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ARSENIC

OVERVIEW

Arsenic (As) is an element stemming predominantly from natural sources occurring ubiquitously in the earth’s crust with a concentration of 1.0-2.0 ppm which is why it is considered a rare element (Lebensmittelchemisches Institut, 2010). Arsenic can occur in its elemental form, but usually does not occur in large deposits rather as a component in other minerals. It may be obtained as a by-product from copper, gold and lead smelter flue dust, as well as from roasting arsenopyrite, the most abundant ore mineral of arsenic (USGS, since 2000).

Table 1. Arsenic metal supply and demand in metric tonnes, 2016-2020 average (As content)

<table>
<thead>
<tr>
<th>Global production</th>
<th>Global Producers</th>
<th>EU consumption</th>
<th>EU Share</th>
<th>EU Suppliers</th>
<th>Import reliance</th>
</tr>
</thead>
<tbody>
<tr>
<td>41,693 tonnes</td>
<td>China 44%</td>
<td>1,286 tonnes</td>
<td>3%</td>
<td>Belgium 59%</td>
<td>39%</td>
</tr>
<tr>
<td></td>
<td>Peru 40%</td>
<td></td>
<td></td>
<td>China 39%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Morocco 11%</td>
<td></td>
<td></td>
<td>Japan 1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Honk Kong 1%</td>
<td></td>
</tr>
</tbody>
</table>

Prices: Arsenic prices are dependent on the form in which it is brought on to the market (either as arsenic metal from China or arsenic trioxide from China or Morocco). From 2012 to 2016, prices for arsenic metal increased from € 1.3/kg to € 1.7/kg. This is due to the increased demand for gallium-arsenide driven by high-tech applications and the growth of the digital industry (USGS, 2014).

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1 JRC elaboration on multiple sources, 2012-2016

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Figure 2. Annual average price of arsenic metal between 2000 and 2020, in US$/kg and €/kg (based on USGS, 2021). Dash lines indicate average price for 2000-2020.

Primary supply: The recovery of arsenic is mainly done by heating arsenopyrite (FeAsS) or loellingite (FeAs2) under exclusion of air at 700°C in horizontal clay pipes. Thereby arsenic is sublimated and collected in cooled collectors and condensed. However, the production of diarsenic trioxide as a by-product in the extraction, processing and purification of copper, lead, cobalt and gold is the most important method of producing arsenic (Lebensmittelchemisches Institut, 2010). The further reduction of diarsenic trioxide to arsenic metal was believed to have accounted for all world output of commercial-grade (99%-pure) arsenic metal (USGS, 2018a).

Figure 3. Global mine production and EU import of Arsenic (WMD and Eurostat), average 2016-2020, As content

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Secondary supply: There is no mentionable documented recycling of arsenic taking place. According to UNEP (2013) report “Recycling Rates of Metals” Old Scrap Ratio, Recycled Content and End-of-Life Recycling Rate are all below 1%. There are no data in respect to the methodologies that are used for the recycling of arsenic in EU.

Uses: The major application area for arsenic compounds in the EU is the production of zinc together with the manufacture of glass (European Commission, 2018).

![Figure 4: EU uses of Arsenic](image)

**Table 2. Uses and possible substitutes**

<table>
<thead>
<tr>
<th>Application</th>
<th>Share</th>
<th>Substitutes</th>
<th>SubShare</th>
<th>Cost</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassmaking</td>
<td>18%</td>
<td>Sodium nitrate</td>
<td>25%</td>
<td>Similar or lower costs</td>
<td>Similar</td>
</tr>
<tr>
<td>Glassmaking</td>
<td>18%</td>
<td>Potassium nitrate</td>
<td>25%</td>
<td>Similar or lower costs</td>
<td>Similar</td>
</tr>
<tr>
<td>Glassmaking</td>
<td>18%</td>
<td>Cerium oxide</td>
<td>25%</td>
<td>Similar or lower costs</td>
<td>Similar</td>
</tr>
<tr>
<td>Glassmaking</td>
<td>18%</td>
<td>No substitute</td>
<td>25%</td>
<td>no substitute</td>
<td></td>
</tr>
<tr>
<td>Electronics</td>
<td>1%</td>
<td>not assessed, under 10%</td>
<td>100%</td>
<td>no substitute</td>
<td></td>
</tr>
<tr>
<td>Chemicals</td>
<td>7%</td>
<td>not assessed, under 10%</td>
<td>100%</td>
<td>no substitute</td>
<td></td>
</tr>
<tr>
<td>Alloys</td>
<td>5%</td>
<td>not assessed, under 10%</td>
<td>100%</td>
<td>no substitute</td>
<td></td>
</tr>
<tr>
<td>Zinc production (Electrowinning of zinc)</td>
<td>69%</td>
<td>Diantimony trioxide (Sb2O3)</td>
<td>25%</td>
<td>Similar or lower costs</td>
<td>Similar</td>
</tr>
<tr>
<td>Zinc production (Electrowinning of zinc)</td>
<td>69%</td>
<td>Antimony potassium tartrate ((K2Sb2(C4H2O6)2))</td>
<td>25%</td>
<td>Similar or lower costs</td>
<td>Similar</td>
</tr>
<tr>
<td>Zinc production (Electrowinning of zinc)</td>
<td>69%</td>
<td>No substitute</td>
<td>50%</td>
<td>no substitute</td>
<td></td>
</tr>
</tbody>
</table>

