SCRREEN2

This project has received funding from the European

Union's Horizon 2020 research and innovation programme

under grant agreement No 958211.

Start date: 2020-11-01 Duration: 36 Months

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

SELENIUM

AUTHOR(S):

TABLE DES MATIÈRES

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

SELENIUM

OVERVIEW

Selenium (chemical symbol Se) is a metalloid or semi-metal that can exist either in grey crystalline form or as a red-black powder. It has a hardness of 2.0 on Mohs scale and a melting point of 220.8°C (494 K). Selenium is photoconductive, meaning that its electrical conductivity increases when exposed to light, and photovoltaic, which means it converts light into electricity. It is rare in the Earth's crust, with an abundance of 30-90 parts per billion and inthe upper crust, its abundance is 90 parts per billion (R. ~L. Rudnick and Gao 2003). Although selenium does occasionally occur in native form, it is more commonly found in compounds that also contain base or precious metals. Approximately 90% of selenium produced in the world is obtained from the anode muds resulting from the electrolytic refining of copper, with the remainder obtained from the processing of lead ores.

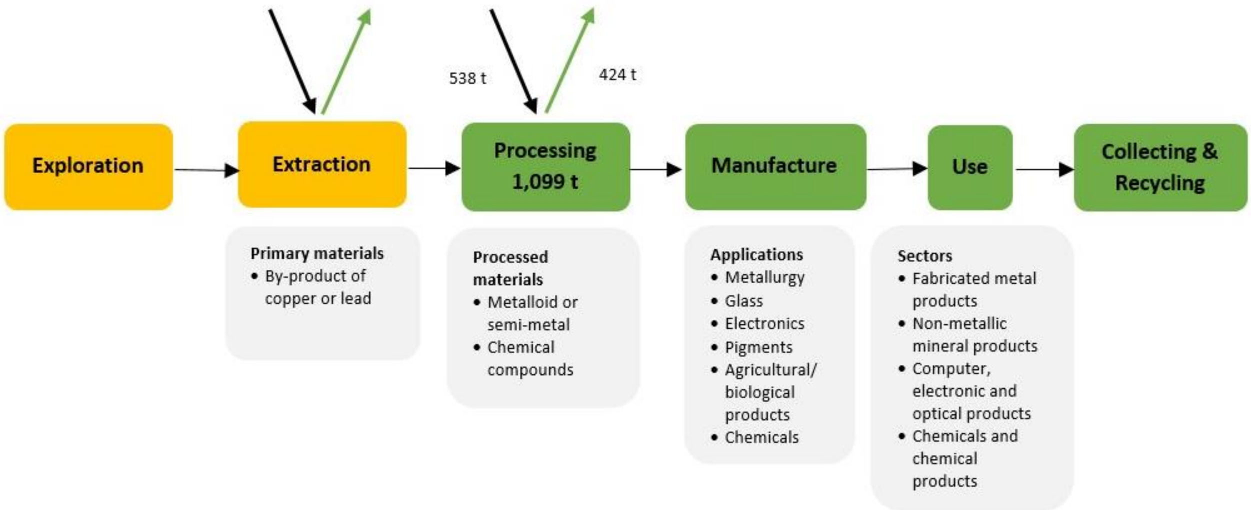

Figure 1. Simplified value chain for selenium in the EU[1]

Table 1. Selenium supply and demand in metric tonnes, 2016-2020 average

Global production	Global Producers	EU consumption	EU Share	EU Suppliers	Import reliance
3,737	China 29% Japan 23% Germany 11% Belgium 6% Russia 6% US 4%	835	22.3%	Russia 23% South Korea 14% Japan 13% China 11% Taiwan 9% Canada 9%	2%

[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

Prices: Selenium prices show very high fluctuations. At the beginning of 2016, the selenium price was stable at around USD 26 per pound whereas the second half of the year prices rose to a monthly average of USD 37 per pound (USGS, 2022). In the 2018-2020 period, selenium prices fluctuated between USD 17 per pound to USD 7 per pound. Moreover, selenium prices are also affected by market supply of copper because selenium is obtained as a by-product of copper refining.

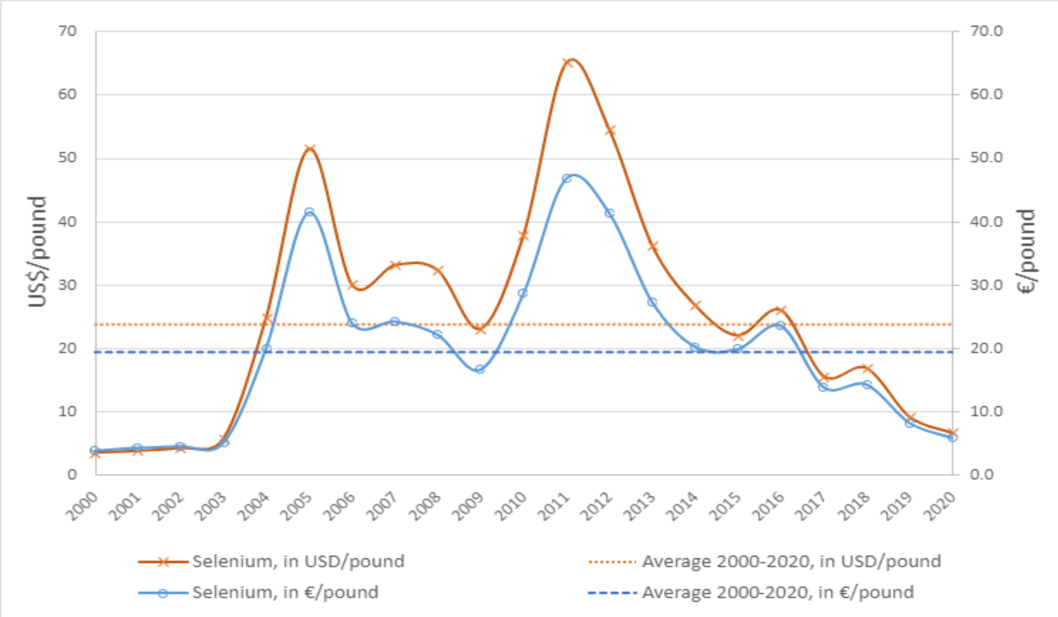

Figure 2. Annual average price of selenium between 2000 and 2020 (USGS, 2021)[2].

Primary supply: Total worldwide production of Selenium, averaged over 2016–2020, amounted to 3,737 t per year and the largest producers are China, Japan, and Germany. The segment for 'other countries' includes Chile, Uzbekistan, India, Serbia and Armenia. Between 2016 and 2020, an average of 815 t of Selenium was produced in EU per year, 23% of global production. Germany and Belgium are the most significant producers (with a production of 300 and 200 tonnes in 2022, respectively). The rest of production is taking place in Poland, Finland and Sweden.

Secondary supply: the recycling rate in Se globally remains very low (<1%). Many of the end uses of selenium are dissipative, meaning that very little material becomes available for recycling. Selenium contents in glass and metallic alloys are too small to be accounted for during recycling processes and selenium-containing scrap from these sources are not normally segregated from other scrap metal or glass with the result that the selenium is further dispersed rather than concentrated. Electronic products are the only secondary source currently available for selenium. The use of selenium in photoreceptors or rectifiers has been declining for some time as selenium-containing compounds are substituted by organic photoreceptors or cheaper silicon-based rectifiers

[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)

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

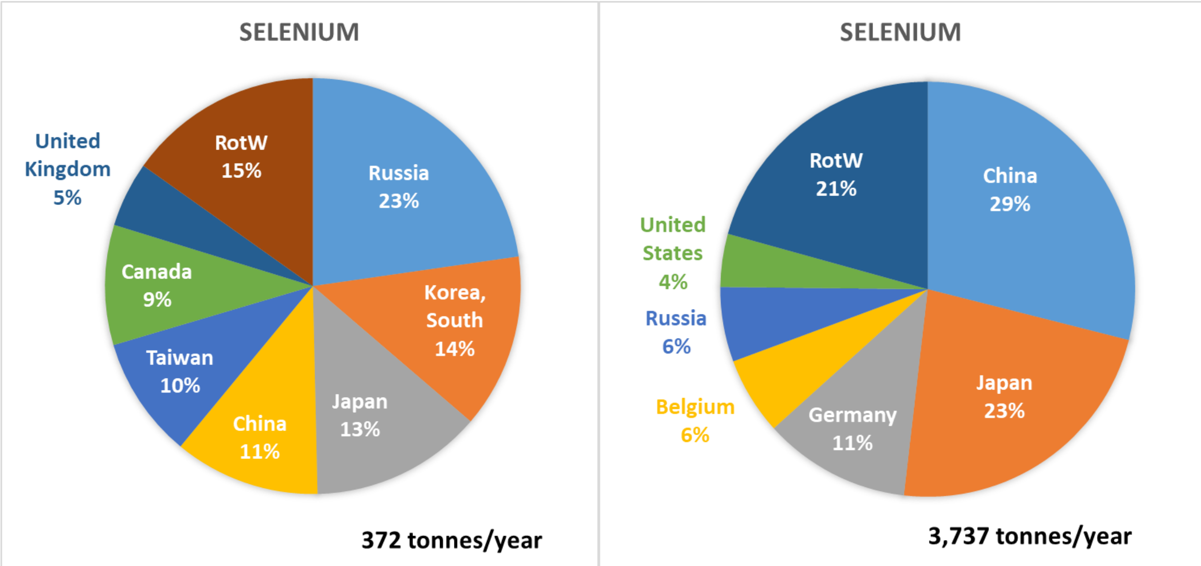

Figure 3. EU sourcing of selenium and global mine production (update)

Uses: End uses for global consumption are metallurgy (including electrolytic manganese production), glass manufacturing, agriculture, chemicals and pigments, electronics, and others (USGS 2022).

