows a reduction of price volatility compared with the 2016-2020 trend, in which zirconium price volatility was around 17%.

Primary supply: The production of zirconium comes essentially from deposits of heavy mineral sands, which are primarily exploited for titanium ore and secondarily for zircon (monazite and further minerals). This circumstance makes zircon output and price somewhat dependent on the demand of titania. Australia, China, South Africa, Indonesia, Mozambique consist the main world producers of zirconium sand the last two decades. United States is a significant producer since 2016.

[1] JRC elaboration on multiple sources (see next sections)

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Secondary supply: Overall end-of life recycling input rate (EoL-RIR), considering each application share, could be indicated around 12% (SCRREEN workshops, 2019). Zirconium included in ceramics, refractories, pigments and alloys cannot be recovered as zirconium compounds. A number of European recycling companies report the Zr recycling contained in: metallic rods, tubes, round bolts, rods, heat exchangers, crystal bars, sputter targets and zirconium alloys (buss-spezialmetalle.de, rsrecycling.eu), however, there are no data concerning the recycling methodologies and the end-product.

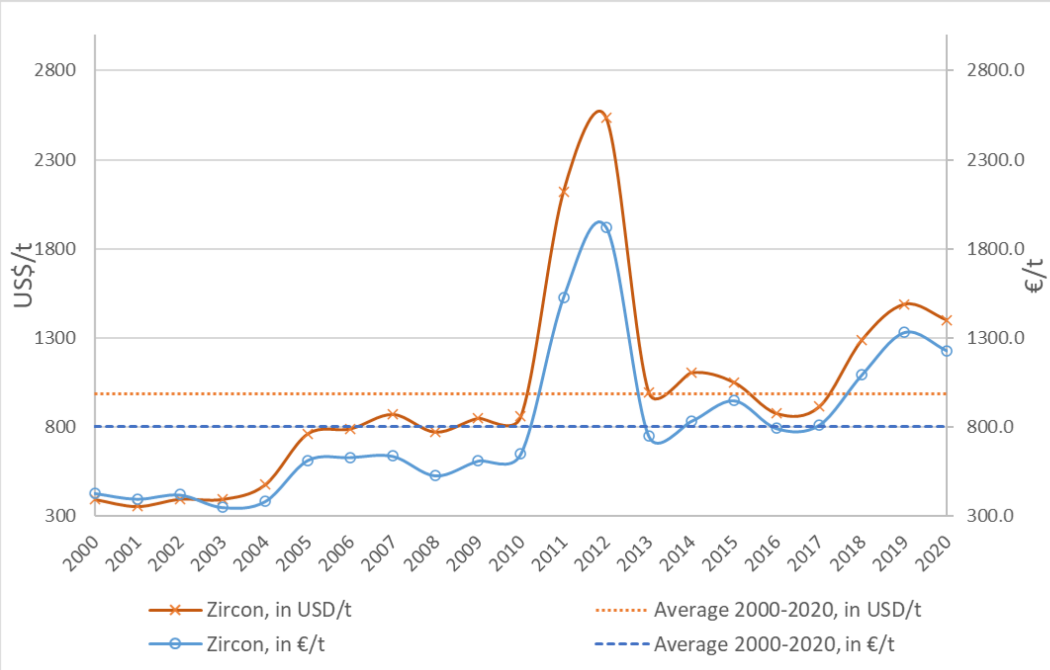

Figure 2. Annual average price of zirconium between 2000 and 2020 (USGS, 2021)2.

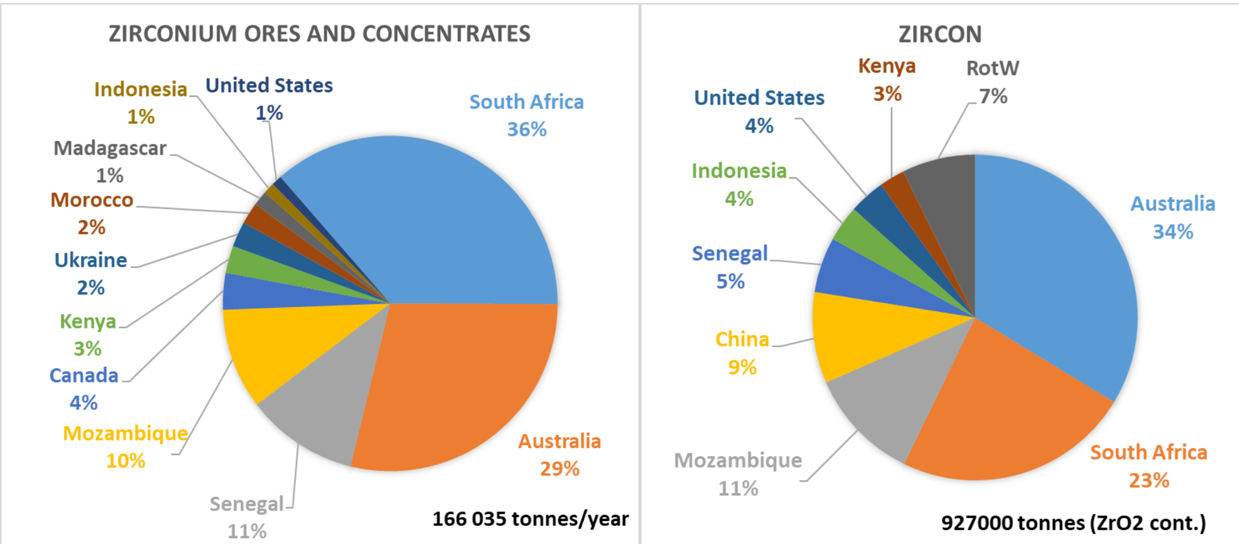

Figure 3. EU sourcing of zirconium and global mine production (ZrO2 cont, average 2016-2020)

[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 (https://www.ecb.europa.eu/stats/policy_and_exchange_rates/euro_reference_exchange_rates/html/eurofxref-graph-usd.en.html)

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Uses: zirconium, as oxide, is mainly used in ceramics, refractories, foundry and pigments. As a metal, it is used in the nuclear industry. It can also be alloys in super alloys.

Substitution: Zirconium compounds find special applications in the manufacturing sector that makes substitution difficult, also because in most cases the alternatives are raw materials with higher price and/or lower production (ILUKA, 2014; Zircon Industry Association, 2015; Kogel, 2006; European Commission, 2017b).

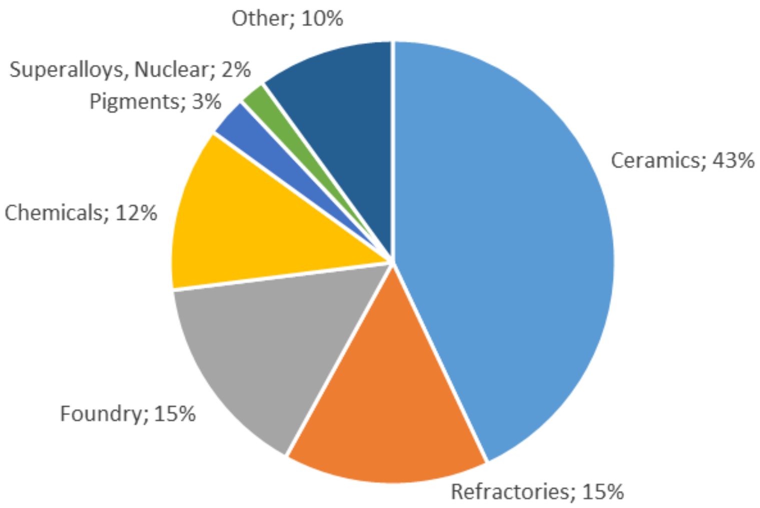

Figure 4: EU uses of zirconium under any forms

Table 2. Uses and possible substitutes

Application	Share	Substitutes	SubShare	Cost	Performance
Foundry	15%	Chromite	20%	Similar or lower costs	Similar
Foundry	15%	Olivine (Magnesium Compound)	10%	Similar or lower costs	Similar
Ceramics	43%	Alumina	10%	Similar or lower costs	Reduced
Ceramics	43%	Wollastonite (Ca, Si, O)	1%	Similar or lower costs	Reduced
Ceramics	43%	Tin	1%	Very high costs (more than 2 times)	Reduced
Ceramics	43%	Tungsten	5%	Similar or lower costs	Similar
Ceramics	43%	Diamond	5%	Very high costs (more than 2 times)	Similar
Refractories	15%	Dolomite, spinel (Magnesium compound)	10%	Similar or lower costs	Reduced
Chemicals	12%	Various substances (titanium, synthetic materials)	10%		

Other issues: The level of toxicity and phytotoxicity associated with Zr is moderately low (Ghosh et al., 1992; Shahid et al., 2013). Yet Zr is also observed to potentially significantly reduce plant growth and affect plant enzyme activity (Shahid et al., 2013). Moreover, zircon is a naturally occurring radioactive material (NORM) and as such is subject to a variety of regulations around the world (Harlow, 2017). Only Senegal (2.4 %) and

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Mozambique (1.4 %) export zirconium whose value represents more than 1 % of the total value of their exports. Mesoporous Zirconium Hydroxide was reported as a material with high CO_2 capacity and sustainable adsorption-desorption performance (Kamikura et al., 2016). Great potential in the carbon capture process has also been reported in mixed matrix membranes (MMMs) with zirconium-based metal-oxide frameworks (MOFs) (Elhenawy et al., 2020).