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SCRREEN2 [Title] | 5
Substitution: Depending on the application there are different possibilities of substituting arsenic. (European Commission, 2018b; ECHA, 2010; USGS, 2019)

Other issues: Arsenic is an element of earth’s crust and a component of many minerals. It is naturally released into the environment naturally through the weathering, oxidation and erosion of sulfide minerals. These sulfide minerals can form soils with very high concentrations of arsenic, and the arsenic can dissolve in water (Wang et al., 2006). An estimated 25% of arsenic emissions into the atmosphere come from natural sources, mostly volcanoes. The majority of the arsenic released by all sources end up in the soil and the ocean. The rate of arsenic release from sulfide minerals can be accelerated by mining activities, which expose the minerals to weathering processes during excavation (Wang et al., 2001). Arsenic oxide dust is produced during copper and gold smelting, and coal combustion. When coal is burned, ash is produced which contains most of the naturally occurring arsenic. More than 99% of the ash is collected and is either sent to specially designed ash ponds or disposal sites or recycled into commercial products. Arsenic can also be leached out of some metal ores by cyanide or acid rock drainage but can be captured and removed from wastewater before it is released into the environment.

EU TRADE

For the purpose of this assessment, Arsenic is evaluated at both extraction and processing stage.

Table 4. Relevant Eurostat CN trade codes for Arsenic.

<table>
<thead>
<tr>
<th>CN trade code</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>28048000</td>
<td>Arsenic</td>
</tr>
</tbody>
</table>

Eurostat (2021) reports two trade codes including arsenic: CN8 28048000 “Arsenic” and CN8 28112910 “Sulphur Trioxide "Sulphuric Anhydride"; Diarsenic Trioxide”. As indicated in the previous criticality assessment and factsheet, it has been decided not to use the trade code 28112910 in further evaluation of criticality, as it could not be determined whether this code measures only diarsenic trioxide or Sulphur trioxide as well. UNCOMTRADE database provides trade data under the code 281219 as arsenic trichloride and other chloride and chlorides oxides. It is difficult to derive arsenic trichloride data from this. Therefore, the following trade figure is based solely on arsenic metal.

Figure 5 presents the imports and exports of arsenic. The EU is a net importer of arsenic metal (CN8 28048000) between 2016 and 2020. The annual imports of arsenic metal during this period were above 500 with a peak in 2017 reaching 716 tonnes. The exports ranged between 36 and 51 tonnes over the same period.

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The main supplier of arsenic metal for the EU is China covering 90% of the total imports. On average EU imported about 400 tonnes of Arsenic metals from China in past 20 years. The import from other suppliers are Japan (6%) and USA (8%) (Eurostat, 2022).

There are no export quotas or restrictions by suppliers of the EU; however, Morocco imposes taxes of up to 25% on arsenic and arsenic sulphides. The EU has trade agreements with Namibia and Japan in place. (OECD, 2019).
PRICE AND PRICE VOLATILITY

Arsenic prices are dependent on the form in which it is brought on to the market (either as arsenic metal from China or arsenic trioxide from China or Morocco). From 2012 to 2016, prices for arsenic metal increased from €1.3/kg to €1.7/kg. This is due to the increased demand for gallium-arsenide driven by high-tech applications and the growth of the digital industry (USGS, 2014). In 2017 and 2018, arsenic metal prices showed a relatively strong decrease to €1.4/kg and €1.2/kg, respectively (USGS, 2017). Price drivers can be attributed to a combination of high supply risk and diversified market policy of China. On the other hand, there is a growing demand for China increasing its need for imports from overseas sources. Arsenic price volatility was around 22% between 2016 and 2020. In this period, price volatility was mostly disturbed by the price changes from €1.2/kg in 2018 to €1.7/kg in 2019. After 2019, the arsenic price started to decrease again, which turns into a relatively high volatility in the 2016-2020 period.