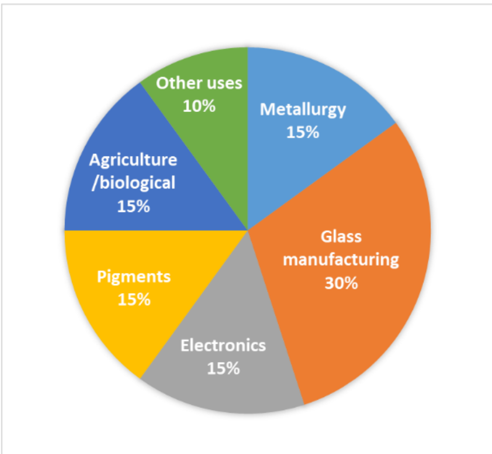

Figure 4: EU uses of selenium

Substitution: in metallurgy, bismuth, lead, and tellurium can substitute selenium to improve the machinability of alloys. In glass, cerium oxide and manganese have been identified as possible alternatives for decolourising glass, while gold chloride and copper-in will add red colouration to glass. Silicon is a major alternative to selenium in many electronic applications, especially solar cells and in rectifiers.

Table 2. Uses and possible substitutes

Use	Share*	Substitutes	Sub share	Cost	Performance
Agriculture/biological	10%	No substitute	100%		No substitute
Electronics	10%	Wafer-based crystalline silicon (substitution for CIGS PV)	47%	Similar or lower costs	Similar

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

		Silicon in low- and medium voltage rectifiers	9%	Similar or lower costs	Similar
		Cadmium telluride (substitution for CIGS PV)	2%	Similar or lower costs	Similar
		Amorphous silicon (substitution for CIGS PV)	0%	Similar or lower costs	Similar
Glass manufacturing	25%	Copper-tin	12%	Similar or lower costs	Similar
		Manganese	13%	Similar or lower costs	Similar
		Gold chloride	12%	Very high costs (more than 2 times)	Similar
		Cerium oxide	13%	Similar or lower costs	Similar
Metallurgy	40%	Sulphur dioxide for electrolytic manganese	1%	Similar or lower costs	Similar
		Bismuth in free-machining alloys	12%	Similar or lower costs	Similar
		Lead in free-machining alloys	12%	Similar or lower costs	Similar
		Tellurium in free-machining alloys	12%	Slightly higher costs (up to 2 times)	Similar
		Sulphur dioxide in free-machining alloys	5%	Similar or lower costs	Similar
		Se-free electrolytic manganese production (functional) of electrolytic manganese: South Africa, CN	1%	Very high costs (more than 2 times)	Similar
Other uses	5%	Tellurium for rubber production	5%	Slightly higher costs (up to 2 times)	Similar
Pigments	10%	Organic materials	50%	Similar or lower costs	Similar

*Global end use shares of selenium (USGS, 2022).

Other issues: all products containing selenium shall be labelled as acutely toxic, as they are classified as toxic if inhaled (H331), toxic if swallowed (H301) and may cause damage to organs through prolonged or repeated exposure (H373). The concentration limit for selenium in drinking water has been set at 10 µg/l by the Drinking Water EU Directive (2020). Selenium is released to the environment primarily by the mining industry. The extraction of coal, precious metals and metallic sulphides provoke emissions of this element to the soil and air, which could eventually diffuse to groundwater and the nearby water bodies (Khamkhash, A. et al., 2017). Under alkaline and oxidising conditions, elemental selenium is transformed into selenates (oxidation state VI) and selenites (oxidation state IV), which are soluble in water

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

MARKET ANALYSIS, TRADE AND PRICES

GLOBAL MARKET

Table 3. Selenium supply and demand (processing) in metric tonnes, 2016-2020 average

Global production	Global Producers	EU consumption	EU Share	EU Suppliers	Import reliance
3,737	China 29% Japan 23% Germany 11% Belgium 6% Russia 6% US 4%	835	22.3%	Russia 23% South Korea 14% Japan 13% China 11% Taiwan 9% Canada 9%	2%

The estimated average world annual production of selenium in the period 2016-2020 was about 3,700 t per year. China and Japan are the leading processing countries, but there is also significant selenium production in Europe. The average EU annual production of selenium in the period 2016-2020 is about 815 t, production takes place mainly in Germany (Retorte GmbH part of Aurubis Group) and Belgium (Umicore).

End uses for global consumption are metallurgy (including electrolytic manganese production), glass manufacturing, agriculture, chemicals and pigments, electronics, and others (USGS 2022). In China, the largest consumer and producer of selenium, selenium dioxide is used to produce manganese flakes. The average amount of selenium (CN8 code 28049000 "Selenium") imported by the EU between 2016 and 2020 was 531 t per year. Selenium EU imports originated from Russia (21 %), Japan (15 %) and South Korea (14 %) as well as various other countries. The average amount of selenium exported by the EU was about 503 t per year, with India, the USA and China as the main destinations. Selenium materials are not traded on exchanges. Purchase contracts are typically negotiated between buyer and seller.

EU TRADE

For this assessment, selenium is evaluated at processing/refining stage.

Table 4. Relevant Eurostat CN trade codes for selenium.

Processing/refining	
CN trade code	**title**
280490	Selenium

Figure 5 shows the import and export trend of selenium. Although it has been fluctuating, the average EU import and export of Selenium in the past two decades (2000-2021) was similar in quantity at approximately 10,000 tonnes. Figure 6 illustrates the share of import in EU for Selenium from various countries. The main suppliers to EU in the past two decades (2000-2021) have varied between the major and minor suppliers. The main suppliers to the EU are Russia (23%), South Korea (14%), Japan (13%), China (11%), Taiwan (9%), Canada (9%) and UK (5%). The share of other countries is 15%. No trade restrictions related to selenium were reported in 2022 (OECD 2022).

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

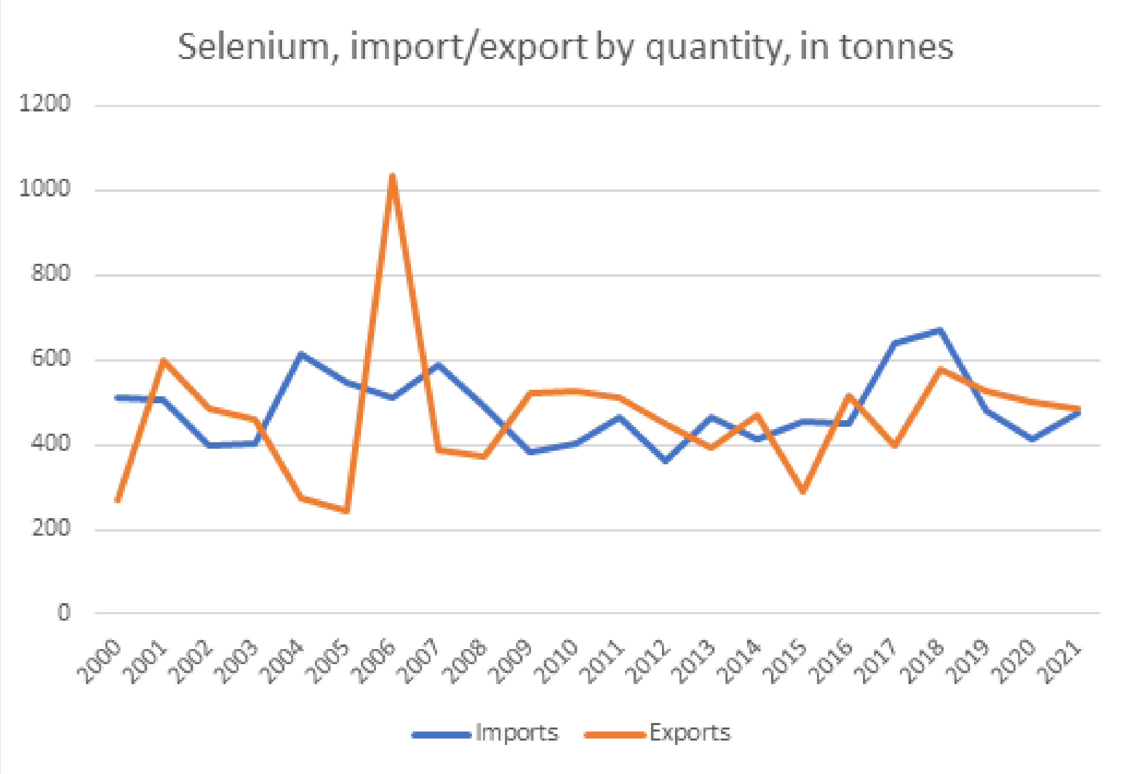

Figure 5. EU trade flows of selenium (CN 280490) from 2000 to 2021 (Eurostat, 2022)