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MARKET ANALYSIS, TRADE AND PRICES

GLOBAL MARKET

Table 3. Zircon production (ZrO_2 content) and EU demand (extraction) in metric tonnes, 2016-2020 average

Global production	Global Producers	EU consumption	EU Share	EU Suppliers	Import reliance
927000	Australia 34% South Africa 23% Mozambique 11% China 9%	149000	16%	South Africa 42% Australia 32% Mozambique 10% Senegal 9%	81%

Zirconium (together with hafnium) appears in nature as mineral zircon ($ZrSiO_4$), and less abundantly in the form of baddeleyite (ZrO_2) (Xu et al., 2015). However, the market is divided by occurrence and product type. In terms of occurrence, the market is distributed in three categories: zircon, zirconia, and others (Mordor Intelligence, 2021). For product type, the market divided in zircon sand, zircon opacifier, refractories, zircon chemicals, and zircon metal (Mordor Intelligence, 2021).

Zircon is retrieved as by-product of the mining of titanium minerals, ilmenite and rutile, or tin minerals (USGS, 2021). The main uses of zircon are refractories, foundry sands, and ceramic opacification (USGS, 2021). For nuclear applications, the production of zirconium comprises ore cracking, hafnium separation, calcination, pure chlorination and reduction to the pure metal (Xu et al., 2015)

In 2020, the main producers of zircon were Australia, South Africa, and China (USGS, 2021). Furthermore, new countries joined the list of zircon producers in the last decade, especially from Africa (such as Kenya, Madagascar, Mozambique, Senegal, Sierra Leone), which brings an expansion of the bottleneck in zircon supply occurred in the 2000s (European Commission, 2020).

EU TRADE

Table 4. Relevant Eurostat CN trade codes for Zirconium.

Processing/refining	
CN trade code	**title**
26151000	Zirconium ores and concentrates
81092000	Zirconium unwrought, powders

There are two major items of Zirconium that the trade data is available. The items are Zirconium ores and concentrate, and Zirconium articles including powders, unwrought zirconium. Zirconium oxide could be a major trade item but there is no separate trade code for this as it is clubbed together with Germanium oxide in trade databases.

The EU is a net importer of Zirconium ores and concentrates with an average 318000 tonnes of import per year (average 2000-2021). Import was twelve times higher than export in the same period (Eurostat, 2000-2021). Export is about a yearly average 27 kt per year.

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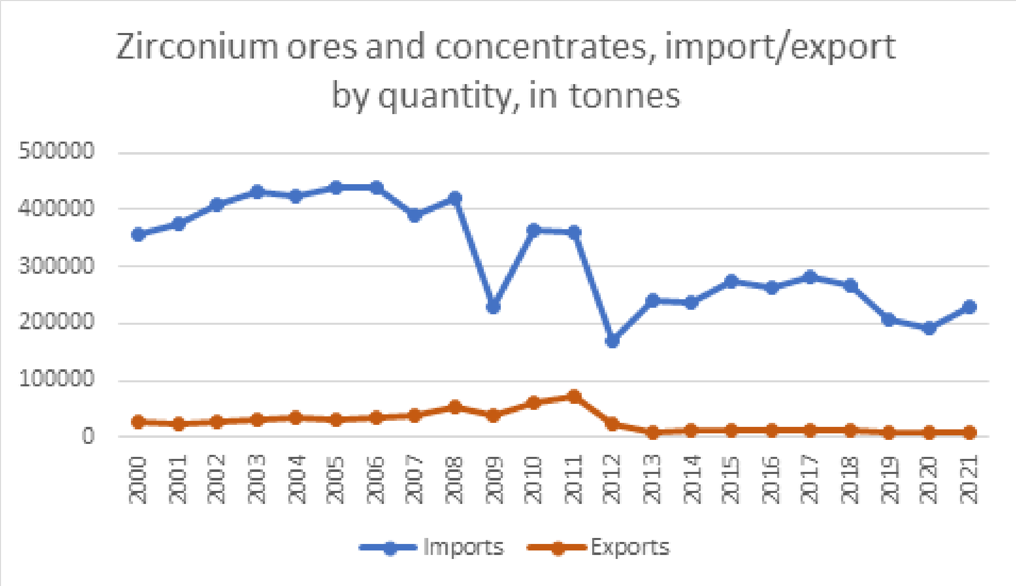

Figure 5. EU trade flows of Zirconium ores and concentrate (CN 25041000) from 2000 to 2021 (Eurostat, 2022)

The main suppliers of Zirconium ore and concentrates between 2000 and 2021 were mainly South Africa and Australia. On an average South Africa supplied about 147 kt followed by Australia 112 kt, Mozambique 20 kt during 2000-2021. African counties provided more than 60 percent of EU Zirconium supply including Madagascar, Kenya, Malawi, Nigeria Morocco and Egypt providing considerable quantities. It should be mentioned that import from Mozambique has been started since 2008 and increased from 4,801 t in 2008 to 27,317 t in 2021. Also, Senegal has been exported Zirconium ore concentrates to EU since 2014. Import from South Africa has been declining over the years. The EU's import from South Africa was 159 kt in 2000 which declined almost half to 66 kt in 2021.

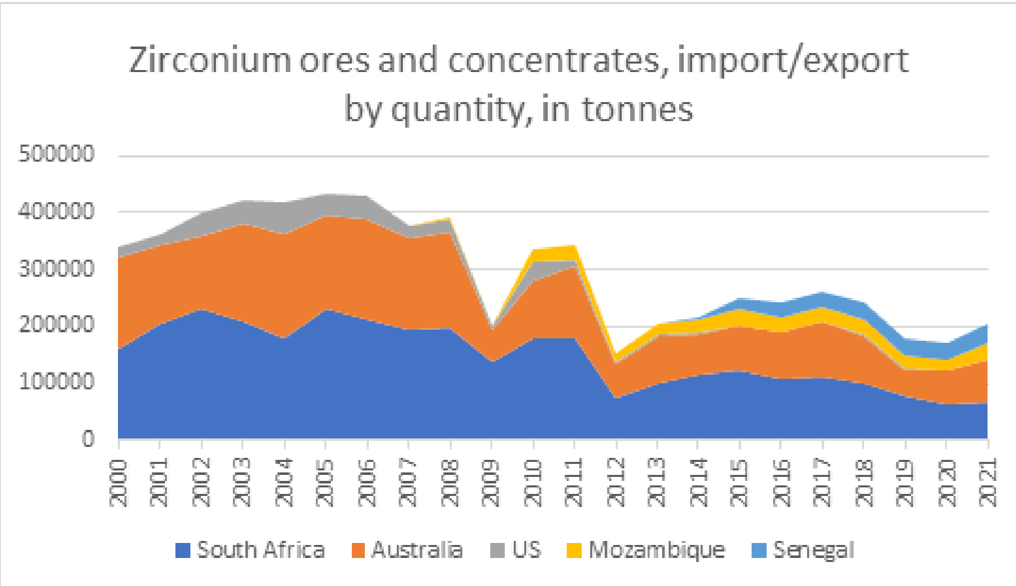

Figure 6. EU imports of Zirconium ores and concentrate (CN 25041000) by country between 2000-2021 (Eurostat, 2021).

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Other than Zirconium ore and concentrates, EU also import and export Zirconium articles including powders, unwrought Zirconium. The average yearly import of these items were equal to 280 tonnes between the period 2002-2021.

The trade data shows that EU also exported an average 280 tonnes of Zirconium articles of powders and unwrought during this period.