![Graph showing annual average price of arsenic metal between 2000 and 2020](image)

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

OUTLOOK

Arsenic trioxide production experienced fluctuations in recent years but the overall trend shows a decline. The arsenic world market is foreseen to shrink due to the tighter environmental regulations which are to be applied (MCGroup, 2022). At the same time, it is expected that specific industrial applications, such as marine timber,
plywood roofing, and utility poles, will continue to use CCA-treated wood. The use of high-purity arsenic metal will also continue to be an important input for military, space, and telecommunications, and in solar cells. In addition, new prospects for arsenic trioxide arise from the increased penetration of GaAs-based LEDs and GaAs wafers in Wi-Fi applications (MCGroup, 2022; USGS, 2019). The EU is heavily dependent on arsenic metal from China (about 90%), in addition to Japan and Hong Kong. There are potential mineral resources and producing mines for arsenic within EU that are mainly related to gold-bearing volcanic mass sulphide deposits or carbonate replacement as well as gold epithermal mineral systems. An example is the Olympias mine in northern Greece which hosts a gold-rich polymetallic (Pb, Zn, Au, Ag) carbonate replacement deposit and produces sphalerite, galena and arsenopyrite concentrates. The mine produces approximately 120,000 tonnes of gold arsenopyrite-pyrite concentrate with Au grade ranging from 18 to 35 g/t and As from 7 to 14%. The majority of such concentrates from the EU are shipped to China with some quantities delivered to Russia as well. Concentrate producers are however not paid for the presence of As but are penalized instead. The COVID-19 pandemic did not seem to have any real impact on production however delays in the shipment of pure arsenic from Asia to Europe as well as a rise in transport costs were reported.

DEMAND

GLOBAL AND EU DEMAND AND CONSUMPTION

Figure 8. Arsenic (CN 28048000) processing stage apparent EU consumption. There is no EU production reported in WMD (2022) before 2008. Consumption is calculated in arsenic content (EU production+import-export).

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Arsenic processing stage EU consumption is presented by HS code CN 280480 Arsenic. Import and export data is extracted from UNComtrade (2021). Production data is extracted from WMD (2022) for extraction stage diarsenic trioxide (arsenic content 75.7%).

This demand is mainly covered by only one domestic source – Belgium is producing 59% of EU supplies of arsenic (content) (Eurostat 2022; WMD, 2022).

Based on UNComtrade (2022) and WMD (2022) average import reliance of arsenic is 39.0 % for 2016-2020.

EU USES AND END-USES

The major application area for arsenic compounds in the EU is the production of zinc together with the manufacture of glass (European Commission, 2018).

In this assessment, the share of arsenic by application was estimated based on the manufacturing and use mass flow of diarsenic trioxide in the EU, reported by ECHA (2010). According to this study, the main application of diarsenic trioxide in the EU is zinc production.

Another important sector using diarsenic trioxide in the EU is special glass production.

The chemicals industry mainly produces other arsenic compounds, as well as ultra-pure arsenic metal for the semiconductor and electronics industry.

The connectivity to the raw materials gallium and indium through the use as gallium and indium arsenide in semiconductors should be mentioned here. However, quantitatively this only plays a minor role in the use of arsenic in the EU (0.1%).

Arsenic metal is used for alloys, e.g. in lead alloys. It is also used in building & construction work and municipal supply (e.g. electricity, steam, gas, water) and sewage treatment (ECHA, 2019).

The breakdown of arsenic by application in the EU can be seen in Figure 9.

Figure 9. End-uses of Arsenic in the EU, calculation based on (ECHA 2010) by JRC.

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No more recent data on the arsenic end use distribution in the EU is available. Presented numbers were cross-checked for current validity in an expert consultation (SCRREEN workshop 2021).

Table 5 Arsenic applications, 2-digit and associated 4-digit NACE sectors, and value added per sector for 2018 (* for 2014) (Eurostat, 2021)

<table>
<thead>
<tr>
<th>Applications (As compounds, ultra-pure arsenic metal)</th>
<th>2-digit NACE sector</th>
<th>4-digit CPA</th>
<th>Value added of NACE 2 sector (M€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc production (Electrowinning of zinc)</td>
<td>C24 – Manufacture of basic metals</td>
<td>C2443 – Lead, zinc and tin production</td>
<td>71,391</td>
</tr>
<tr>
<td>Glassmaking</td>
<td>C23 – Manufacture of non-metallic mineral products</td>
<td>C2319 – Manufacture and processing of other glass, including technical glassware</td>
<td>69,888</td>
</tr>
<tr>
<td>Chemicals</td>
<td>C20 – Manufacture of chemicals and chemical products</td>
<td>C2013 – Manufacture of other inorganic basic chemicals; C2059 – Manufacture of other chemical products n.e.c.</td>
<td>117,093*</td>
</tr>
<tr>
<td>Alloys</td>
<td>C24 - Manufacture of basic metals</td>
<td>C2443 – Lead, zinc and tin production; C2445 – Other non-ferrous metal production</td>
<td>71,391</td>
</tr>
<tr>
<td>Electronics (Circuit boards, GaAs wafers and semiconductors)</td>
<td>C26 – Manufacture of computer, electronic and optical products</td>
<td>C2611 – Manufacture of electronic components; C2612 – Manufacture of loaded electronic boards</td>
<td>84,021*</td>
</tr>
</tbody>
</table>