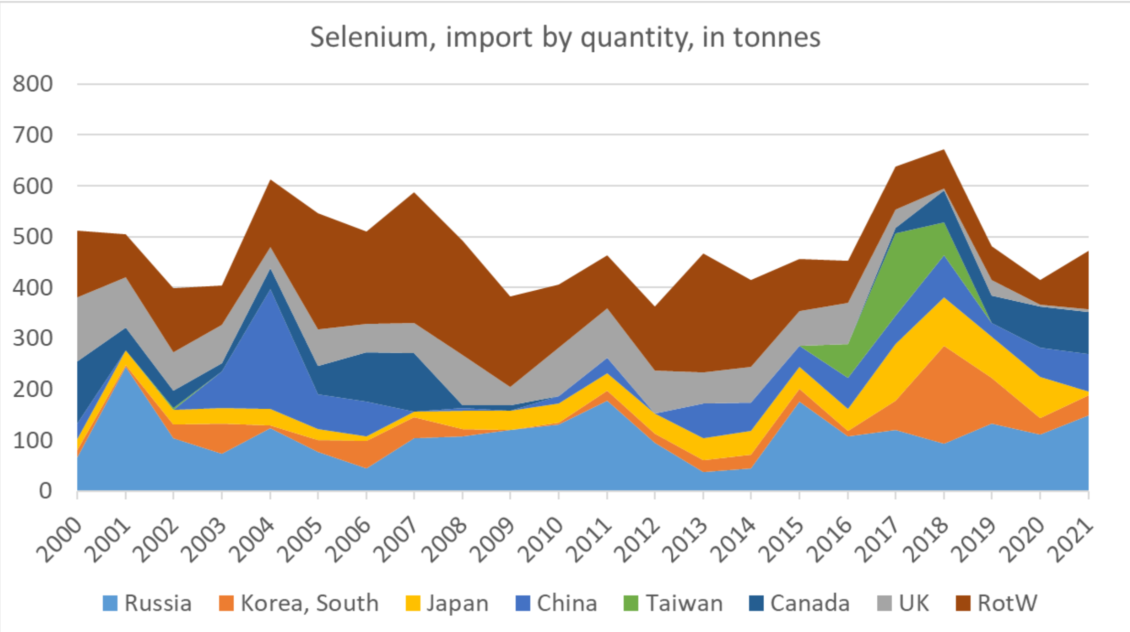

Figure 6. EU imports of selenium (CN 280490) by country from 2000 to 2021 (Eurostat, 2022)

PRICE AND PRICE VOLATILITY

Selenium prices show very high fluctuations. At the beginning of 2016, the selenium price was stable at around USD 26 per pound whereas the second half of the year prices rose to a monthly average of USD 37 per pound

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

(USGS, 2022). In the 2018-2020 period, selenium prices fluctuated between USD 17 per pound to USD 7 per pound. Moreover, selenium prices are also affected by market supply of copper because selenium is obtained as a by-product of copper refining. An increase in the supply of copper tends to reduce prices for selenium while a restriction in the supply of copper will generally result in increasing selenium prices (USGS, 2022).

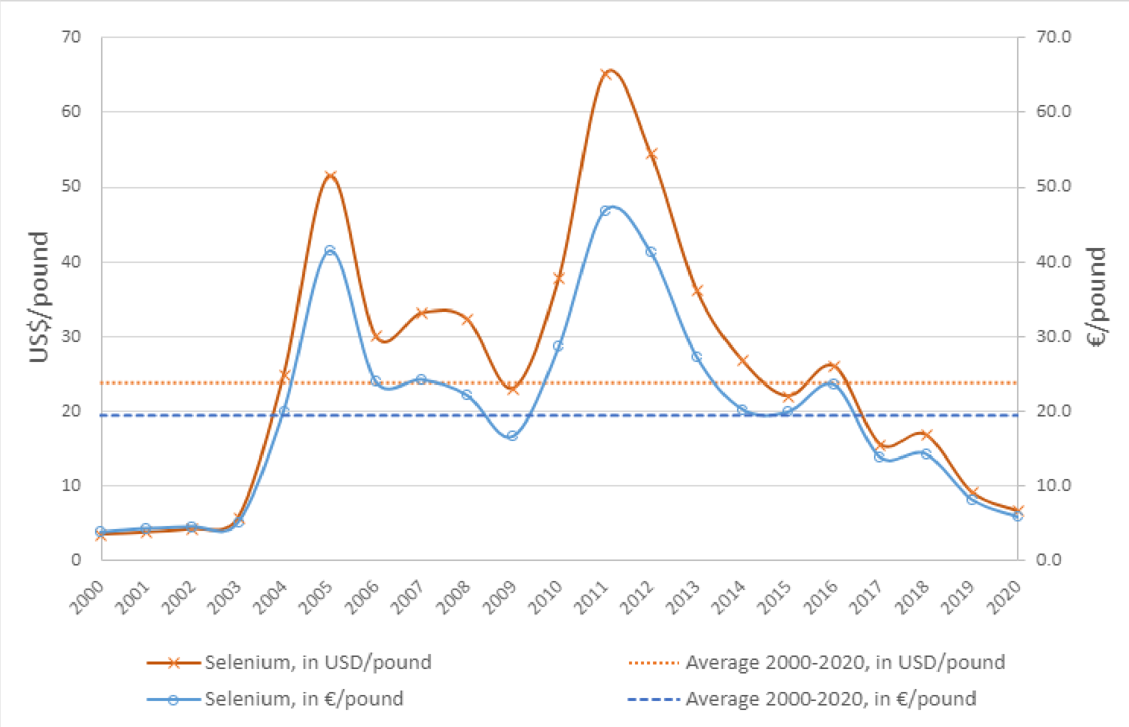

Figure 7. Annual average price of selenium between 2000 and 2020, in US$/pound and €/pound[3]. Dash lines indicate average price for 2000-2020 (USGS, 2022)

DEMAND

GLOBAL AND EU DEMAND AND CONSUMPTION

Selenium EU consumption is assessed at processing stage. Selenium processing stage EU consumption is presented by HS code CN 28049000 - Selenium. Import and export data is extracted from Eurostat Comext (2022). Production data is extracted from WMD (2022).

Average import reliance of selenium at processing stage 2 % for 2016-2020.

[3] Values in €/pound are converted from original data in US$/pound 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)

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

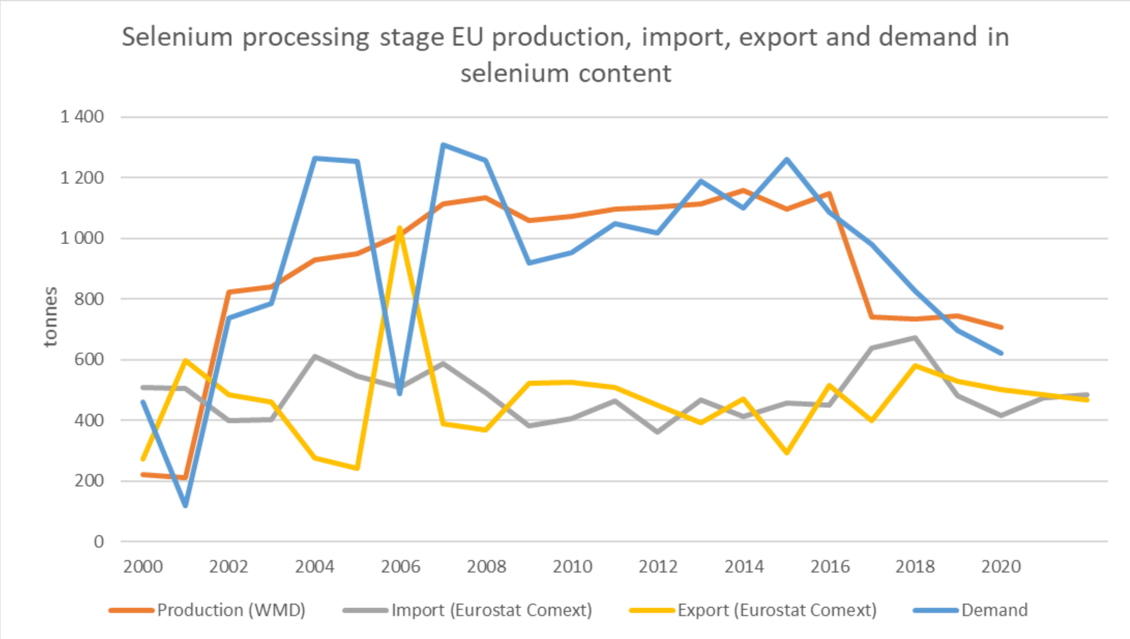

Figure 8. Selenium (CN 28049000) processing stage apparent EU consumption. Production data is available from WMD (2022). Consumption is calculated in selenium content (EU production+import-export).

EU USES AND END-USES

End uses for global consumption are metallurgy (including electrolytic manganese production), glass manufacturing, agriculture, chemicals and pigments, electronics, and others (USGS 2022). Figure 9 presents the main end-uses of selenium.