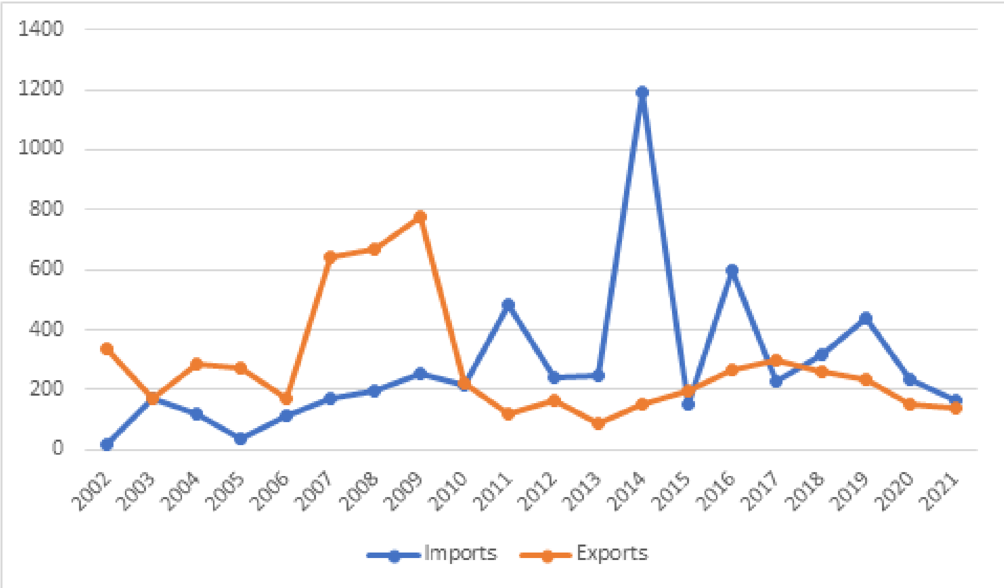

Figure 7. EU trade flows of Zirconium articles unwrought, powders (CN 81092000) from 2000 to 2021 (Eurostat, 2022)

The major source of import for EU was UK, US and China.

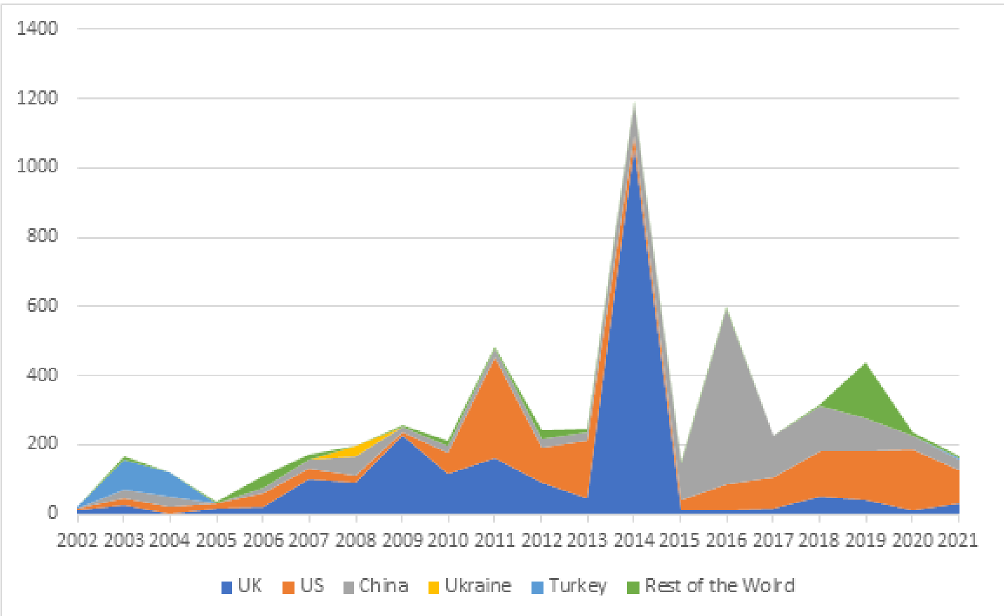

Figure 8. EU imports of Zirconium articles unwrought, powders (CN 81092000) from 2000 to 2021 (based on Eurostat, 2022)

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As per the previous factsheet, there are EU free trade agreements in place with South Africa and Ukraine (bilateral agreement) as well as with Mozambique and Madagascar (Economic Partnership Agreements); a Market Access Regulation concerns Kenya (European Commission, 2019). There are no exports quotas or prohibition in place between the EU and its suppliers (OECD, 2019). An export prohibition from Indonesia took place in 2014, but apparently it was not applied, as exports from the country to the EU continued. Export taxes (below 25%) are applied in China and Vietnam.

PRICE AND PRICE VOLATILITY

In 2020, the global production and demand of zirconium was marginally reduced because of COVID-19 outbreak (USGS, 2021). Although the COVID-19 impacts, there were several mining projects for zirconium worldwide (ILUKA Resources, 2021; USGS, 2021). However, the new mining projects are under construction, which implies that the capacity is still unavailable by 2021. Together with the COVID-19 situation, price trend up to 2021 suggests that zirconium dioxide prices will slightly decrease for 2022 (DERA, 2021a). The price volatility of zirconium dioxide was 5% between June 2020 and May 2021 (DERA, 2021b). This shows a reduction of price volatility compared with the 2016-2020 trend, in which zirconium price volatility was around 17%.

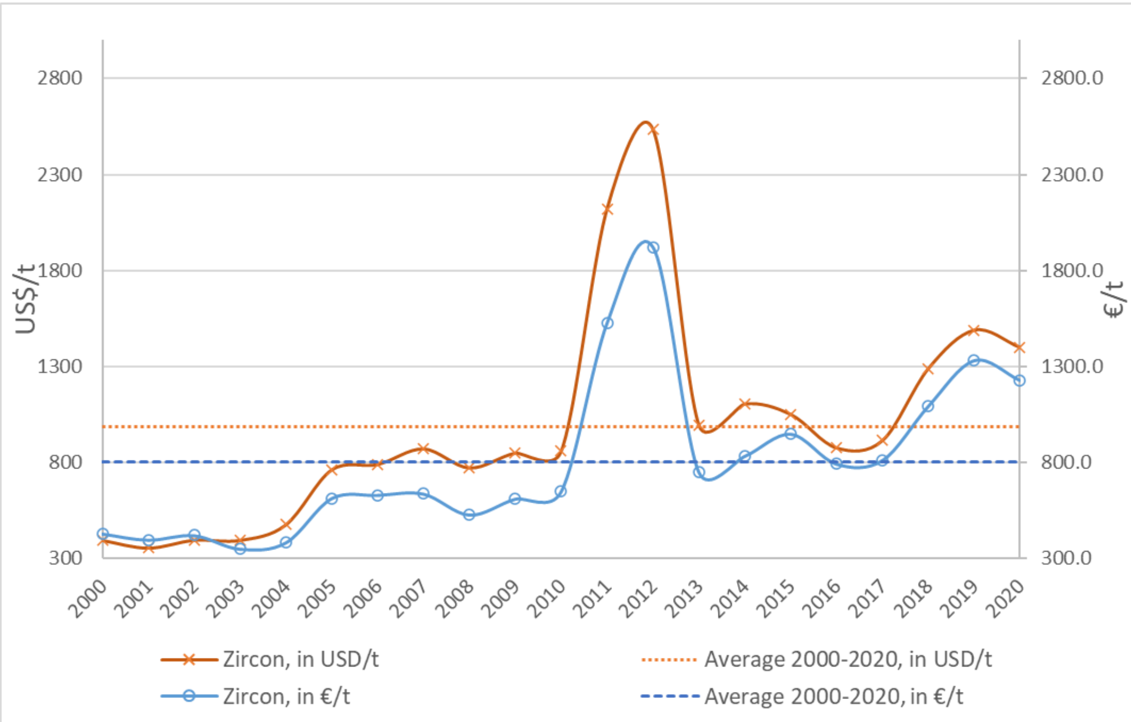

Figure 9. Annual average price of zircon between 2000 and 2020, in US$/t and €/t (USGS, 2021) [3]. Dash lines indicate average prices for 2000-2020.

[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 (https://www.ecb.europa.eu/stats/policy_and_exchange_rates/euro_reference_exchange_rates/html/eurofxref-graph-usd.en.html)

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OUTLOOK FOR SUPPLY AND DEMAND

In general, the drivers of zircon market depends on changes in the ceramic manufacturing and the titanium market (European Commission, 2020). Any forecast is difficult because market fluctuations are only partially linked to economic geology or technological issues concerning zirconium end-use. The outlook for ceramic ware is of continuous growth of global production, by now driven by demographic pressure in transition and developing countries. Nevertheless, zircon market is expected to slow down in the next years as key sectors (such as ceramic tiles) are expected to decreasing as well (European Commission, 2020). During the COVID-19 pandemic in 2020, zircon production was already slightly lower compared with the 2019 production as result of reduced consumption, and power and impacts on labour (USGS, 2021). The conversion to digital decoration has been reducing the fraction of zircon used in ceramic tile making, because of lower amounts of glazes, pigments and opacifiers applied on tiles (European Commission, 2020).

DEMAND

GLOBAL AND EU DEMAND AND CONSUMPTION

The apparent EU annual Zirconium demand is averaged 149 kt per year between 2019 and 2020.

