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Germanium: Current and Novel Recovery Processes

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Abstract

Germanium (Ge) is considered a critical element due to its many industrial applications; Ge is a metalloid used in solar cells, fiber optics, metallurgy, chemotherapy, and polymerization catalysis. The main sources of Ge are sulfides ores of Zn, Pb, and Cu, coal deposits, as well as by-products and residues from the processing of these ores and coals (e.g., smelting flue dust and coal fly ashes). Indeed, over 30% of global Ge consumed come from recycling processes. The recovery of Ge from sulfide ores is mostly based on hydrometallurgical processes followed by a number of mass transfer techniques to concentrate Ge (e.g., solvent extraction). However, environmental-friendly extraction methods of Ge from coal fly ashes and copper smelting flue dust have recently been proposed in order to reduce environmental impacts. In addition, novel processes based on absorption of Ge with ribbon grass have become an interesting option not only to produce Ge but also to boost soil decontamination and biogas production. This chapter presents a general description of Ge occurrence, associations, and chemistry as well as a review of the current and novel recovery processes of Ge. The main sources of Ge and its main industrial applications are also discussed.

Keywords: germanium, residues, by-products, hydrometallurgical processes

1. Introduction

Germanium (Ge) was discovered in Freiberg in 1885. One year later, it was isolated from the uncommon mineral argyrodite (Ag_8GeS_6) by the chemist Clemens Winkler [1]. Ge is a chemical element with a grayish-white color whose position in the periodic table indicates that it has physicochemical properties similar to silicon (Si) and tin (Sn). Germanium has five

naturally occurring isotopes, ^{70}Ge , ^{72}Ge , ^{73}Ge , ^{74}Ge , and ^{76}Ge , the latter being slightly radioactive, with a half-life of 1.58×10^{21} years [2]. However, ^{74}Ge is the most common isotope, having a natural abundance of approximately 36% [3].

Germanium is a scarce element in the Earth's crust (about 1.6 ppm Ge crustal average) that rarely forms its own minerals [6]. It often appears in the form of the oxide (GeO_2) or the sulfide (GeS_2) and in solution as germanic acid [7, 8]. However, most Ge is dispersed through silicate minerals due to the substitution of Ge^{4+} for the geochemically similar Si^{4+} . Ge is also associated with minerals or ores containing graphite (C), zinc (Zn), copper (Cu), iron (Fe), tin (Sn), and silver (Ag) [8]. Germanium can be classified either as a semimetal or metalloid because it shows both metal and nonmetal properties [4, 5]. As pure element, Ge has a metallic appearance at room temperature and behaves brittle with increasing mechanical deformation. In addition, Ge has a high refractive index and low chromatic dispersion and ability to form extended three-dimensional networks of Ge-O tetrahedra like Si-O [1, 9]. These physical properties determine the high economic importance of Ge and compounds in the industry sector. In this regard, the European Commission included Ge in a list of raw materials of critical concern for members of the European Union (EU) not only because of its high economic importance [10] but also because its industrial production is focalized in a small number of countries (mainly in China), and the world's demand pressure is increasingly growing.

2. Germanium-bearing minerals and residues

Nearly 30 minerals are known to contain Ge, mostly sulfides (**Table 1**). Germanium is a substituting element in Zn-sulfide structures (up to 3000 ppm in sphalerite and wurtzite ($(\text{Zn,Fe})\text{S}$) and Cu sulfides (up to 5000 ppm in enargite, tennantite, bornite, and chalcopyrite) [3]. Germanium is also present as a substituting element in oxides (e.g., up to 7000 ppm in hematite (Fe_2O_3)), hydroxides (up to 5310 ppm in goethite (FeOOH)), phosphates, arsenates, vanadates, tungstates, and sulfates [3, 11].