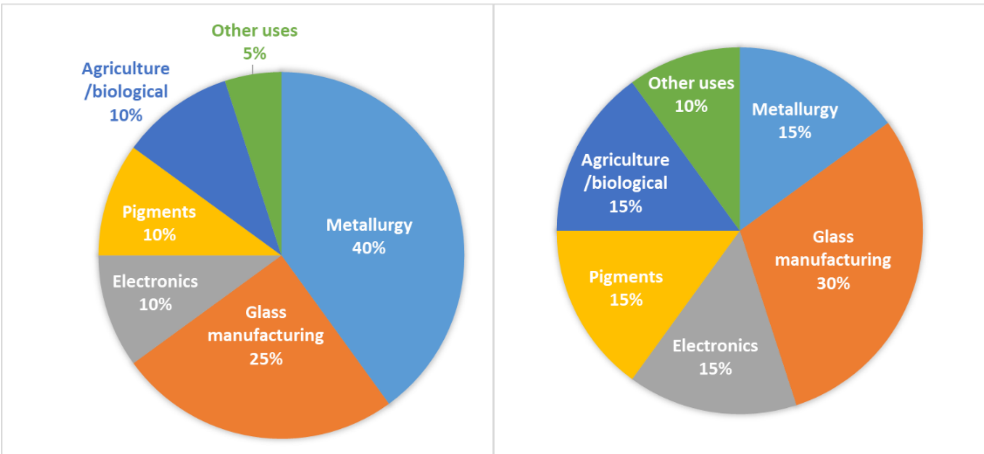

Figure 9. Left: Global end uses of Selenium 2020 (USGS, 2022). Right: EU end uses of selenium, 2020 (SCRREEN experts 2022)

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 (Table 5).

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

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

Applications	2-digit NACE sector	Value-added of sector (millions €) - 2019	Examples of 4-digit NACE sector
Metallurgy	C25 – Manufacture of fabricated metal products, except machinery and equipment	183,015	C2511 – Manufacture of metal structures and parts of structures; C2599 – Manufacture of other fabricated metal products n.e.c.
Glass manufacturing	C23 – Manufacture of other non-metallic mineral products	69,888	C2311 – Manufacture of flat glass; C2313 – Manufacture of hollow glass; C2319 – Manufacture and processing of other glass, including technical glassware
Electronics	C26 – Manufacture of computer, electronic and optical products	84,020	C2611 – Manufacture of electronic components; C2660 – Manufacture of irradiation, electromedical and electrotherapeutic equipment; C2670 – Manufacture of optical instruments and photographic equipment
Pigments	C20 – Manufacture of chemicals and chemical products	117,093	C2012 – Manufacture of dyes and pigments
Agricultural / biological products	C20 – Manufacture of chemicals and chemical products	117,093.2	C2015 – Manufacture of fertilisers and nitrogen compounds; C2110 Manufacture of basic pharmaceutical products.
Chemical manufacture	C20 – Manufacture of chemicals and chemical products	117,093.2	C2059 – Manufacture of other chemical products n.e.c.

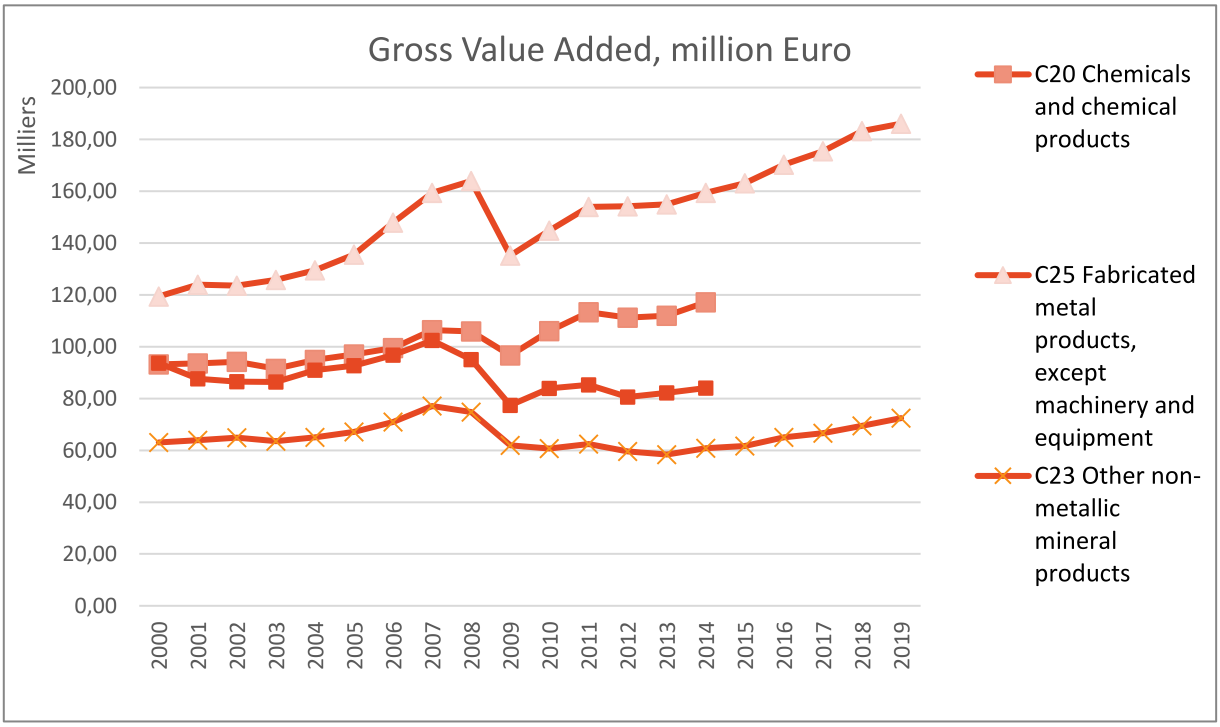

Figure 10. Value added per 2-digit NACE sector over time (Eurostat, 2022)

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

METALLURGY

Uses in metallurgical application include:

- Production of electrolytic manganese (high purity manganese metal) where the addition of selenium dioxide improves energy efficiency.
- The addition of selenium to carbon steel, stainless steel and copper improves their machinability.
- The use of selenium with bismuth as a substitute for lead in brass plumbing fixtures
- The use of selenium as a grain refiner in the grids of lead-acid batteries.

GLASS MANUFACTURING

Selenium is used as a decolouriser to remove the green tint caused by iron impurities and to produce a red colour. It also reduces solar heat transmission through glass.

ELECTRONICS

Selenium is used in rectifiers (devices that convert alternating current (AC) into direct current (DC) in voltage surge protection devices.

High purity selenium and selenium alloys are used in the photoreceptor of photocopiers and laser printers.

It is used in photovoltaic (solar) cells – thin-film CIGS cells (copper indium gallium selenide).

PIGMENTS

Selenium-containing pigments have good heat stability and are resistant to ultraviolet light or chemical exposure. They are used to impart red, orange or maroon colours to plastics, ceramics, glazes and paints.

AGRICULTURAL BIOLOGICAL PRODUCTS

As an essential nutrient for animal and human health, selenium is used as a food additive or applied with fertiliser to grassland for grazing animals if the soil is selenium poor.

Selenium is available as a dietary supplement and can be used as a fungicide to control dermatitis.

CHEMICAL MANUFACTURE

Selenium is used as a catalyst for selective oxidation; in plastic caps; as a plating alloy to improve appearance and durability; gun bluing; and in a compound used to improve the abrasion resistance in vulcanised rubbers.

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

Table 6. Uses and possible substitutes

Use	Share*	Substitutes	Sub share	Cost	Performance
Agriculture/biological	10%	No substitute	100%		No substitute
Electronics	10%	Wafer-based crystalline silicon (substitution for CIGS PV)	47%	Similar or lower costs	Similar
		Silicon in low- and medium voltage rectifiers	9%	Similar or lower costs	Similar
		Cadmium telluride (substitution for CIGS PV)	2%	Similar or lower costs	Similar
		Amorphous silicon (substitution for CIGS PV)	0%	Similar or lower costs	Similar
Glass manufacturing	25%	Copper-tin	12%	Similar or lower costs	Similar
		Manganese	13%	Similar or lower costs	Similar
		Gold chloride	12%	Very high costs (more than 2 times)	Similar
		Cerium oxide	13%	Similar or lower costs	Similar
Metallurgy	40%	Sulphur dioxide for electrolytic manganese	1%	Similar or lower costs	Similar
		Bismuth in free-machining alloys	12%	Similar or lower costs	Similar
		Lead in free-machining alloys	12%	Similar or lower costs	Similar
		Tellurium in free-machining alloys	12%	Slightly higher costs (up to 2 times)	Similar
		Sulphur dioxide in free-machining alloys	5%	Similar or lower costs	Similar
		Se-free electrolytic manganese production (functional) of electrolytic manganese: South Africa, CN	1%	Very high costs (more than 2 times)	Similar
Other uses	5%	Tellurium for rubber production	5%	Slightly higher costs (up to 2 times)	Similar
Pigments	10%	Organic materials	50%	Similar or lower costs	Similar

*Global end use shares of selenium (USGS, 2022).

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

METALLURGY

Bismuth, lead, and tellurium can substitute selenium to improve the machinability of alloys.
Sulphur dioxide can be used in the electrolytic production of manganese.
Costs and performance are considered to be similar with the exception of tellurium, which is more expensive.

GLASS MANUFCATURE

Cerium oxide and manganese have been identified as possible alternatives for decolourising glass, while gold chloride and copper-in will add red colouration to glass. All will provide similar performance to selenium, but gold chloride is considerably more expensive.

ELECTRONICS

Organic photoreceptors in photocopies and printers can substitute for selenium.
Silicon is a major alternative to selenium in many electronic applications, especially solar cells and in rectifiers.
Cadmium telluride is a potential substitute for CIGS in thin film photovoltaic solar cells.

PIGMENTS

Organic pigments are a potential substitute for selenium.

AGRICULTURE/BIOLOGICAL

There are no substitutes for selenium in the agricultural or biological applications because selenium is an essential nutrient.