Zirconium extraction stage EU consumption is presented by HS code CN 26151000 zirconium ores and concentrates. Import and export data is extracted from Eurostat Comext (2021). Production data is extracted from Eurostat Prodcom (2021) using PRCCODE 07291935.

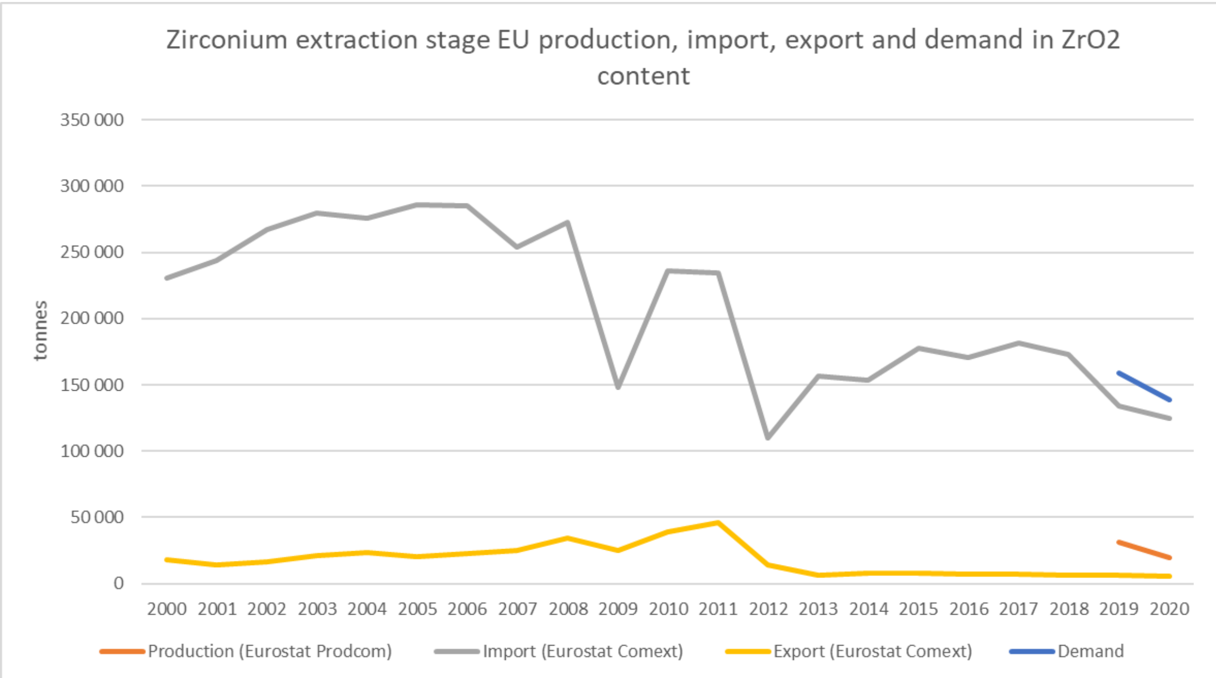

Figure 10. Zirconium (CN 26151000 zirconium ores and concentrates) extraction stage apparent EU consumption. Production data from Eurostat Prodcom (2021) is available on for 2019-2020 and is presented by sold production. Consumption is calculated in ZrO_2 content (EU production+import-export).

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Based on Eurostat Comext (2021) and Eurostat Prodcom (2021) average import reliance of zirconium at extraction stage is 83.1 % for 2019-2020. The share of zirconium metal consumed annually in the EU is around 3,200 t (average 2012-2016). Zirconium processing stage EU consumption cannot be presented due to lack of information on zirconium metal production at the processing stage in the EU27.

EU USES AND END-USES

Erreur ! Source du renvoi introuvable. presents the main uses of zirconium in the EU as an average of 2012 to 2 016. To the best of our knowledge, there does not exist more recent data on the zirconium consumption pattern in the EU. The numbers were reviewed and confirmed for current validity by the Zircon Industry Association (2021).

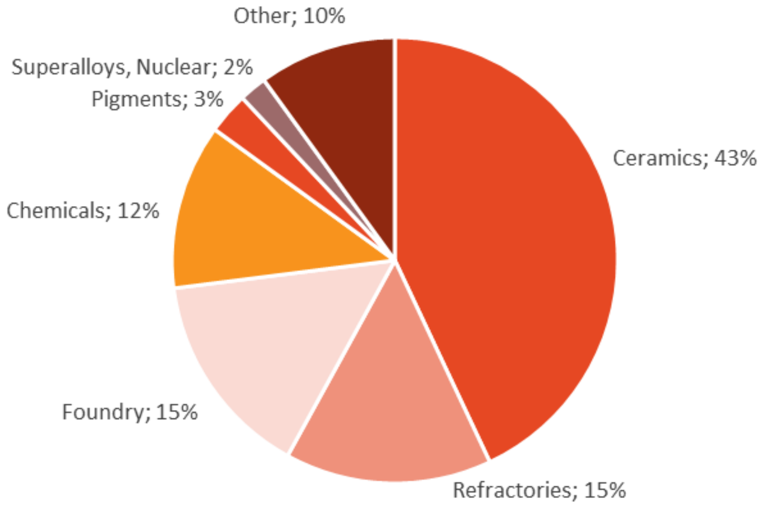

Figure 11. EU end uses of zirconium (Zircon Industry Association, 2015). Average figures for 2012-2016, reviewed on current validity by the Zircon Industry Association.

Industry sectors relevant for zirconium demand analysis are described in **Erreur ! Source du renvoi introuvable.** using the NACE sector codes (Eurostat, 2021). The development of gross value added by these sectors since 2000 is shown in **Erreur ! Source du renvoi introuvable.**.

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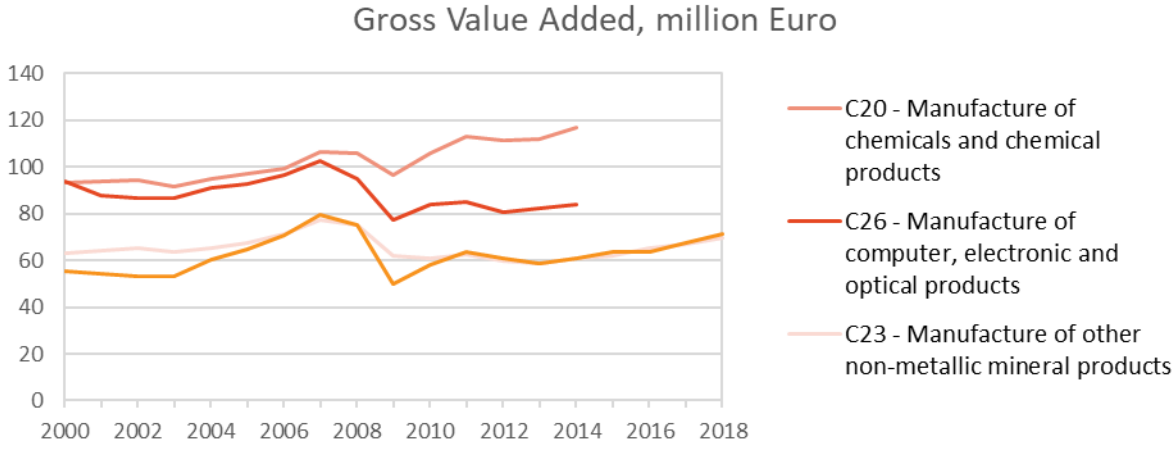

Figure 12. Value added per 2-digit NACE sector over time (Eurostat, 2021)

Table 5. Zirconium applications, 2-digit and associated 4-digit NACE sectors, and value added per sector 2019 (Eurostat, 2022).

Applications	2-digit NACE sector	Value added of NACE 2 sector (M€)	4-digit CPA
Ceramics	C23 - Manufacture of other non-metallic mineral products	69,888	C23.31 - Manufacture of ceramic tiles and flag; C2341 - Manufacture of ceramic household and ornamental articles; C2342 - Manufacture of ceramic sanitary fixtures; C2344 - Manufacture of other technical ceramic products; 23.91 - Production of abrasive products
Refractories	C23 - Manufacture of other non-metallic mineral products	69,888	C2320 - Manufacture of refractory products
Foundry	C24 - Manufacture of basic metals	71,391	C2454 - Casting of other non-ferrous metals
Chemicals	C20 - Manufacture of chemicals and chemical products	117,093*	C2013 - Manufacture of other inorganic basic chemicals
Pigments	C20 - Manufacture of chemicals and chemical products	117,093*	C2012 - Manufacture of dyes and pigments
Superalloys, Nuclear	C24 - Manufacture of basic metals	71,391	C2445 - Other non-ferrous metal production; C2446 - Processing of nuclear fuel
Others	C26 - Manufacture of computer, electronic and optical products	84,021*	

APPLICATIONS OF ZIRCONIUM IN THE EU

CERAMICS

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Zircon, a mineral containing zirconium silicate, is used as an opacity enhancer and whitener in ceramic production. The main application is the manufacturing of tiles, accounting for 85 % of zirconium consumption for ceramics. Other end uses are sanitary ware, tableware, frit and glazes, and technical ceramics including abrasives and dentistry. Beside zircon, zirconia (zirconium dioxide) is used as a pigment in the ceramic products described above and in fabrication of special electro-ceramics, due to its piezoelectric property (Zircon Industry Association 2019).