Germanium can also occur in rare minerals such as argyrodite (Ag_8GeS_6), germanite ($\text{Cu}_{13}\text{Fe}_2\text{Ge}_2\text{S}_{16}$), renierite ($(\text{Cu,Zn})_{11}(\text{Ge,As})_2\text{Fe}_4\text{S}_{16}$), or briartite ($\text{Cu}_2(\text{Fe,Zn})\text{GeS}_4$). Germanium-bearing ores are hosted in a variety of deposit that contains Au, Pb, and Ag, apart from those of Cu and Zn. Deposit types that contain significant amounts of Ge include volcanogenic-hosted massive sulfide (VMS), sedimentary exhalative (SEDEX), Mississippi Valley-type (MVT), Pb-Zn (including Irish-type Zn-Pb deposits), Kipushi-type Zn-Pb-Cu replacement bodies in carbonate rocks, polymetallic Zn-Sn vein, and coal deposits [9].

The VMS deposits are major sources of Zn, Cu, Pb, Ag, and Au and significant sources for Ge. They typically occur as lenses of polymetallic massive sulfides that form at or near the seafloor in submarine volcanic environments and are classified according to base metal content, Au content, or host-rock lithology [12]. There are close to 350 known VMS deposits in Canada and over 800 known worldwide. The most common feature among all types of VMS deposits is that they are formed in extensional tectonic settings, including both oceanic seafloor spreading and arc environments. Sedimentary-exhalative (SEDEX) deposits, on the other

% germanium	Mineral name	Chemical formula	MW
69.41% Ge	Argutite	GeO ₂	104.61
53.91% Ge	Eyselite	Fe ⁺⁺⁺ Ge ⁺⁺⁺ O ₇ (OH)	401.40
45.27% Ge	Otjissimeite	PbGe ₄ O ₉	641.63
35.78% Ge	Bartelkeite	PbFe ⁺⁺ Ge ₃ O ₈	608.87
31.50% Ge	Stottite	Fe ⁺⁺ Ge(OH) ₆	230.50
24.49% Ge	Carboirite-III	Fe ⁺⁺ A ₁₂ GeO ₅ (OH) ₂	296.43
23.59% Ge	Krieselite	(Al,Ga) ₂ (Ge,C)O ₄ (OH) ₂	230.81
22.36% Ge	Carboirite-VIII	Fe ⁺⁺ (Al,Ge) ₂ O[(Ge,Si)O ₄](OH) ₂	292.20
22.31% Ge	Brunogeierite	(Ge ⁺⁺ ,Fe ⁺⁺)Fe ⁺⁺⁺ ₂ O ₄	244.11
18.57% Ge	Briartite	Cu ₂ (Zn,Fe)GeS ₄	390.97
16.49% Ge	Barquillite	Cu ₂ CdGeS ₄	440.38
13.42% Ge	Schaurteite	Ca ₃ Ge ⁺⁺⁺ (SO ₄) ₂ (OH) ₆ •3(H ₂ O)	541.06
10.83% Ge	Carraraite	Ca ₃ Ge(OH) ₆ (SO ₄)(CO ₃)•12H ₂ O	670.75
10.79% Ge	Maikainite	Cu ₂₀ (Fe,Cu) ₆ Mo ₂ Ge ₆ S ₃₂	3296.63
10.15% Ge	Germanocolusite	Cu ₁₃ V(Ge,As) ₃ S ₁₆	1609.66
10.03% Ge	Polkovicite	(Fe,Pb) ₃ (Ge,Fe) _{1-x} S ₄	470.48
9.86% Ge	Ovamboite	Cu ₂₀ (Fe,Cu,Zn) ₆ W ₂ Ge ₆ S ₃₂	3470.24
9.78% Ge	Morozeviczite	(Pb,Fe) ₃ Ge _{1-x} S ₄	705.33
9.10% Ge	Germanite	Cu ₂₆ Fe ₄ Ge ₄ S ₃₂	3192.14
7.89% Ge	Catamarcaite	Cu ₆ GeWS ₈	902.31
7.76% Ge	Putzite	(Cu _{4.7} Ag _{3.3})GeS ₆	925.86
7.62% Ge	Itoite	Pb ₃ [GeO ₂ (OH) ₂](SO ₄) ₂	952.35
7.21% Ge	Fleischerite	Pb ₃ Ge(SO ₄) ₂ (OH) ₆ •3(H ₂ O)	1006.40
6.58% Ge	Renierite	(Cu,Zn) ₁₁ (Ge,As) ₂ Fe ₄ S ₁₆	1655.51
6.44% Ge	Argyrodite	Ag ₈ GeS ₆	1127.95
5.60% Ge	Calvertite	Cu ₅ Ge _{0.5} S ₄	495.06
2.90% Ge	Tsumgallite	GaO(OH)	100.05
2.71% Ge	Mathewrogersite	Pb ₇ (Fe,Cu)Al ₃ GeSi ₁₂ O ₃₆ •(OH,H ₂ O) ₆	2678.79
1.30% Ge	Colusite	Cu ₁₂₋₁₃ V(As,Sb,Sn,Ge) ₃ S ₁₆	1673.29
0.32% Ge	Cadmoidite	CdIn ₂ S ₄	