CHEMICAL MANUFACTURE / OTHERS

No substitutes were considered for the chemical applications because less than 10% of selenium production is used in this category (USGS 2019) (SCRREEN workshops 2019, 2022).

SUPPLY

EU SUPPLY CHAIN

The average production of selenium in EU at the processing stage in the period 2016-2020 was 815.2 tonnes. Germany and Belgium are the most significant producers (with a production of 300 and 200 tonnes in 2022, respectively). The rest of production is taking place in Poland, Finland and Sweden. The average imported elemental selenium amount in EU was 536 tonnes during the period 2017-2021. Russia, Canada and China are the main trade partners (149, 83, 74 tonnes were imported respectively by these countries in 2021). The average exported amount of elemental selenium was 498 tonnes in the same period. India, China and Iran are the main countries were selenium is exported. The recycling rate of selenium globally is negligible (<1%). There are no data concerning the specific recycling rate in EU (Eurostat data, 2021).

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

The selenium production in EU represents about the 25% of the global production (year 2020) (WMD, since 1984). It is produced as a by-product in copper refineries in EU such as in: Rönnskär, Sweden, Harjavalta, Finland (Boliden 2019) and in Poland. When selenium is rapidly melted it forms a black vitreous form structured by irregular and complex polymeric rings. The black selenium powder is used in pharmaceuticals, for soil improvement, paint manufacturing, staining and detaining, and in the steel industry. The source material for the copper refineries is partly from Boliden's own mines in Scandinavia and partly from non-EU sources.

Aurubis operates three copper smelters/refineries in Europe: Hamburg, Germany; Olen, Belgium; and Pirdop, Bulgaria. Aurubis reports that they recover by-product metals, including selenium, from copper smelting operations but it is not stated whether this occurs at all three smelters. The copper concentrates for these operations are sourced primarily outside the EU. Retorte, a subsidiary of Aurubis located in Rothenbach a.d. Pegnitz, Germany, specialises in refining selenium into a wide range of products including high purity selenium and alloys, powder and pellets, chemicals, animal feed additives and pharmaceuticals.

KGHM recover selenium with a purity of 99.40% from refining copper at its Głogów Copper Smelter/Refinery in Poland. KGHM operates three copper mines in Poland, one in Canada, two in the USA and one in Chile. After processing, the selenium is used in the glass, fodder, pharmaceutical, and cosmetics industries.

SUPPLY FROM PRIMARY MATERIALS

GEOLOGY, RESOURCES AND RESERVES

GEOLOGICAL OCCURRENCE:

Selenium is relatively rare in the earth's crust with an average abundance of only 30–90 parts per billion (ppb) in the uppercrust (R. L. Rudnick and Gao 2003). It is also widely distributed meaning it is unlikely to be sufficiently concentrated to allow economic extraction in its own right and consequently selenium is only extracted as a by-product, usually of copper, but also of lead or occasionally nickel. Although it does rarely occur as a native material, it is most commonly found in compounds with base or precious metals which are classified as selenides or sulphoselenides (a number of other compounds also exist). Selenium tends to replace the element sulphur in its compounds and can occur in a relatively large number of the sulphur mineral albeit in very small quantities.

Selenium is a chalcophile element, meaning it preferentially combines with sulphur rather than oxygen, but it can be readily separated from sulphur because it has a lower oxidation potential. It can occur in a wide range of different deposit types including (based on Luttrell, 1959):

- Hydrothermal base metal sulphide deposits
- Disseminated porphyry copper deposits
- Vein and replacement copper deposits
- Volcanic-hosted massive sulphide deposits
- Copper-lead sulphide veins
- Epithermal silver-gold veins

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

- Mercury-antimony deposits
- Sandstone-type uranium-vanadium deposits
- Sedimentary deposits, including coals, volcanic tuffs, phosphates and some shales

Selenium derived from these deposits can also be concentrated in soils or vegetation.

Various alterative ("unconventional" called) natural Se sources have recently been identified from which the metal can potentially recovered in medium term. Among these, so far non exploited, sources can be mentioned: volcanogenic massive sulphides, sedimentary bedrocks, phosphorites, black shales and organic-rich sediments, Cu–Zn–Pb deposits in ophiolites and polymetallic nodules (Funari et al. 2021).

GLOBAL RESOURCES AND RESERVES

Reserves for selenium are based on identified copper deposits and average selenium content. Coal generally contains between 500 and 1,200 ppb of selenium, or about 80 to 90 times the average of copper deposits. The recovery of selenium from coal fly ash, although technically feasible, does not appear likely to be economical in the foreseeable future (USGS, since 2000).

Table 7. Global reserves of Selenium in year 2021 (USGS, since 2000)

Country	Selenium Reserves (t)	Country	Selenium Reserves (t)
China	26,000	Canada	6,000
Russia	20,000	Poland	3,000
Peru	13,000	Sweden	20,000
United States	10,000	Other Countries*	22,000
World total (rounded)	100,000		

EU RESOURCES AND RESERVES

During the Minerals4EU (2019) project, no selenium resources were reported by any of the 40 European countries surveyed, irrespective of the different international or national systems of reporting used. However, resources may exist in countries that did not respond to the survey. Copper resources are known to exist in at least 19 European countries and it is highly likely that some of these deposits will contain selenium, but it is not included in reported resources because it is a by-product. There were two active exploration licences reported for Slovakia investigating resources of precious metals with various by-products including Selenium.

None of the 40 European countries surveyed reported selenium reserves, but reserves may exist in countries that did not respond to the survey. Nine European countries reported reserves of copper (Minerals4EU, 2019).

WORLD AND EU PRIMARY PRODUCTION

Total worldwide production of Selenium, averaged over 2016–2020, amounted to 3,737 t per year and the largest producers are China, Japan, and Germany. The segment for 'other countries' includes Chile, Uzbekistan, India, Serbia and Armenia (Figure 11, Figure 12). Between 2016 and 2020, an average of 815 t of Selenium was

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

produced in EU per year, 23% of global production. The distribution of selenium production by country in EU in 2020 can be seen in Figure 13.

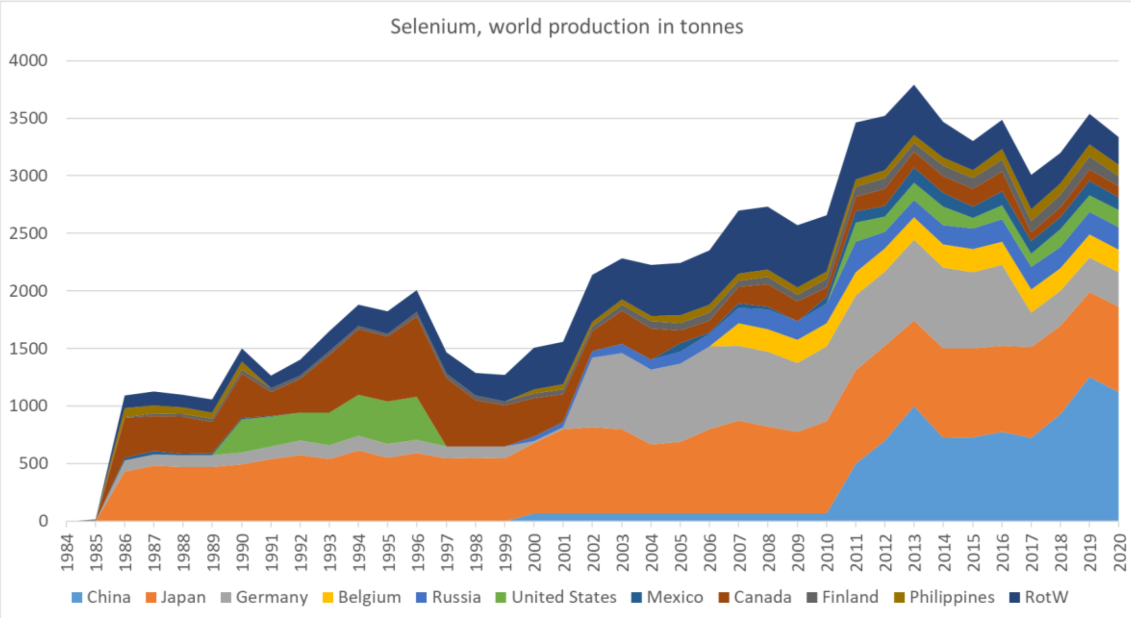

Figure 11. Global production of selenium since 1984 (WMD, since 1984)