REFRACTORIES

The inertness, corrosion resistance and low defect potential make zirconium oxides appropriate materials for refractories. The zirconium silicate mineral zircon is used as bricks, lining and mortar in furnaces for molten glass or metals (Zircon Industry Association 2019).

FOUNDRY

Zircon sands and flours are used as facing and surface coating of moulds. 67 % of the zircon in foundry is used for sand casting, 29 % for investment casting and the remaining 4 % for aluminium Cosworth casting (Zircon Industry Association 2019).

CHEMICALS

Zirconium chemicals encompass zirconium oxychloride, boride, nitride, sulphate, carbonate, and hydride (among others) used in several application fields, e.g. coatings, cosmetics, paper, paint and ink or catalysis.

PIGMENTS

In the pigment industry, zirconium oxide is used for ceramic pigments, inks, paper coatings, paint driers, etc.

SUPERALLOYS

Zirconium metal is used in superalloys in two distinct forms: Hafnium-bearing zirconium metal is used in specialty alloys and for application in corrosive environments, while hafnium-free zirconium metal is used as cladding for nuclear fuel rods and for structural materials in nuclear reactors.

OTHER

In addition, there are miscellaneous applications of zircon, zirconia and zirconium, including glasses, sensors, catalysts, materials for electronics and fuel cells. In glass, zirconium functions as an X-ray absorber (Zircon Industry Association 2019). Zirconium powder is used for pyrotechnics, e.g. for airbag inflators and ammunition (Nielsen and Wilfing 2012).

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Table 6. Uses and possible substitutes of zirconium or zirconium oxide

Application	Share	Substitutes	SubShare	Cost	Performance
Foundry	15%	Chromite	20%	Similar or lower costs	Similar
Foundry	15%	Olivine (Mg Compound)	10%	Similar or lower costs	Similar
Ceramics	43%	Alumina	10%	Similar or lower costs	Reduced
Ceramics	43%	Wollastonite (Ca, Si, O)	1%	Similar or lower costs	Reduced
Ceramics	43%	Tin	1%	Very high costs (more than 2 times)	Reduced
Ceramics	43%	Tungsten	5%	Similar or lower costs	Similar
Ceramics	43%	Diamond	5%	Very high costs (more than 2 times)	Similar
Refractories	15%	Dolomite, spinel	10%	Similar or lower costs	Reduced
Chemicals	12%	Various substances (titanium, synthetic materials)	10%		

Zirconium compounds find special applications in the manufacturing sector that makes substitution difficult, also because in most cases the alternatives are raw materials with higher price and/or lower production (ILUKA, 2014; Zircon Industry Association, 2015; Kogel, 2006; European Commission, 2017b).

In the ceramic field, zircon can be substituted mainly by alumina, wollastonite, and tin dioxide in coatings for tiles, sanitaryware, and tableware. Alumina, tungsten (tungsten carbide) and diamond are valid alternatives in abrasives and some technical ceramics.

In some cases, the substitution of zirconia, as in dentistry, would imply a step behind to old technologies (using porcelain, hence kaolin-silica-feldspar).

In the refractories industry, zirconium silicate can be replaced by magnesium compounds, namely dolomite or spinel in certain high-temperature applications. However, zirconium oxide cannot find any prompt substitution in fused alumina-zirconia refractories for the lining of glass furnaces.

Chromite and olivine can be used instead of zircon for some foundry applications.

In pigment manufacture, zirconium is hardly replaceable, even though tin oxide doped with vanadium may substitute yellow zircon (doped with praseodymium) as well as cobalt aluminate might substitute turquoise zircon (doped with vanadium).

Niobium, stainless steel and tantalum provide limited substitution for nuclear applications (for Zirconium metals).

Silver-cadmium-indium control rods are used in lieu of hafnium at numerous nuclear powerplants.

Zirconium can be used interchangeably with hafnium in certain superalloys. (USGS, Zirconium factsheet 2022)

Chemical processing plant applications have several possible substitutes, including titanium and synthetic materials

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SUPPLY

EU SUPPLY CHAIN

The production of zirconium comes essentially from deposits of heavy mineral sands, which are primarily exploited for titanium ore and secondarily for zircon (monazite and further minerals). This circumstance makes zircon output and price somewhat dependent on the demand of titania. EU zircon imports as ZrO_2 during the period 2016-2020 were ranged between 124.000 and 182.000 tonnes, while the average produced amount in the years 2019 and 2020 was around 25.000 tonnes (Eurostat, 2020). The main consumers are Spain (≈124 kt), Italy (≈51 kt), France (≈21 kt) and Germany (≈15 kt). Zircon sand is imported mainly from South Africa, Australia, Senegal and Mozambique (Eurostat, 2019). The zirconium metal consumed annually in the EU was 3,200 t (average 2012-2016), with France accounting for ~86%, followed by Romania (~5%), Italy (~3%) and Belgium (~2.5%). The import of zirconium metal to the EU comes from the United States (~1300 t, 37%), China (~1278 t, 36%), and the United Kingdom (~534 t, 15%), plus minor contribution from South Korea, Canada and Russia (Eurostat, 2019). The EU exports about 343 t per year (average 2017-2018) mostly by Germany (~94%).

SUPPLY FROM PRIMARY MATERIALS

GEOLOGY, RESOURCES AND RESERVES OF ZIRCONIUM

GEOLOGICAL OCCURRENCE

Zirconium deposits exploit concentrations of zircon ($ZrSiO4$) or baddeleyite ($ZrO2$) of economic importance (USGS, 2017; Minerals4EU, 2019). Other zirconium minerals (e.g., eudyalite, zirkelite, vlasovite, etc) are rare and never reach a concentration high enough to be commercially significant. Zircon is a common accessory mineral in most igneous rocks, especially in granitic suites and corresponding metamorphics, where it is usually present in small amount. Nevertheless, being highly resistant to weathering and physical degradation, zircon tends to be enriched in some sedimentary rocks, particularly in river and beach sands, where it can be found in the heavy minerals fraction (together with tourmaline, rutile, ilmenite, leucoxene, etc). Such placer deposits are essentially located along coastlines of stable cratons, where the action of the waves for long time gave rise to sands enriched in heavy minerals (up to 10-20%). Both strand line (active or fossil beaches) and aeolian dune deposits are exploited. In these deposits, zircon is always associated to titanium minerals, which represent the main target of mining operations. The zircon-to-rutile ratio is on average 1:5, even though it can be sometimes higher, up to 2:1 (ILUKA, 2014). Deposits in operation are along the coasts of Australia, Africa, southern Asia and the Americas. Baddeleyite deposits are very rare and found only in peculiar alkaline igneous complexes (USGS, 2017; Murphy, 2006): Kovdor in the Kola Peninsula (Russia), Poço de Caldas, Minas Gerais (Brazil), and Phalaborwa (South Africa).

GLOBAL RESOURCES AND RESERVE

Table 7. Global reserves of zircon sand in 2021 (USGS, since 2000

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Country	Zircon Reserves (thousand metric tonnes in ZrO_2 content)
Australia	50000
China	500
South Africa	21.0
Kenya	50
Mozambique	1800
USA	500
Others	11000
World total	70000

Identified world zirconium resources mostly consist of zircon placers and major deposits are preferentially distributed in the Austral hemisphere (Australia, South Africa, Brazil) and southern Asia (India, China). World known reserves of zircon sand are estimated at approximately 150 million tonnes, corresponding to about 100 million tonnes of ZrO2 (USGS, since 2000. Australia has the world's largest zirconium reserves, followed by India and South Africa; these three countries account for 80% of global reserves.

EU RESOURCES AND RESERVES

Table 8. Resource data for the EU and surrounding countries compiled in the European Minerals Yearbook of the Minerals4EU website (Minerals4EU, 2019)

Deposit group (type)		Country	Area	Resource number	Commodity Minerals
Placer (paleoplacer)	D	France	Bretagne, Normandie	65	Ti, Zr (zircon)
		non-EU	Ukraine, Greenland	4	
Alkaline igneous rocks (syenite, alkali granite)	O	Finland	Sokli, Katajakangas	3	REE, Nb, Ta, Zr (eudyalite), P, U, etc.
		Sweden	Norra Kärr	1	
		non-EU	Greenland	8	
Residual (bauxite)	O	Greece	Macedonia, Thrace	9	Al, Cr, Fe, Ni, Zr, REE, etc.
Felsic-intermediate igneous rocks (granite, pegmatite)	O	Sweden	Näverån, Björkråmyran	2	REE, U, Th, Y, Zr (zircon)
		France	Squiffiec	1	Zr (zircon)
		Greece	Pagoni Rachi	1	Cu, Mo, Nb, Zr
		non-EU	Norway (Høgtuva)	1	REE, Be, U, Zr
Others (epithermal, metasomatics)	O	Sweden	Tunbyholm, etc.	3	Nb, Ta, U, V, Zr

D = deposit; O = occurrence.