MW: molecular weight.

Adapted from [13].

Table 1. Mineral species sorted by the element Ge.

hand, occur as tabular Zn-Pb-Ag deposits that contain laminated, stratiform mineralization and may be hosted in shale, carbonate, or carbonate- or organic-rich clastic rocks (siltstone and less commonly sandstone and conglomerate rich).

Most SEDEX deposits are hosted either by bimodal volcanic and clastic sedimentary sequence that is commonly metamorphosed to amphibolite-granulite facies, as at Broken Hill, Australia, or by basinal marine, fine-grained sedimentary rocks comprised mostly of carbonaceous chert, shales, and siltstones, less commonly by sandstones and conglomerates [14]. Mineralogy of the SEDEX deposits includes sulfides, carbonates, barite, and quartz. The most common sulfide mineral is pyrite, but the main ore minerals are invariably sphalerite and galena. SEDEX deposits account for 50% of the Pb and Zn reserves and about 25% of the global production of these metals [14]. There are more than 120 SEDEX deposits worldwide with known grade and tonnage figures, and of these 45 have geological resources greater than 20 million tons of Pb + Zn [15].

The Mississippi Valley-type (MVT) deposits can be found in the Gordonsville-Elmwood Zn-Pb district in Tennessee. These deposits, on average, have grades of 400 ppm Ge in Zn ore concentrate, while other MVT deposits in the USA may contain 50 ppm Ge in sphalerite. The Huize MVT deposit, which is located in China (Yunnan Province), is one of the largest MVT deposits in China and produces zinc-lead and Ag, Ge, and Cd by-products [16].

The most significant carbonate-hosted Zn-Pb-Cu deposits that contain notable amounts of Ge are the Kipushi deposit in the Democratic Republic of the Congo and the Kabwe deposits in Zambia [9]. Germanium averages 68 ppm in bulk samples in the Kipushi deposit and occurs substituted in sulfide minerals, although it sometimes occurs in separate Cu-Fe-Ge sulfide minerals [17].

Coal and lignite deposits are also a significant source of Ge. The Lincang lignite mine (Yunnan Province) produces 16 metric tons of high-grade GeO_2 annually, of which 90% is exported [11]. Germanium-rich coal seams are interblended with siliceous rocks that have oxygen and carbon isotope characteristics which suggested a hydrothermal origin. However, it has also been proposed that hydrothermal fluids were then discharged first as hot springs along fault zones into Miocene basins where the Ge was concentrated in lignite seams within stratiform siliceous and siliceous-limestone deposits [18].

Among the deposits containing well-constrained Ge reserves, sulfidic Pb-Zn (> 5000 tons) and high Ge lignite deposits (> 19,000 tons) constitute the two most important types of known Ge deposits [19].

Germanium can exhibit siderophile, lithophile, chalcophile, and/or organophile behavior depending on the geologic environment where it is hosted [11]. Thus, Ge shows a siderophilic behavior due to its relatively high Ge contents (up to 250 ppm) in Fe oxides such as Fe_2O_3 and Fe_3O_4 [8]. The lithophile behavior is shown by slight enrichment of Ge in the continental crust relative to the oceanic crust and the upper mantle, while the chalcophilic property of Ge is evident for its economic level in Zn- and Cu-rich sulfide hydrothermal systems. The organophile behavior of Ge, one of the highest affinities for organic matter of all the elements commonly associated with carbonaceous sediments, is marked from its enrichment in organic matter (coal and lignite deposits), which is comparable with some Zn-sulfide ores [2, 8, 11, 20, 21].