Figure 10. Value added per 2-digit NACE sector over time (Eurostat, 2022)
APPLICATIONS OF ARSENIC IN THE EU:

Uses of inorganic arsenic are widespread and occur in many different sectors (ECHA, 2010; ISE, 2019; USGS, 2019).

METALLURGY

The main application of diarsenic trioxide in the EU is the electrowinning process for zinc production. Its main purpose is the removal for impurities such as copper, cobalt, nickel, etc. Arsenic metal is also used in lead alloys to improve strength and castability. Furthermore, it is used as antifriction additive in alloys for bearings.

GLASS SECTOR

Diarsenic trioxide is used in the special glass sector to produce lighting glass, optical glass, laboratory and technical glassware, etc. for the purpose of decolourization purposes, as enamel or as fining agent. Germanium-arsenide-selenide or gallium arsenide is used for specialty optical materials. Gallium arsenide is additionally an alternative for zinc selenide in laser systems for lenses and rear mirrors, providing high toughness and durability.

CHEMICALS FOR THE ELECTRONIC SECTOR

There is a production of arsenic compounds for application in the electronics sector. High-purity arsenic metal is used to produce gallium-arsenide, indium-arsenide, and indium-gallium-arsenide semiconductors. These semiconductors have many applications in the electronics sector, e.g. in LEDs, infrared detectors, lasers, computer or biomedical, communications. They are also used to produce photovoltaic panels. Additionally, arsenic is investigated as a doping agent for cadmium telluride solar panels for increasing cell voltage of these thin film solar devices. Traditionally copper is used for this treatment. However, studies have shown great potential for arsenic, phosphorus, and antimony. (Kartopu, G. et al., 2019). Most of the arsenic consumption for semiconductors takes place in China (SCRREEN 2021). Arsenic is also used in the production of lead-acid batteries (Grund et al., 2012).

FURTHER ARSENIC USES OUTSIDE THE EU

The use of arsenic in the electronics sector takes mainly place in China but is not completely absent in the EU and thus already described in the applications of arsenic in the EU. Applications of arsenic, which are not at all relevant in the EU production, are within the agricultural sector.

AGRICULTURE

Chromated copper arsenate can be used in forestry as a wood preservation and as herbicide and insecticide in agriculture (Grund et al., 2012). Due to environmental implications, this use is highly restricted in the EU but still applied in some countries like the US. The same applies to the use of arsenic in fertilizers, fireworks and pesticides.
Depending on the application there are different possibilities of substituting arsenic. (European Commission, 2018b; ECHA, 2010; USGS, 2019)

**METALLURGY**

Zinc production: possible alternatives for diarsenic trioxide in the electrowinning of zinc are diantimony trioxide (Sb$_2$O$_3$) and antimony potassium tartrate (K$_2$Sb$_2$(C$_4$H$_2$O$_6$)$_2$).

Alloys: There is no current option to substitute in the application in lead alloys as these are being phased out.

Copper foil: The study by the European Commission on Inorganic arsenic compounds (2018b) found an application of an alternative for arsenic in copper foils, the name was not disclosed. At the time of the study, it has been used for approx. 30% of the production showing similar physical properties.

Gold electroplating: no suitable alternatives considering technical and economic feasibility have been found.

**GLASS SECTOR**

Glass production: there is continuous research going on into replacing arsenic in special glass production, however, alternatives are currently not available, where very high-quality glass is required.
There are no alternatives for arsenic in some optical filter glass, as they rely on the intrinsic properties for arsenic.

Some glass-ceramic hobs are now arsenic-free but producing clear glass hobs without arsenic remains a difficult challenge.

There are alternatives for fining agents: sodium sulphate and antimony trioxide for lead crystal, sodium/potassium nitrates with antimony trioxides in special glasses, as well as cerium oxide.

There are also alternative decolourising agents: antimony trioxide as decolourising agent for glass and as opacifier in ceramics and enamels, selenium for lead crystal, cerium oxide in special glass and as opacifier in ceramics and enamels.

**ELECTRONICS SECTOR**

Semiconductors: Gallium-arsenide can be replaced by indium-phosphide, gallium- nitrate and silicon-germanium. (USGS, 2019).