Further occurrences exist in other countries, not covered by this database. In most cases, just the zircon sand placers are classified as deposits. Overall, these resources cannot be summed because no quantitative estimation is available for reserves (Minerals4EU, 2019).

Leading Edge Materials Company estimates that about 10,200 tonnes of zirconium dioxide are going annually to be produces through the metallurgical processing of Norra Karr REE deposit in Sweden (leadingedgematerials, 2021). Zirconium dioxide will be produced as a mixture with REOs and Nb oxide after

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the leaching and the solvent extraction stages. The potentially exploitable Kringlerne REEs deposit in Greenland contains a significant amount zircon. Kringlerne is located in the southern part of the Ilĺmaussaq Complex, containing eudialyte-group minerals and their alteration products (notably catapleiite and nacareniobsite-(Ce)) as the main target minerals. The inferred resources have been estimated at 4300 Mt with a 1.8 wt.% Zr_2O_5 content (Goodenough et al. 2016).

WORLD AND EU MINE PRODUCTION

The primary zirconium production (mainly zircon) by country since 1984 according to WMD data and since 2000 according to USGS data can be seen in **Erreur ! Source du renvoi introuvable.** and **Erreur ! Source du renvoi introuvable.**, respectively. Australia, China, South Africa, Indonesia, Mozambique consist the main world producers of zirconium sand the last two decades. United States is a significant producer since 2016.

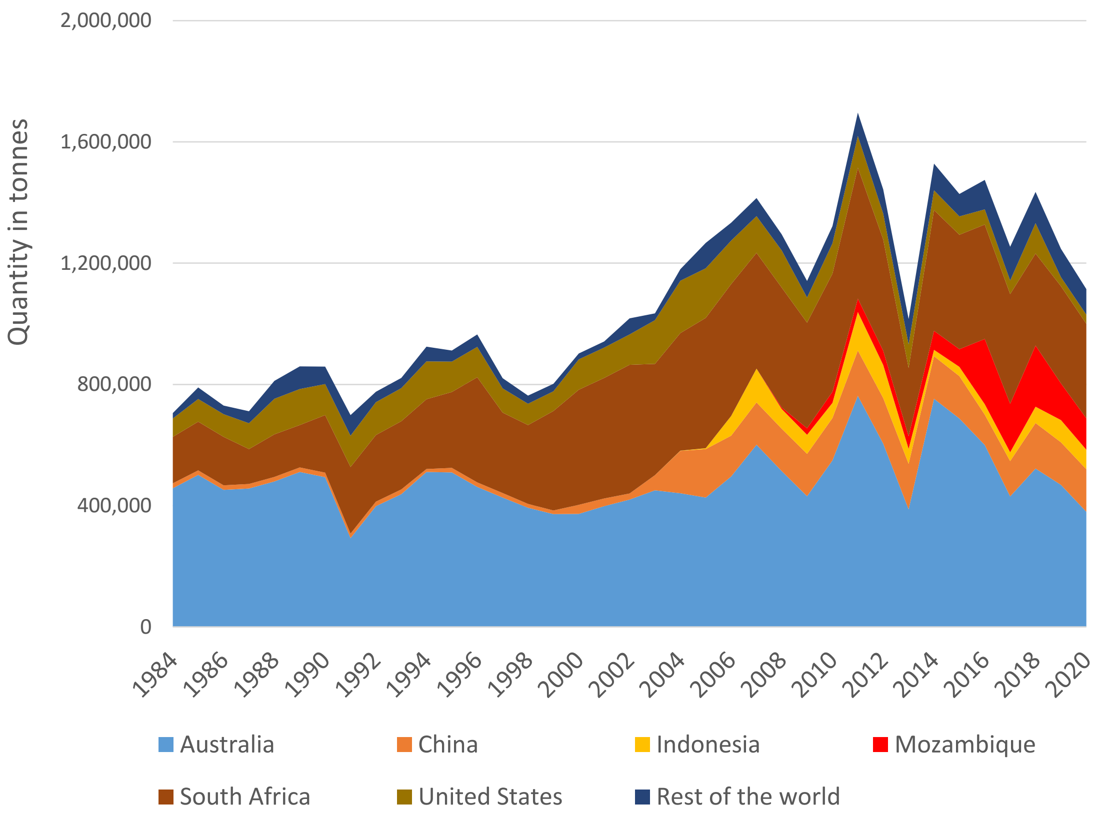

Figure 13. Global primary zirconium production since 1984 (WMD, since 1984).

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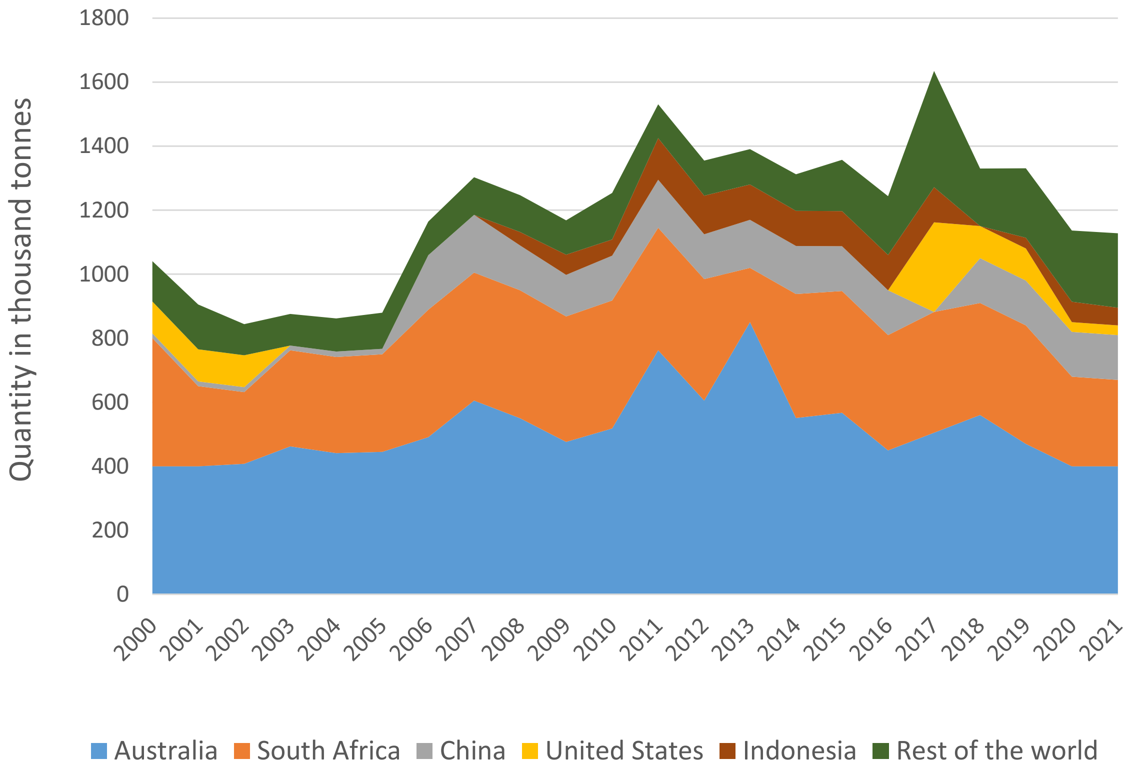

Figure 14. Global primary zirconium production since 2000 (USGS, since 2000).

The following companies are the major producers of primary zirconium concentrates (**Zircomet, 2020**):

- Iluka's zircon production is mainly from it's Jacinth-Ambrosia mine in south Australia
- Rio Tinto owns Richards Bay Minerals in South Africa
- Tronox/Cristal owns mines in both South Africa and Australia
- Kenmare owns the Moma mine in Mozambique
- TiZr operates a mine in Senegal

OUTLOOK FOR SUPPLY

The global demand for zircon sand in 2019 was 1.2 Mt. The annual growth rate in demand estimated to increase to 2.7% until 2023. Zirconium oxide demand is expected to increase by 3-6% until 2025. On the other hand, the supply annual growth forecast until 2025 is -3.6%. Additionally, there is currently a general lack of quality mineral sand projects, particularly with high zircon assemblage, and a depletion of existing operations. The zirconium compounds is planned to overcome via substitution actions (Zircomet, 2020). Advanced exploration and development projects with planned production of zircon concentrates are taking place in Australia, Madagascar, Mozambique, Senegal, Tanzania, and elsewhere. In the United States, mining and heavy-mineral-processing operations were expanded near Starke, FL, and prefeasibility studies were underway at the Titan heavy-mineral-sands project near Camden, TN. (USGS, 2022).