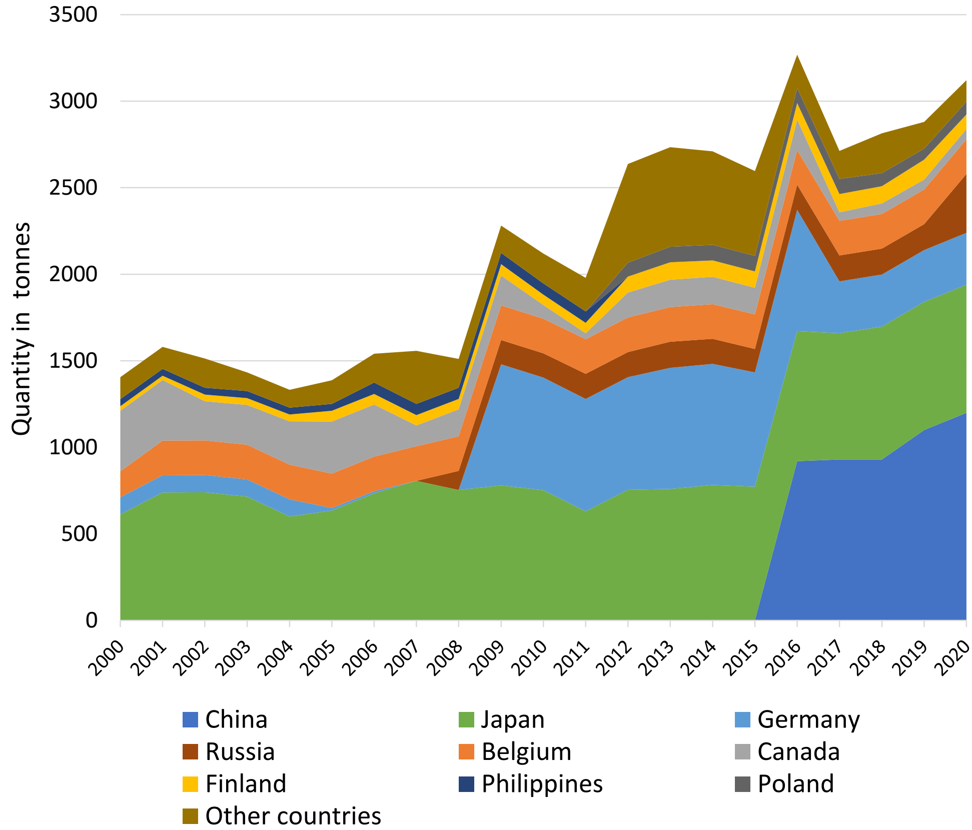

Figure 12. Global production of selenium since 2000 (USGS, since 2000)

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

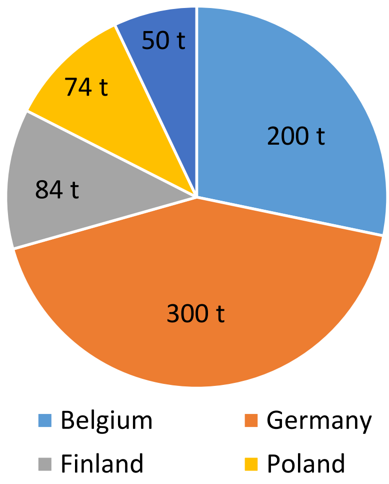

Figure 13. Selenium production in EU by country in 2020 (WMD, since 1984)

More than 90% of global selenium production is won as a by-product from electrolytic refining of copper. To reach this stage the copper, and its associated by-products including selenium, undergo a number of processing stages. These include traditional mining techniques (either underground or from surface mines), crushing and grinding, froth flotation, roasting, smelting, and the conversion of matte to copper blister. At each stage a proportion of selenium is lost in tailings or residues (Kavlak and Graedel 2013).

Electrolytic refining uses slabs of copper blister as anodes and pure copper as cathodes immersed in an electrolyte. An electrical current is passed through the electrolyte and as the anodes dissolve, copper atoms transfer to the cathodes. Selenium is insoluble during this process and settles at the bottom of the electrolytic cell into what is known as ‘anode slimes’ or muds. These slimes can subsequently be treated to recover selenium and/or other metals such as silver, gold, or platinum group metals.

Selenium content in these anode slimes has been reported as ranging from 0.4% to 19% (Moats, M. et al 2007). The selenium is recovered from these slimes using a number of available roasting methods followed by grinding and leaching, separation using scrubbers or filters, or vaporisation and precipitation (Willig 2014). Exact processes will depend on the individual composition of the anode slimes and details are not normally published because they contain proprietary information.

Selenium can also be recovered from sludge arising in sulphuric acid plants where base metal ores are roasted, and from electrostatic dust precipitators in copper or lead smelters (Willig 2014).

(Kavlak and Graedel 2013) reported that the recovery rate during the initial concentration is as low as 10%, during the smelting and converting stages the recovery is 50%, and during the treatment of anode slimes as much as 90% of the available selenium is recovered. This is a reflection of the degree of attention focused on selenium at each stage. During the initial concentration phases, the focus lies on recovering copper or other base metals which are more economically rewarding due to the larger quantities available. In contrast, where recovery of selenium from anode slimes is carried out the equipment used is optimised to ensure the highest possible recovery rate of selenium as this has become the focus.

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

Once recovered, selenium normally needs to be refined further to obtain the high purity levels needed for many applications. These refining methods may involve selective precipitation; selective leaching and recrystallization; or oxide, hydride or chloride purification (Willig 2014).

OUTLOOK FOR SUPPLY

The supply of selenium is directly affected by the supply of copper and, to a lesser extent, nickel from which is produced as by-product, while it is also directly affected by the number of facilities that recover selenium. Despite the increase of Se price (>20% since 2021), copper producers in China stopped selling it from their inventories, reducing availability of selenium. Selenium prices increased owing to a rise in crude selenium feedstock costs (USGS, since 2000).

SUPPLY FROM SECONDARY MATERIALS/RECYCLING

Many of the end uses of selenium are dissipative, meaning that very little material becomes available for recycling. Selenium contents in glass and metallic alloys are too small to be accounted for during recycling processes and selenium-containing scrap from these sources are not normally segregated from other scrap metal or glass with the result that the selenium is further dispersed rather than concentrated. Selenium used in pigments, chemicals, agricultural and biological products are dissipated in the environment and not recovered (George, M.W. and Wagner 2004).

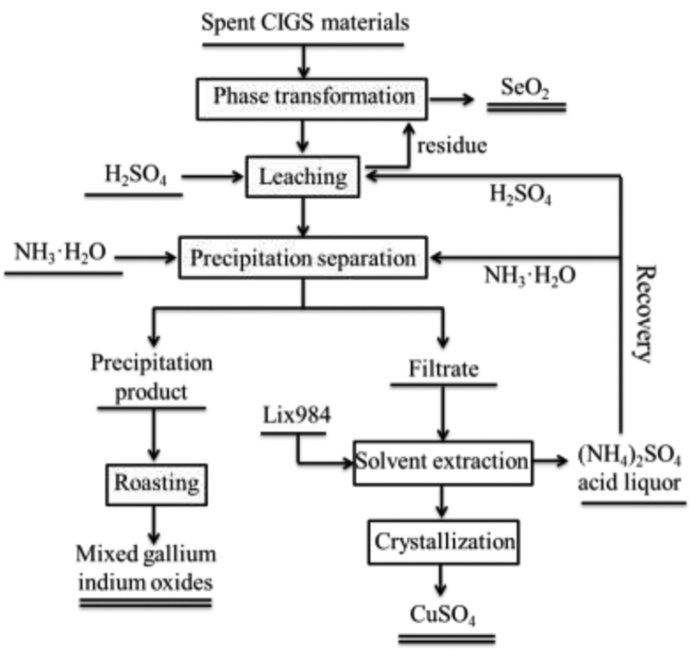

Figure 14. Proposed methodology for the recovery of selenium by spent photovoltaic cells (Lv et al. 2019)

Electronic products are, therefore, the only secondary source currently available for selenium. The use of selenium in photoreceptors or rectifiers has been declining for some time as selenium-containing compounds are substituted by organic photoreceptors or cheaper silicon-based rectifiers (George, M.W. and Wagner 2004). As a consequence, the availability of material for the recycling of selenium from these products is very

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

minor (personal communication from industry sources). One potential source for recycled selenium are a type of photovoltaic cells known as CIGS (copper indium gallium selenide) but as this is a relatively new technology the quantities of these cells that have reached their end-of-life is still quite small. However, in the longer term supplies of recycled selenium from this source could increase if the use of this type of solar cells increases.

Selenium recovery by spent CIGS is relatively simple and involves the roasting of the end-of-life material at 1000 °C (Lv et al. 2019). At this temperature, the 99.9 wt.% Se content volatilized and recovered via oxidation into selenium dioxide. At the same time, the other valuable metals are converted from selenides to oxides. Subsequently, the indium and gallium and recovered through hydrometallurgy (leaching with H_2SO_4 and precipitation) (Figure 14). Nevertheless, the sustainability of the methodology should be examined in terms of its energy cost and the efficient co-recovery of all the valuable metals.

The quantities involved with both types of scrap are very small (personal communication from industry sources). The UNEP report quotes recycled content, which represents the 'old scrap' plus 'new scrap' as a proportion of the total quantity of a material available to manufacturers (which would also include primary material). For selenium this is estimated as 1–10% (UNEP 2011). According to Eurostat data (Eurostat, 2021), the recycling rate in Se globally remains very low (<1%).

POST-CONSUMER RECYCLING (OLD SCRAP)

End-of-life scrap or 'old scrap' is defined as scrap arising from products that have been used but are no longer required because they have been worn out or become obsolete.

There are many different indicators that can be used to assess the level of recycling taking place for any material. The United Nations Environment Programme (UNEP) estimated the 'end-of-life recycling rate' of selenium as <5%. This is measured as 'old scrap' sent for recycling as a proportion of 'old scrap' generated.

For this criticality assessment, a slightly different indicator was required: the end-of-life recycling input rate (EOL-RIR). This measures the quantity of end-of-life scrap (i.e. 'old scrap') contained within the total quantity of metal available to manufacturers (which would also include primary metal and 'new scrap'). For selenium, insufficient data was found to enable the calculation of EOL-RIR but as (UNEP 2011) estimated EOL-RR as <5% and the figures quoted by George and Wagner (2004) are also very small, it was concluded that EOL-RIR must be low. Therefore a figure of 1% was used in the assessment (UNEP 2011) (SCRREEN workshops 2019).