Specifically, for power amplifiers Ga-As, can be replaced with silicon based complementary metal oxides for midtier third generation handsets (USGS, 2021)

Defence-related applications: So far, no effective substitute for gallium-arsenide based integrated circuits exists.

For heterojunction bipolar transistors, silicon-germanium is also an effective substitute for GaAs use (USGS 2021).

Alternatives for GaAs laser diodes include indium phosphide for some specific wavelengths, and helium-neon laser compete with GaAs in visible laser diode applications (USGS 2021)

**OTHER: AGRICULTURE, FIREWORKS, AND WOOD PRESERVATION**

There are a number of copper-based alternativites to CCA as well as boron-based preservatives. Also, timber itself can be replaced by concrete, plastic composite materials etc. negating the need for wood preservatives altogether. USGS (2021).

**SUPPLY**

**EU SUPPLY CHAIN**

According to (WMD, 2022) the EU production of arsenic oxide was 1000 tonnes produced through the smelting or roasting of nonferrous metal ores, concentrates or copper smelter dusts in Belgium (Valenzula, 2000). This production corresponds to 732 tonnes of elemental arsenic. The EU demand for 2020 was 1600 tonnes which was covered by the importing of about 600 tonnes corresponding to an import reliance of 37.5% (Eurostat, 2022). However, this estimation is incomplete for arsenic because there were no figures on the
trade of diarsenic trioxide. Therefore, in this assessment, the EU supply risk, calculated mainly based on EU import and domestic production, was excluded.

The company Vital Materials Co. based in Belgium manufactures gallium arsenide substrates which are used as semiconductors in wireless communication applications for example. Another Belgian company KBM Affilips manufactures a wide range of master alloys, such as lead-arsenic, copper arsenic, or lead-arsenic-antimony alloys. Overall, there are eight companies having registered arsenic use with ECHA in Belgium, France, Spain, Slovakia, Germany, and Luxembourg (ECHA, 2019; Vital Materials Co., 2019; KBM Affilips, 2019).

Only two companies produce diarsenic trioxide in the EU. Also, the number of importers is very limited. ECHA’s study concludes a very low level of complexity of the arsenic supply chain, as 88% of arsenic used in the EU is concentrated in the industry sectors of: glass production and recycling, electronics, chemicals and copper and zinc metallurgy (as As is used for the manufacturing of specific alloys). About few dozen of Companies use arsenic trioxide in their production chain (European Commission, 2018b).

**SUPPLY FROM PRIMARY MATERIALS**

**GEOLOGY, RESOURCES AND RESERVES OF ARSENIC**

**GEOLOGICAL OCCURRENCE**

Arsenic is an element stemming predominantly from natural sources occurring ubiquitously in the earth’s crust with a concentration of 1.0-2.0 ppm which is why it is considered a rare element. (Lebensmittelchemisches Institut, 2010) Arsenic can occur in its elemental form, but usually does not occur in large deposits rather as a component in other minerals. It may be obtained as a by-product from copper, gold and lead smelter flue dust, as well as from roasting arsenopyrite, the most abundant ore mineral of arsenic (USGS, 2021).

**GLOBAL RESOURCES AND RESERVES**

World reserves data are unavailable, as arsenic is mainly produced as a by-product via the processing of various ores but are thought to be more than 20 times of the annual world production in 2021 (59,000 t) according to USGS data (USGS, since 2000).

There are recoveries of orpiment (As2S3) and realgar (AsS) occurrences in China, Peru and the Philippines. China has stockpiled orpiment and realgar from gold mines for later recovery of arsenic. Arsenic occurrences are associated with copper-gold ores in Chile and gold deposits in Canada. It can also be recovered from enargite, a copper mineral. Diarsenic trioxide was produced at the hydrometallurgical complex of Guemassa, Morocco, from cobalt arsenide ore (USGS, 2021).

**EU RESOURCES AND RESERVES**

For the EU there is only resource data available for Poland (Table 7).
According to Minerals4EU (2019) there is exploration activity both in Portugal and in Poland. In Portugal there were 10 active exploration licences in 2013 for occurrences including arsenic with various other commodities. In 2013 in Poland there was one exploration licence active exploring an occurrence of arsenic with other minerals.

### WORLD AND EU PRODUCTION

Arsenic is an element of the earth’s crust and can be found in its elemental form, but commonly it is found as inorganic arsenic in the form of its sulphides. Additionally, it can occur in form of its oxides and in arsenic alloys as metal arsenide and arsenate. The recovery of arsenic is mainly done by heating arsenopyrite (FeAsS) or loellingite (FeAs2) under exclusion of air at 700°C in horizontal clay pipes. Thereby arsenic is sublimated and collected in cooled collectors and condensed.