SUPPLY FROM SECONDARY MATERIALS/RECYCLING

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Overall end-of life recycling input rate (EoL-RIR), considering each application share, could be indicated around 12% (SCRREEN workshops, 2019). Zirconium included in ceramics, refractories, pigments and alloys cannot be recovered as zirconium compounds. However, when refractories and steel alloys are recycled the zirconium remains in the recycled product. Therefore these recycling rates are applicable also for the zirconium which would results in estimated rate of 70% of zirconium utilized.

A number of European recycling companies report the Zr recycling contained in: metallic rods, tubes, round bolts, rods, heat exchangers, crystal bars, sputter targets and zirconium alloys (buss-spezialmetalle.de, rsrecycling.eu), however, there are no data concerning the recycling methodologies and the end-product.

The recycling (purification) of Zr-containing cladding components in nuclear reactors has been the subject of researches. The purification is preformed through chlorination or hydrochlorination, therefore the process could be incorporated into the process of metallic Zr production which involves the formation and purification of ZrCl4 as an intermediate product (Collins et al., 2012) (**Erreur ! Source du renvoi introuvable.**). The involving of the chlorination/hydrochlorination process in the recycling concept, will enable the linking between the recycling and the primary production of metallic cladding hulls which are also produced through a chlorination process as it will be described in the following "processing" subsection.

The recycling of Zry-4 scrap alloy (containing Sn) in terms of chemical and microstructure upgrading has been tested using electron beam (EB) and vacuum induction (VIM) technologies. The laboratory-scale results showed that it is feasible to obtain alloys having suitable chemical characteristics, microstructure and mechanical properties for various applications in the nuclear area, chemical industry and medicine such as dental prostheses (Pereira et al. 2020).

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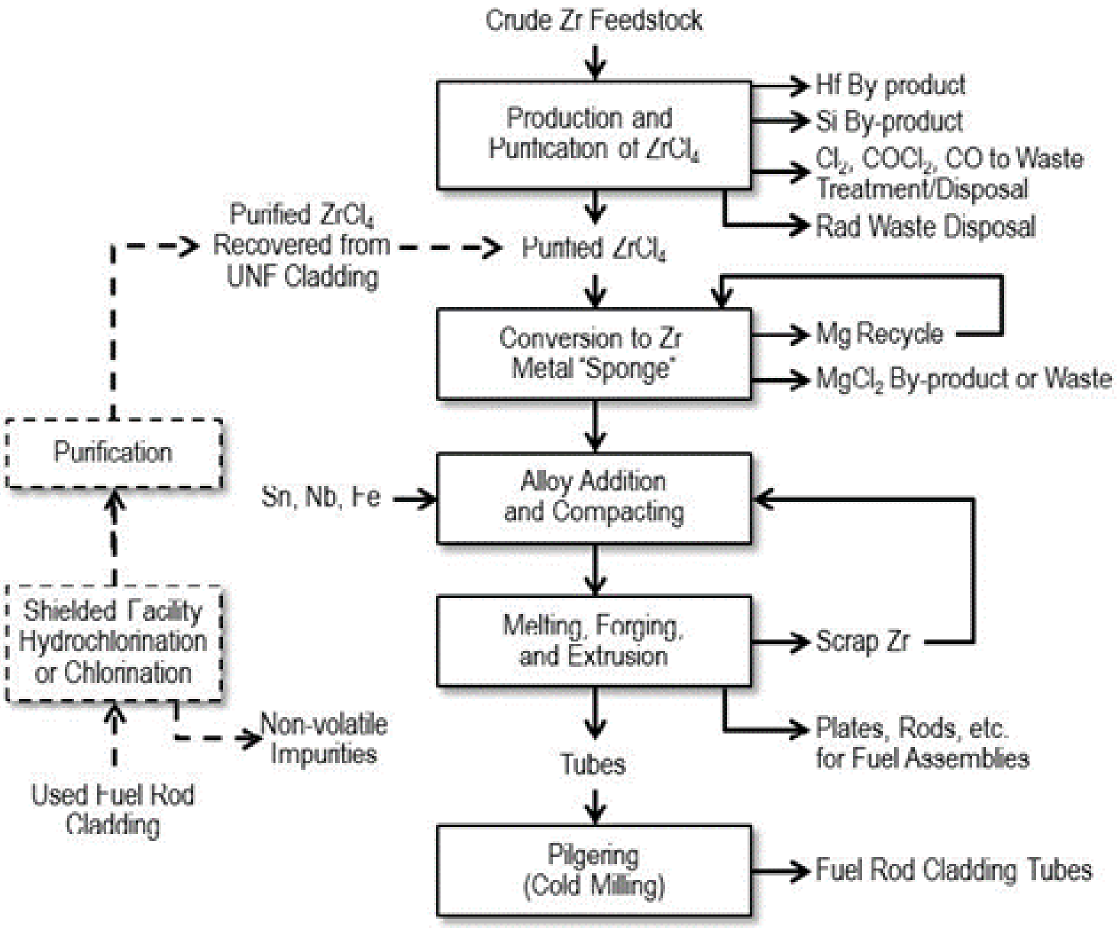

Figure 15. Proposed methodology for the recycling (purification) of zirconium contained in nuclear fuel rod components and the incorporation of the purification into the process of metallic Zr production (Collins et al., 2012).

PROCESSING OF ZIRCONIUM

Heavy minerals sands contain both zircon and titanium minerals (commonly in the 1-10% range by weight). Mining by dredging or dry mining techniques (Murphy, 2006) is followed by washing the sand, then concentrates containing 90-95% heavy minerals are separated from

The silica sand by wet gravity concentration techniques. Specific processes are employed to get zircon sand: electrostatic separation (typically used for separating zircon from rutile); magnetic separation (zircon from leucoxene, monazite and ilmenite), gravity separation (zircon from kyanite, feldspars and quartz). Iron and aluminum oxide coatings at the surface of zircon grains are removed by hot acid leaching. In some cases, the final product is calcined at approximately 900°C to render the zircon whiter.

Zirconia is the main end-product of zircon processing directly suitable for many uses in a variety of ceramics and coatings. The decomposition of zircon by the reaction with sodium hydroxide is the most common method

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for obtaining the pure oxide (Blanchart, 2018). At temperatures above 600 °C, sodium hydroxide and zircon react to form sodium zirconate and sodium silicate according to the reaction:

$ZrO_2.SiO_2 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O$

The sodium silicate is removed by leaching with water and sodium zirconate is hydrolyzed to produce a hydrated Zr hydroxide. The last is calcined to form impure zirconium oxide which is purified by leaching with sulfuric acid.

Altrenatively, zirconia is produced via high-temperature processing through the reaction of zircon with lime at 1600 °C according to the reaction (Blanchart, 2018):

$2CaO + ZrO_2.SiO_2 \rightarrow ZrO_2 + CaSiO_4$

Calcium silicate is removed by leaching with hydrochloric acid, while zirconia is washed and dried.

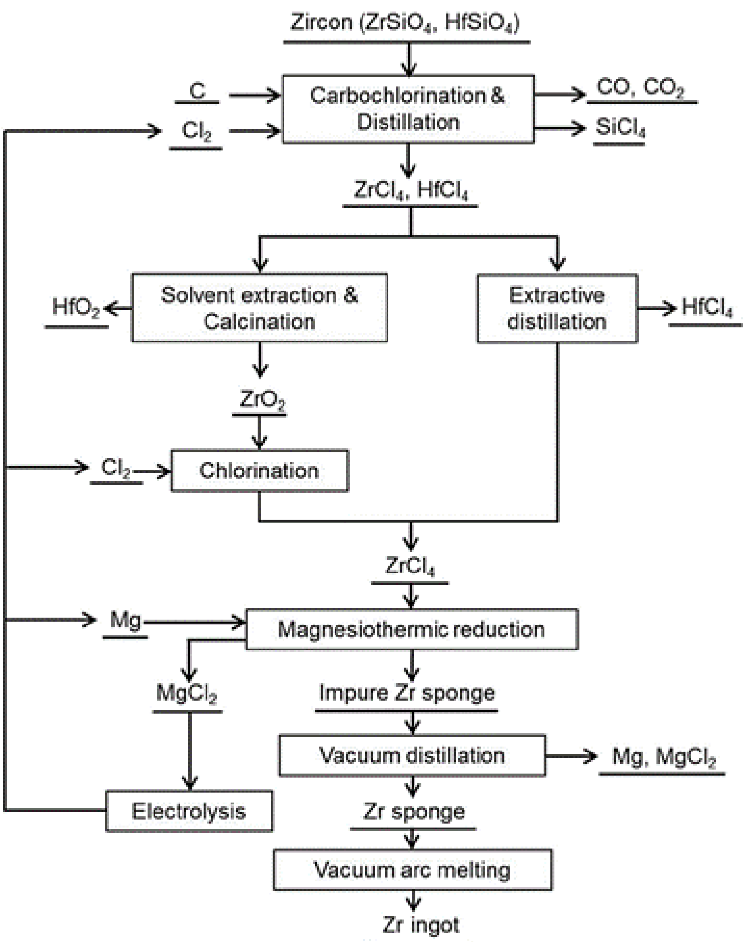

Figure 16. Metallurgical processing for the production of elemental Zr by zircon ore (Xu et al. 2015).