INDUSTRIAL RECYCLING (NEW SCRAP)

Scrap and other wastes are also generated during the fabrication and manufacture of products (sometimes referred to as 'new scrap' or 'processing scrap'). For selenium 'new scrap' represents the largest source of material for recycling (European Commission 2017).

METALLURGICAL RESIDUES

Selenium is contained at significant amounts in the residues of the antimony extractive industry and more specifically at the residues formed through the antimony-arsenic separation. Arsenic in antimony ores is

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

initially separated as crude antimony by oxidation, volatilization and reduction smelting, and then crude antimony is further refined by adding sodium carbonate or sodium hydroxide to remove arsenic, causing the generation of waste residue named as arsenic-alkali residue. At present, the total storage of arsenic-alkali residue has reached 200,000 tons in China, while the generation rate of the residue is about 5,000 tons per year. A typical Se concentration in the antimony residue is around 0.18 wt.%. The efficient Se separation is possible through hydrometallurgical processing involving the successive leaching, initially with hot water, and crystallization (with CO_2 and at a second step with H_2SO_4) of the residue (Long et al. 2020).

PRODUCTION OF SELENIUM

Selenium is mainly recovered as by product through the processing of copper refinery anode slimes. The most widely applied method involves the hydrometallurgical treatment with dilute sulphuric acid. Selenium in solution, together with tellurium, is extracted via cementation. The leaching residue, containing the remaining selenium, is further treated through oxidative roasting in a shaft furnace at the temperature range of 700-800°C. The oxidation roasting converts copper, nickel and tellurium into acid soluble forms (Figure 15). Alternatively, to the leaching with sulphuric acid, anode slimes can be processed via: (a) sulphatizing roasting followed by reduction of the selenium under Se^{+4}, (b) oxidative roasting followed by sulphuric acid leaching, (c) H_2SO_4 pressure leaching followed by soda roasting and (d) caustic pressure leaching followed by Se^{+4} reduction (Cooper, 1990).

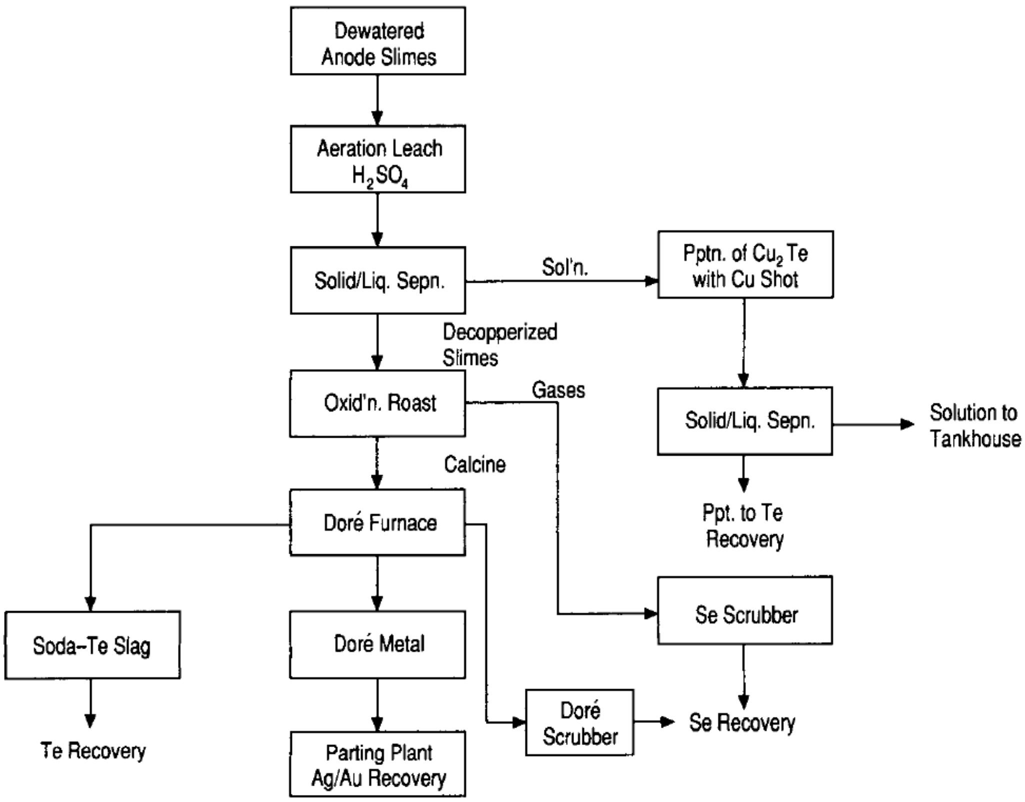

Figure 15. Recovery of selenium through the hydrometallurgical processing of copper refinery anode slimes (Cooper, 1990)

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

OTHER CONSIDERATIONS

HEALTH AND SAFETY ISSUES

Selenium is included by the International Agency for Research on Cancer (1987) in Group 3 (not classifiable as to its carcinogenicity to humans), providing that there are no suggestions of its carcinogenicity to humans. On the other side, in accordance with the Classification, Packaging and Labelling EU Regulation (2008) all products containing selenium shall be labelled as acutely toxic, as they are classified as toxic if inhaled (H331), toxic if swallowed (H301) and may cause damage to organs through prolonged or repeated exposure (H373). The concentration limit for selenium in drinking water has been set at 10 µg/l by the Drinking Water EU Directive (2020).

ENVIRONMENTAL ISSUES

Selenium is released to the environment primarily by the mining industry. The extraction of coal, precious metals and metallic sulphides provoke emissions of this element to the soil and air, which could eventually diffuse to groundwater and the nearby water bodies (Khamkhash, A. et al., 2017). Under alkaline and oxidising conditions, elemental selenium is transformed into selenates (oxidation state VI) and selenites (oxidation state IV), which are soluble in water (Etteieb, S. et al., 2019; World Health Organization, 2011).

In accordance with the (Classification, Packaging and Labelling EU Regulation, 2008) selenium products shall be labelled as toxic for aquatic ecosystems since they may cause long-lasting harmful effects on aquatic life.

Vertebrates exposed to selenium-contaminated water bodies are affected by its teratogenicity and potential to bioaccumulate (Etteieb, S. et al, 2019; Getachew Dagnew. G. et al., 2019). Selenium toxicity in fish results in growth rate reduction, behavioural changes, deformities, and increased mortality in early ages. Selenium toxicity in aquatic birds reduces egg hatchability and deformity in offspring (Canadian Ministry of Environment, 2014). (Sharma, V. et al., 2020) report that a chronic excessive selenium intake is known as selenosis. This poisoning was noted for example in herds of horses in the 1930s and it was linked to grazing on grains with disproportionate levels of selenium. It caused impairment in gait and vision, known as “blind staggers” and dystrophic hooves. In addition, the authors allege that selenium is toxic to aquatic organisms and can be transferred from the mother to the eggs of oviparous vertebrates, causing oxidative stress and cellular dysfunction. This might lead to embryo mortality or teratogenic deformities and thus reduce the fish population in polluted marine ecosystems.

SOCIO-ECONOMIC AND ETHICAL ISSUES

In 2021, there were no countries for which the economic value of exports of this selenium products represented more than 0.1 % of the total value of their exports. (COMTRADE 2023)

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

RESEARCH AND DEVELOPMENT TRENDS

RESEARCH AND DEVELOPMENT TRENDS FOR LOW-CARBON AND GREEN TECHNOLOGIES

- Selenophene for organic solar cells

Many researchers consider that organic solar cells (OSCs) will be the third generation of solar cells due to their low production cost, light weight, strong design-ability of the organic molecular structure, and easy production processes (Amador-Bedolla, C. et al., 2013). Selenophene, an aromatic ring with four carbon and one selenium atom, is currently being studied to be used as an active layer in bulk heterojunction OSCs. It has a narrow optical band gap, which guarantees a high light adsorption capacity, and a high stacking order, ensuring improved carrier transport efficiency. The power conversion capacity of OSCs with a selenophene active layer is close to 18 %, in line with that of currently commercialized solar cells. This value is higher than other OSCs modules since efficiency is increased by selenophene properties, such as narrow band gap, high molecular order, and crystallinity (Liu, X. et al., 2022).

- High-energy lithium-selenium batteries

In recent years, the application of selenium in energy storage devices has gained scientific attention. It is considered an alternative to sulphur as cathode material in lithium batteries, in order to overcome limitations related to the usage of sulphur, namely its extremely low electrical conductivity (5×10^{-30} S/cm). Lithium-selenium batteries (LSeBs) present higher energy density than lithium-ion batteries (2528 Wh/L and 1190 Wh/L, respectively). Selenium cathodes show high energy capacity, comparable to sulphur cathodes (3254 mAh/cm^3 and 3467 mAh/cm^3, respectively) and high electronic conductivity, comparable to $LiCoO_2$ cathodes (1×10^{-5} S/cm and 1×10^{-4} S/cm, respectively). Also, the high melting point (221 ºC) of selenium makes it suitable for elevated temperature applications. Finally, LSeBs perform better with carbonate electrolytes than with ether-based ones, guaranteeing high voltage stability and low cost (Jinmeng, S. et al., 2021; Eftekhari, A., 2017).