![Figure 11. Global arsenic trioxide production between 1984 and 2020 [WMD (since 1984)].](image)

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However, the production of diarsenic trioxide as a by-product in the extraction, processing and purification of copper, lead, cobalt and gold is the most important method of producing arsenic (Lebensmittelchemisches Institut, 2010).

The further reduction of diarsenic trioxide to arsenic metal was believed to have accounted for all world output of commercial-grade (99%-pure) arsenic metal (USGS, 2019).

The arsenic trioxide production per country according to WMD between 1984 and 2020 and according to USGS between 2000 and 2020 is presented in Figure 11 and Figure 12, respectively [WMD, 2022; USGS, 2021].

![Figure 12. Global arsenic trioxide production between 2000 and 2020 (USGS since 2000).](image)

**SUPPLY FROM SECONDARY MATERIALS/RECYCLING**

There is no mentionable documented recycling of arsenic taking place. According to UNEP (2013) report “Recycling Rates of Metals” Old Scrap Ratio, Recycled Content and End-of-Life Recycling Rate are all below 1%. There are no data in respect to the methodologies that used for the recycling of arsenic in EU. Vacuum pyrolysis has been proposed as environmentally technique for the recovery of As by GaAs-based e-waste such as end-of-life light-emitting diodes (LEDs). Arsenic and gallium can be recovered efficiently at the heating temperature of 1273 K, the processing time of 60 min, and the vacuum pressure of ~20 Pa, while the total recovery efficiency can reach 95 wt %. Ga, As-Ga and As are recovered in district zones into the reactor (Zhan et al. 2018).
PROCESSING OF ARSENIC

Arsenic is produced as a by-product through the thermal treatment of arsenopyrite (i.e. through the oxidative roasting of gold-bearing arsenopyrite or Au-ores containing arsenopyrite aiming to the increase of their leachability). To obtain pure arsenic metal the first step is the thermal reduction of the raw material diarsenic trioxide with coke or iron, producing arsenopyrite (FeAsS) or loellingite (FeAs₂). This is then heated in vacuum in horizontal sound tubes where elemental arsenic sublimes and returns to its solid state on the cold surface. In order to obtain arsenic metal with a purity greater 99.99999% necessary for semiconductor applications, multi-distilled diarsenic trichloride is reduced in hydrogen (ISE, 2019).

OTHER CONSIDERATIONS

HEALTH AND SAFETY ISSUES

People are also exposed to elevated levels of inorganic arsenic (As) through contaminated drinking water, using contaminated water in food preparation and irrigation of food crops, industrial processes, eating contaminated food and smoking tobacco. Long-term exposure to inorganic arsenic, mainly through drinking-water and food, can lead to chronic arsenic poisoning. Skin lesions and skin cancer are the most characteristic effects. WHO (2019) provides guidelines for values of arsenic in drinking water and risk management recommendations. The EU has regulations in place limiting the amount of arsenic in water and food.

Occupational exposure to arsenic would be via inhalation and dermal contact. Occupational exposure to inorganic arsenic compounds may take place, for example, in the formation of the substances involving alloys with arsenic metal or in thermal processes where arsenic is present as unintentional impurity in raw materials. Furthermore, arsenic compounds are present in dust formed by the processes. The number of workers potentially exposed to inorganic arsenic in the workplace is high. (European Commission, 2018).

**DIRECTIVE (EU) 2019/983** regulates the protection of workers from the risks related to exposure to carcinogens or mutagens at work. According to the EU harmonised classification and labelling (CLP), this substance is toxic if swallowed, is toxic if inhaled, is very toxic to aquatic life and is very toxic to aquatic life with long lasting effects. Moreover, some uses of this substance are restricted under Annex XVII of REACH.

**Regulation (EC) No 1223/2009** lists in its Annex II substances that are prohibited for use in cosmetics, among others arsenic and its compounds. **Directive 2009/48/EC** on the safety of toys (formerly 88/378/EEC) include 55 allergenic substances that are prohibited in toys, allergenic substances that require labelling, and migration limits for other substances which may not be exceeded.

Maximum levels for arsenic in certain foods have been established by **Commission Regulation (EC) No 2015/1006** (future section 3.5 of the Annex to Regulation (EC) No 2006/1881, applicable from 1 January 2016 onwards). **Regulation (EU) 2019/1009** sets limits for arsenic in fertilising products.

The arsenic content of copper concentrates on the world market has been increasing and there is a competition for concentrates with low content of arsenic. Around 30 % of world copper concentrates contain more than 0.1 % arsenic. Complex copper concentrates have an arsenic content greater than 0.2 % with no

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upper limit. Many copper smelters able to process complex concentrates with high arsenic content prior to the 1990s, have either stopped this practice or closed for environmental reasons. Currently only a few copper smelters in the world can process complex concentrates, and there are ongoing attempts to reduce arsenic contents in concentrates.