A small fraction of the mineral zircon is processed to the metallic zirconium, which is mainly used for nuclear applications due to its low neutron-absorption cross-section and excellent corrosion resistance properties. The metallurgical processing of zircon ore for the production of elemental Zr is complex and comprises the

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main stages of: Carbochlorination, solvent extraction-calcination, Hf separation, pure chlorination and metallothermic reduction to the pure metal (Xu et al. 2015) (**Erreur ! Source du renvoi introuvable.**). Carbochlorination is processed by heating zircon sand and carbon in a fluidized bed at 1200 °C under the fluidizing gas of chlorine. Its product is a mixture $ZrCl_4$ and $HfCl_4$ and liquid silicon tetrachloride which collected as a by-product and used to produce fiber optic cable, fumed silica and silicon metal for PV panels. The separation of hafnium from zirconium is the crucial step of the nuclear grade zirconium production. The commercially used separation methods consist of various hydrometallurgical routes, including fractional crystallization, methyl isobutyl ketone extraction and tributyl phosphate extraction. Fractional crystallization has also been used at some extent.

OTHER CONSIDERATIONS

HEALTH AND SAFETY ISSUES

The level of toxicity and phytotoxicity associated with Zr is moderately low (Ghosh et al., 1992; Shahid et al., 2013). Yet Zr is also observed to potentially significantly reduce plant growth and affect plant enzyme activity (Shahid et al., 2013). In a context of increasing amounts of Zr emissions to the environment, more data on the plant-soil behaviour of Zr are needed. This will enable to better understand the mechanisms involved in uptake and phytotoxicity of Zr, and accordingly to better assess the potential health risks associated with Zr-polluted plants consumed by humans (Shahid et al., 2013).

Moreover, zircon is a naturally occurring radioactive material (NORM) and as such is subject to a variety of regulations around the world (Harlow, 2017). So far little data enables us to accurately quantify the impacts associated with natural ionising radiation during the production phase of zircon sand in Life Cycle Assessment (Gediga et al., 2019). The NORM issue during the production of zircon sand will be a topic for future research in the LCA field, in terms of reliable data collection and associated assessment of natural occurring radioactivity (Gediga et al., 2019). However, generally, regarding the production of zircon sand, volumes of residues are relatively limited and their activity relatively low (AFCN, 2020). In particular, the measure of the radioactivity in the soil nearby a zircon mineral processing plant, in the North East part of Italy, and the associated estimation of the absorbed dose, showed that the induced radiological impact on the environment and on the population was negligible (Righi et al., 2002).
The use/ban of Zirconium is not restricted under REACH Regulation (EC) No 1907/2006 Annex XVII (Deutsche Forschungsgemeinschaft and Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, 2002).

ENVIRONMENTAL ISSUES

Besides impacts associated with natural occurring radioactivity as mentioned above, the production of Zr metal implies a number of other environmental impacts as classically observed for metals. Only a limited number of studies are available in the literature regarding the environmental impacts of Zr production in a Life Cycle perspective. As for other elements in their metallic form (either metals or alloys), the environmental burden associated with the cradle-to-gate production of Zr metal is calculated to be largely due to the refining

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stage (Nuss and Eckelman, 2014). Considering the 5 impact categories global warming potential, cumulative energy demand, terrestrial acidification, freshwater eutrophication, and human toxicity (cancer and non-cancer), the impact intensity (that is, per kg produced) of Zr (in oxide and metal forms, weighted by the 2008 supply mix) is in the lower range as compared to other elements (Nuss and Eckelman, 2014). The global warming impact of Zr metal is however in the average range as compared to other elements. Moreover, in a more recent study, the production of 1 kg of zircon sand was calculated to generate 0.32 kg-CO_2 equivalent in a life-cycle perspective (Gediga et al., 2019).

NORMATIVE REQUIREMENTS RELATED TO THE USE AND PROCESSING OF ZIRCONIUM

Technical rules for the use of Zirconium powder (pyrophoric) and Zirconium powder (non-pyrophoric) can be found in the GESTIS Substance database[4],[5]. International limit values for zirconium, zirconium compounds, zirconium dioxide, zirconium powder are non-stabilized and zirconium powder that is stabilized can be found in the GESTIS international limit values database[6].

SOCIO-ECONOMIC AND ETHICAL ISSUES

ECONOMIC IMPORTANCE OF ZIRCONIUM FOR EXPORTING COUNTRIES

Table 9 lists the countries for which exports of phosphate and/or phosphate rocks represent a considerable share of the total value of their exports.

Table 9: Share of zirconium exports in total exports

Country	Export value (USD)	Share in total exports (%)
Senegal	93,822,823	2.4
Mozambique	49,530,985	1.4
Madagascar	18,689,124	0.95
Kenya	40,272,403	0.67
South Africa	415,779,751	0.49

Source: COMTRADE (2022), based on data for 2020

Only Senegal (2.4 %) and Mozambique (1.4 %) export zirconium whose value represents more than 1 % of the total value of their exports. For Madagascar (0.95 %), Kenya (0.67 %) and South Africa (0.49 %), the value of their zirconium exports still accounts for more than 0.1 % of their total exports. For all other exporting countries, this share remains below 0.1 %.

SOCIAL AND ETHICAL ASPECTS

[4] See https://gestis-database.dguv.de/data?name=007400
[5] See https://gestis-database.dguv.de/data?name=520040
[6] See https://limitvalue.ifa.dguv.de/WebForm_ueliste2.aspx

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No information available that links zirconium to particular social or ethic aspects.

RESEARCH AND DEVELOPMENT TRENDS

RESEARCH AND DEVELOPMENT TRENDS FOR LOW-CARBON AND GREEN TECHNOLOGIES

a. R&D trends in terms of emerging LCGT

No data available

b. R&D trends in terms of emerging application of RM in already existing LCGT

- **Zr application in photovoltaics**

Zirconium oxide (ZrO_2) films can be used as insulation layers in solar cells (Waghmare, 2017), and nano-ZrO_2 pastes are commercially available to fabricate insulating layers in dye-sensitized solar cell assemblies or perovskite solar cell assemblies. ZrO_2 micro/nanoparticles and other kinds of Zr-based chemicals, like zirconium acetylacetonate ($Zr(C_5H_7O_2)_4$) and barium zirconium sulfide ($BaZrS_3$), are studied for possible use in solar cells and photodetectors (Syrrokostas et al., 2019; Yerramilli et al., 2019; Wei et al., 2020). Zirconium can also be used as a dopant in electron transport layers (ETL) of organic solar cells (OSCs), like in ZnO ETL, to enhance their photovoltaic performance (Song et al., 2021).

- **Zirconium-based catalysts**

Zirconia-based compounds are widely studied as catalysts in different processes, e.g. in biomass conversion, which is of great importance in the sustainable manufacturing of green chemicals and represents a viable way to reduce the use of fossil fuels and carbon emissions (Zhang et al., 2021). Zirconium nitride (ZrN) nanoparticles have been recently shown to result in higher efficiency than the most common Pt catalyst in devices using oxygen reduction reaction (ORR), like fuel cells and metal-air batteries (Yuan et al., 2020).

- **Zirconium application in CO_2 capture**

Mesoporous Zirconium Hydroxide was reported as a material with high CO_2 capacity and sustainable adsorption-desorption performance (Kamikura et al., 2016). Great potential in the carbon capture process has also been reported in mixed matrix membranes (MMMs) with zirconium-based metal-oxide frameworks (MOFs) (Elhenawy et al., 2020).

OTHER RESEARCH AND DEVELOPMENT TRENDS

- Metal-Organic Frameworks as multifunctional materials toward P-sustainability[7]

The EU-funded PSust-MOF project aims to improve the circular use of phosphate-based fertilizers. On top of that the project will use water as the reaction medium for Zr-MOF synthesis compatible with the requirements of industrial production.

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[7] See https://cordis.europa.eu/project/id/888972

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