OTHER RESEARCH AND DEVELOPMENT TRENDS

- RUPTURE[4] project: Selenium Containing Rupturing Dendritic Prodrugs for Therapeutic Applications (EU, 2023 – 2025)

Reactive oxygen species (ROS) are free radicals containing oxygen that reacts with other cell molecules. Under normal physiological conditions, ROS drive regulatory pathways, and cells control the generation of ROS via scavenging systems. Elevated ROS levels are present in almost all cancer cells, where they promote proliferation. However, high levels of ROS can suppress the growth of cancer cells and kill them via activation of cell-cycle inhibitors. Selenium derivatives show chemotherapeutic potential, based on the ability to act as a pro-oxidant at high dosages. The RUPTURE project aims to develop novel anticancer agents based on selenium-containing dendritic carriers, targeting ROS signalling and inducing cell death.

[4] CORDIS EU research results, 10.3030/101064084

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

- Se4All[5] project: Se-bioFORtified ALfaLfa for Se-enriched Dairy products (EU, 2021 – 2025)

About 3 billion people worldwide are affected by low intakes of the essential nutrient selenium (Se). The Se present in our diet its intimately linked with the amount of Se in soils, and therefore related crops, which can vary dramatically from region to region. Inadequate dietary Se intake is related to the risk of developing chronic degenerative diseases. The Se4All project will explore Se-enriched edible plants as a solution to overcome this issue. Specifically, it will produce Se-enriched dairy products and cheese as functional foods through Se-biofortified alfalfa hay for feeding milking cows. Se will be applied directly to the plant (foliar application), instead of to the soil, in order to achieve transferability of the methodology to different regions.

- Evaluation of adsorption behaviour of selenium onto zeolite-based composite barrier material for intermediate deep radioactive waste repository (Durmus et al. 2023)

The radionuclide ^{79}Se is a potential radio-ecological concern due to its long half-lives and its capacity to be readily incorporated into the natural life cycle from radioactive waste repositories. This study aimed to reveal the role of barrier materials including zeolite in the transfer of selenium from radioactive waste repository areas to the biosphere. The interaction between selenium (IV) and the barrier material was evaluated by examining different parameters. In the event of an accident that may occur, the environmental and health risks that the ^{79}Se may pose were evaluated within the scope of possible dose values using a Monte Carlo-based simulation program. As a result, it has been determined that the composite barrier material used plays an important role in preventing the transfer of selenium from the waste storage area to the biosphere.

- Selenium nanoparticles for therapeutic applications

Selenium nanoparticles (SeNPs) have been used for treating diseases and disorders related tooxidative stress and inflammation like arthritis, cancer, diabetes, and nephropathy. (Khurana, A. et al., 2019) have reviewed the use of SeNPs in disease treatment, which include anti-inflammatory, anti-cancer, anti-diabetic, and antioxidant therapeutic applications. For example, SeNPs may be used to transfer chemotherapeutics to the target site, since they exhibit differential activity against malignant cells and normal cells.

REFERENCES

Aeftekhari, A. (2017), The Rise of Lithium–Selenium Batteries, https://doi.org/10.1039/C6SE00094K , accessed on February 2023

Amador-Bedolla, C. et al. (41467), Organic Photovoltaics, https://doi.org/10.1016/B978-0-12-394399-6.00017-5 , accessed on February 2023

Boliden (2019), By Products. Available at: http://www.boliden.com/operations/products/by-products (Accessed: 7 November 2019).

CLP (39798), Regulation (EC) No 1272/2008, http://data.europa.eu/eli/reg/2008/1272/2022-12-17 , accessed on January 2023

[5] CORDIS EU research results, 10.3030/101007630

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

COMTRADE (2023), United Nations database for international trade data (COMTRADE); datasets for 2021, https://comtrade.un.org/ , accessed on February 2023

Cooper, W.C. (1990), The treatment of copper refinery anode slimes. JOM, 42(8), pp. 45–49.

CRM experts (2022), SCRREEN Experts Workshop. Brussels: 22.09.2022

Drinking water EU directive (2020), DIRECTIVE (EU) 2020/2184, http://data.europa.eu/eli/dir/2020/2184/oj , accessed on February 2023

EU occupational exposure (38106), Directive 2004/37/EC, http://data.europa.eu/eli/dir/2004/37/2022-04-05 , accessed on February 2023

European Commission (2017), Study on the review of the list of critical raw materials. Non-critical raw materials factsheets. European Commission. doi: 10.2873/876644.

Eurostat (2021), Annual detailed enterprise statistics for industry (NACE Rev. 2, B-E), https://ec.europa.eu/eurostat/en/web/products-datasets/-/SBS_NA_IND_R2 , accessed on December 2021

Eurostat Comext (2022), Eurostat database. EU trade since 1988 by HS2-4-6 and CN8 (DS-045409). , http://epp.eurostat.ec.europa.eu/newxtweb/ , accessed on December 2022

Funari, V., Gomes, H.I., Coppola, D., Vitale, G.A., Dinelli, E., de Pascale, D., Rovere, M. (2021), Opportunities and threats of selenium supply from unconventional and low-grade ores: A critical review, Resources, Conservation & Recycling, 170, 105593.

George, M.W. and Wagner, L. A. (2004), 'Selenium recycling in the United States in 2004, chapter T of Sibley, S.R.', Flow studies for recycling metal commodities in the United States, pp. 1–16. Available at: http://pubs.usgs.gov/circ/circ1196-Y/.

Jinmeng, S. et al. (2021), State-Of-The-Art and Future Challenges in High Energy Lithium–Selenium Batteries, https://doi.org/10.1002/adma.202003845 , accessed on February 2023

Kavlak, G. and Graedel, T. E. (2013), 'Global anthropogenic selenium cycles for 1940–2010', Resources, Conservation and Recycling, 73, pp. 17–22. doi: https://doi.org/10.1016/j.resconrec.2013.01.013.

Khurana, A. etnal. (2019), Therapeutic applications of selenium nanoparticles, https://doi.org/10.1016/j.biopha.2018.12.146 , accessed on February 2023

Liu, X. et al. (44873), Recent Advances in Selenophene-Based Materials for Organic Solar Cells, https://doi.org/10.3390/ma15227883 , accessed on February 2023

Long, H., Zheng, Y., Peng, Y., He, H., (2020), Recovery of alkali, selenium and arsenic from antimony smelting arsenic-alkali residue, Journal of Cleaner Production, 251, 119673.

Luttrell, G. W. (1959), Annotated Bibliography on the Geology of Selenium. Bulletin 1019-M Contributions to Bibliography of mineral resources. United States Geological Survey. Available at: https://pubs.usgs.gov/bul/1019m/report.pdf.

Lv, Y., Xing, P., Ma, B., Liu, B., Wang, C., Zhang, Y., Zhang, W. (2019), Separation and Recovery of Valuable Elements from Spent CIGS Materials, ACS Sustainable Chem. Eng., 7, 19816−19823.

Minerals4EU (2019), European Minerals Yearbook. Available at: http://minerals4eu.brgm-rec.fr/m4eu-yearbook/theme_selection.html (Accessed: 9 July 2019).

Moats, M., Davenport, W., Demetrio, S., Robinson, T. and Karcas, G (2007), Electrolytic copper refining 2007 world tankhouse survey. In Houlachi, G.E., Edwards, J.D. and Robinson, T.G. (Eds), Copper 2007. Vol

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

V: Copper electrorefining and electrowinning (pp.105–242). Canadian Institute of Mining, Montreal. Figures quoted in Will'.

Moats, M., Davenport, W., Demetrio, S., Robinson, T. and Karcas, G. (2007), 'Electrolytic copper refining 2007 world tankhouse survey. In Houlachi, G.E., Edwards, J.D. and Robinson, T.G. (Eds), Copper 2007. Vol V: Copper electrorefining and electrowinning (pp.105–242). Canadian Institute of Mining, Montreal. Figures quoted in Will'.

OECD (2022), Export restrictions on Industrial Raw Materials , https://qdd.oecd.org/subject.aspx?Subject=ExportRestrictions_IndustrialRawMaterials, accessed on December 2022

Rudnick, R. ~L. and Gao, S. (2003), 'Composition of the Continental Crust', Treatise on Geochemistry, 3, p. 659. doi: 10.1016/B0-08-043751-6/03016-4.

SCRREEN workshop (2019), 'Validation workshop on Critical Raw Materials, 10-12 September 2019, Thon Hotel Brussels City Centre'. Brussels.

STDA (2010), Sources and applications for selenium and tellurium. Selenium Tellurium Development Association, http://www.stda.org/se_te.html., accessed on

STDA (2022), Selenium and Tellurium Developing Association: Se & Te. , https://stda.org/pages/SE-%26-TE.html , accessed on December 2022

UNEP (2011), Recycling rates of Metals - A status Report, A Report of the Working Group on the Global Metal Flows to the International Resource Panel.

USGS (2022), Mineral Commodity Summaries, https://www.usgs.gov/centers/national-minerals-information-center, accessed on December 2022

USGS (Since 2000), Mineral Commodity Summaries, U.S. Department of the Interior, U.S. Geological Survey

Willig, F. K. (2014), Selenium Recovery in Precious Metal Technology. Thesis for a Degree Project in Engineering Chemistry. Umeå University with Outotec (Sweden) AB. Available at: http://umu.diva-portal.org/smash/get/diva2:703367/FULLTEXT01.pdf.

WMD (2022), Federal Ministry of Agriculture, Regions and Tourism of Austria (Ed.): World Mining Data.-(since 1984)

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