Arsenic is contained in some electrical and electronic components. According to the Technical Rules for Hazardous Substances in Germany, an exposure to cadmium and arsenic compounds is to be expected during treatment and recycling of waste electrical and electronic equipment (WEEE) in particular with recycling of photovoltaic modules which are not silicon-based (European Commission 2018).

**ENVIRONMENTAL ISSUES**

Arsenic is an element of earth’s crust and a component of many minerals. It is naturally released into the environment naturally through the weathering, oxidation and erosion of sulfide minerals. These sulfide minerals can form soils with very high concentrations of arsenic, and the arsenic can dissolve in water (Wang et al., 2006). An estimated 25 % of arsenic emissions into the atmosphere come from natural sources, mostly volcanoes. The majority of the arsenic released by all sources end up in the soil and the ocean.

The rate of arsenic release from sulfide minerals can be accelerated by mining activities, which expose the minerals to weathering processes during excavation (Wang et al., 2001). Arsenic oxide dust is produced during copper and gold smelting, and coal combustion. When coal is burned, ash is produced which contains most of the naturally occurring arsenic. More than 99 % of the ash is collected and is either sent to specially designed ash ponds or disposal sites or recycled into commercial products. Arsenic can also be leached out of some metal ores by cyanide or acid rock drainage but can be captured and removed from wastewater before it is released into the environment.

**NORMATIVE REQUIREMENTS**

Emissions of arsenic and compounds are covered by increasingly stringent regulations, namely the Directive (EU) 2016/2284 on the reduction of national emissions of certain atmospheric pollutants, and Directive 2006/118/EC on the protection of groundwater against pollution and deterioration.

**SOCIO-ECONOMIC AND ETHICAL ISSUES**

**ECONOMIC IMPORTANCE OF THE ARSENIC FOR EXPORTING COUNTRIES**

According to COMTRADE (2022), the shares of exports of Arsenic in the total value of exports remain below 0.1 % in each of the exporting countries so that the economic importance of these exports is limited.

**SOCIAL AND ETHICAL ASPECTS**

The current emphasis of developing countries on policies that favour the intensification of mining exploitation as the main source of incomes has generated negative consequences for ecosystems and rural communities,
mainly due to the release of highly toxic elements into the environment, including arsenic. Specifically in Latin America, the “As [arsenic] problem” is known in all of its 20 countries, resulting in diverse environmental and public health impacts (Bundschuh et al., 2021; Khan et al., 2019). For these reasons, mining conflicts emerge as social conflicts between local populations, mining companies and the governments.

In the last five years, more than four activists were on average killed every week worldwide defending territories against the invasion of industries like mining. More than half of those killings occurred in Latin America. In that region, the mining sector experienced a significant increase in investments in the past decades and the occurrence of mining related conflicts increased accordingly (Temper et al., 2022).

(Manonen et al., 2022) the number of mining conflicts has been on the rise globally and in the EU, most often at the local or regional level, where the conflict focuses on project-specific issues: extraction, processing, waste management, or transport of minerals. The limited literature suggests that there are several and varying reasons which are fuelling mining conflicts in the EU, being one the most important related to metals in the context of planned or realised openings of new mines. Top environmental concerns were: i) loss of landscape or aesthetic degradation, ii) ground water pollution or depletion and, iii) surface water pollution or decreasing water quality. Arsenic pollution of water is the main topic related to metal mining in Europe (Kivinen et al., 2020).

RESEARCH AND DEVELOPMENT TRENDS

RESEARCH AND DEVELOPMENT TRENDS FOR LOW-CARBON AND GREEN TECHNOLOGIES

- Integration of gallium-arsenic solar cells with mini-concentrators
  (Kyunsang, L. et al., 2015) investigated how to reduce production costs and increase the efficiency of thin-film gallium arsenide (GaAs) solar cells (SCs). The researchers integrated SCs with solar light concentrators, using mini-compound parabolic concentrators (CPCs). The SCs were produced with an accelerated non-destructive epitaxial lift-off (ELO) process and integrated with thermoformed mini concentrators. The CPCs were characterized by low cost, ease of production, lightweight and wider acceptance angle for solar light adsorption with respect to conventional concentrators. Compared to conventional SCs, the modules produced by (Kyunsang, L. et al., 2015) showed 2.8 times gain in annual energy harvesting and a production and operation cost reduction of 89 % since they reached a price of 0.34 $/W peak.

- Single-junction gallium-arsenic solar cells
  (Wang, Y. et al., 2017) produced a single junction pilot gallium arsenide (GaAs) solar cell (SC) on a silicon (Si) substrate, aiming at reducing the shortcomings of the integration of GaAs on the Si. Namely, a lattice mismatch between GaAs and Si causes high defect density and a rough contact surface, reducing the carrier’s lifetime, provoking degradation, and reducing the overall SC performance. The single junction GaAs solar cell operated with an open circuit tension (V_{oc}) of 900.2 mV and a short circuit current (J_{sc}) of 19.6 mA/cm^2. The energy conversion efficiency was 16 %, indicating that there are opportunities for applying this structure in large-area and low-cost applications.

OTHER RESEARCH AND DEVELOPMENT TRENDS

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The mechanism of low-level arsenic exposure-induced hypertension: Inhibition of the activity of the angiotensin-converting enzyme \(^2\), Rahaman et al. (2023)

It is well-established that arsenic exposure induces hypertension in humans. Although arsenic-induced hypertension is reported in many epidemiological studies, the underlying molecular mechanism of arsenic-induced hypertension is not fully characterized. In the human body, blood pressure is primarily regulated by a well-known physiological system known as the renin-angiotensin system (RAS). Hence, the potential molecular mechanisms of arsenic-induced hypertension was explored, by investigating the regulatory roles of the RAS.

Spatial distribution of arsenic in surface sediments of the southern Baltic Sea\(^4\), Szubska et al (2023)

Arsenic is a ubiquitous chemical element, occurring naturally worldwide. Yet due to its global cycle, its concentrations in the marine environment are manifold higher than the terrestrial background and may pose harm to biota. This is especially relevant for the Baltic Sea, which is very susceptible to any kind of pollution. Arsenic transported to the sea is adsorbed on iron oxides or precipitating as flocculating particulates and finally bounded in sediments. Therefore, despite the contemporary emission cuts, the existing pollution remains or constantly circulates in marine habitats. The purpose of the research was to recognize the spatial distribution of arsenic in the surface sediments of the southern parts of the Baltic Sea. The number of 483 samples allowed us to prepare reliable interpolation of arsenic contents in surface sediments. Although arsenic concentrations in the Baltic Sea can be considered low, in particular areas the levels are significantly higher. The observed arsenic concentrations distribution pattern could be mostly explained by natural transportation and accumulation bottom-type distribution.

NANOREMOVAS\(^5\): Advanced multifunctional nanostructured materials applied to remove arsenic in Argentinian groundwater (EU, 2015-2018)

Daily intake of arsenic polluted water by cattle in Argentina is becoming of increasing concern, especially due to the important size of the livestock export market where EU is a main customer. Because natural forage or alfalfa grown without irrigation is used to feed livestock, drinking water is considered the main source of arsenic for cattle (several studies reveal arsenic concentrations in phreatic water samples above 0.15 mg/L, the level that suggest causing chronic intoxication in cattle). Therefore, as it has been demonstrated, there is a risk for human health due to the introduction in the food chain through milk or meat. In view of arsenic toxicity and the large number of people exposed to its effects worldwide, there is a clear need for the implementation in remote exploitations of affordable and sustainable treatment methodologies to provide potable water to cattle. To face this problem and provide a solution, NANOREMOVAS pursued to develop and implement a pilot plant for the treatment of arsenic polluted waters based on the application of state-of-art advanced multifunctional nanostructured materials, already tested at the laboratory level. In this sense,
NANOREMOVAS includes the cooperation between the industry and academia of partners from Europe and Argentina.

- AsLife: Life in Arsenic rich environments: Challenge or opportunity? (EU, 2016-2018)

Arsenic (As) is a notorious toxin, and as such may have exerted a strong selective pressure on the distribution and evolution of life on Earth. Despite evidence supporting the high levels and prominent role of As on the primitive Earth, the essentiality and toxicity of As, and its impact on evolutionary processes remains unexplored. AsLife aims at taking a novel approach to assessing microbial As cycling by exploiting two linked «environments». The first are the microbial mats from High-Altitude Andean Lakes, where it is known that As concentrations are far above background levels. Specifically, living and diagenetically modified microbial mats will be investigated using scanning hard X-ray nanoprobes emerging at synchrotron facilities. This non-invasive and non-destructive technique provides data on a sub-micrometer scale by which to tie physiological inference from trace metal(loid)s distribution and speciation patterns directly to the microfossil biomass. Thus, providing a means to understand the interplay between microbial metabolisms and bioavailability of trace metal(loid)s in living and fossil ecosystems. The second environment comprises laboratory cultures, using the sampling power of «adaptive laboratory evolution» to explore how microbes adapt and enhance As detoxification facing the extreme As levels present in Andean Lakes. These results were discussed in light of genomic studies of As-rich microbiota performed by Argentinian colleagues.

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