Because Ge occurs in coal deposits, by-products and residues from coal combustion and/or gasification should also be considered as Ge sources. Fly ashes (FAs) generated by combustion and gasification processes of certain coals may contain important amounts of Ge (**Table 2**). In the same way, Ge is retrieved as a by-product of sulfides ores (e.g., Zn and Cu-Zn-Pb ores); therefore, residues obtained from the ore processing, e.g., smelting flue dust, should also be considered as a potential source of Ge. By including these sources, the potential supply of Ge could exceed its current primary production [22].

Ge-bearing residues/by-products.	Ge mineral phases*	Ge content (mg/kg)	Reference
Zn refinery residue	n.d.	3620	[23]
Cu-cake	n.d.	700	[24]
coal fly ash	GeO ₂	4986	[25]
Gasification fly ash	GeO ₂ , GeS ₂ , GeSnS ₃	<500	[26]
Cu smelting flue dust	n.d.	417	[27]
Waste optical fibers	n.r	1100	[28]

*Mineral phases obtained through X-ray diffraction; n.d., not detected; n.r, not reported.

Table 2. Selection of residues and by-products with a high potential for Ge recovery.

3. Germanium production and its main applications

Germanium was initially used industrially in transistors due to its semiconductor properties. However, it was later replaced by silicon, which has better behavior with respect to temperature [9]. In 2016, Ge applications in solar cells, fiber optics, metallurgy, and chemotherapy and as catalyst for polymerization of polyethylene terephthalate (PET) comprised in 2016 almost 80% of the global consumption of Ge [20, 28–30].

Fiber optics are the major use of Ge worldwide since it is used as a doping element in optical fibers, which contain approximately 4% Ge, the rest being silicon oxide (SiO₂). Germanium increases the refractive index of the optical fiber which helps to contain the light within the fiber and enables the transmission of the digital signal. Germanium can also be used to make lenses and window panes for infrared detectors, infrared devices mainly destined to military guidance, and weapon-sighting applications and cameras because of its transparency to infrared radiation. It can, therefore, be used in numerous applications such as surveillance, night vision, and satellite systems [29–31]. With regard solar cell applications, Ge is used in high-performance multi-junction cells (typically III–V cells) in the domain of photovoltaics (PV) and in the bottom-cell part of triple junction PV, for the substrate, base, and emitter layers, because of its lattice constant, robustness, low cost, abundance, and ease of production.

Other diverse uses of Ge could be as an alloying element (0.35%) for Sn, or Al-Mg alloys, to increase their hardness; soldering material (12%Ge/88%Au) for gold-based dental prosthesis; luminescent material; photographic and wide-angle lenses; ceramics, with Na₂O/TiO₂ or K₂O/Ta₂O₅; gamma-ray detector Bi₂(GeO₃)₃; bismuth germanate oxide crystals (BGO- Bi₄Ge₃O₁₂) for

various detection technologies (scintillation, tomography, gamma spectroscopy); fluorescent paint (MgGeO_3); superconductors (Nb_3Ge); thermocouple; and thermoelectricity. Germanium dioxide is also used as a polymerization catalyst in the production of PET, giving rise to a wide range of PET bottles and containers [29–31].

As explained in last sections, Ge recovery is associated with currently produced Zn and Cu-polymetallic ores and coal deposits [11, 31–33]. None of the Ge-bearing minerals is mined solely for its content, and most of the recovered Ge is a by-product from ores and coal processing [1]. Therefore, the extraction of Ge is mostly carried out through the typical extraction methods by mining facilities (pyro- and hydrometallurgy) [1, 25]. **Figure 1** shows the pathway processing for Ge recovering either by Zn refining residues and scrap. In general, after physical separation or pyro- and hydrometallurgical processes, a concentrate of Ge with around 30% content is obtained. Thus, the Ge concentrate, regardless of its source, is chlorinated, distilled, and purified to form the first usable product, GeCl_4 , which is primarily used in fiber-optic cable production [3]. Germanium tetrachloride can be hydrolyzed and dried to

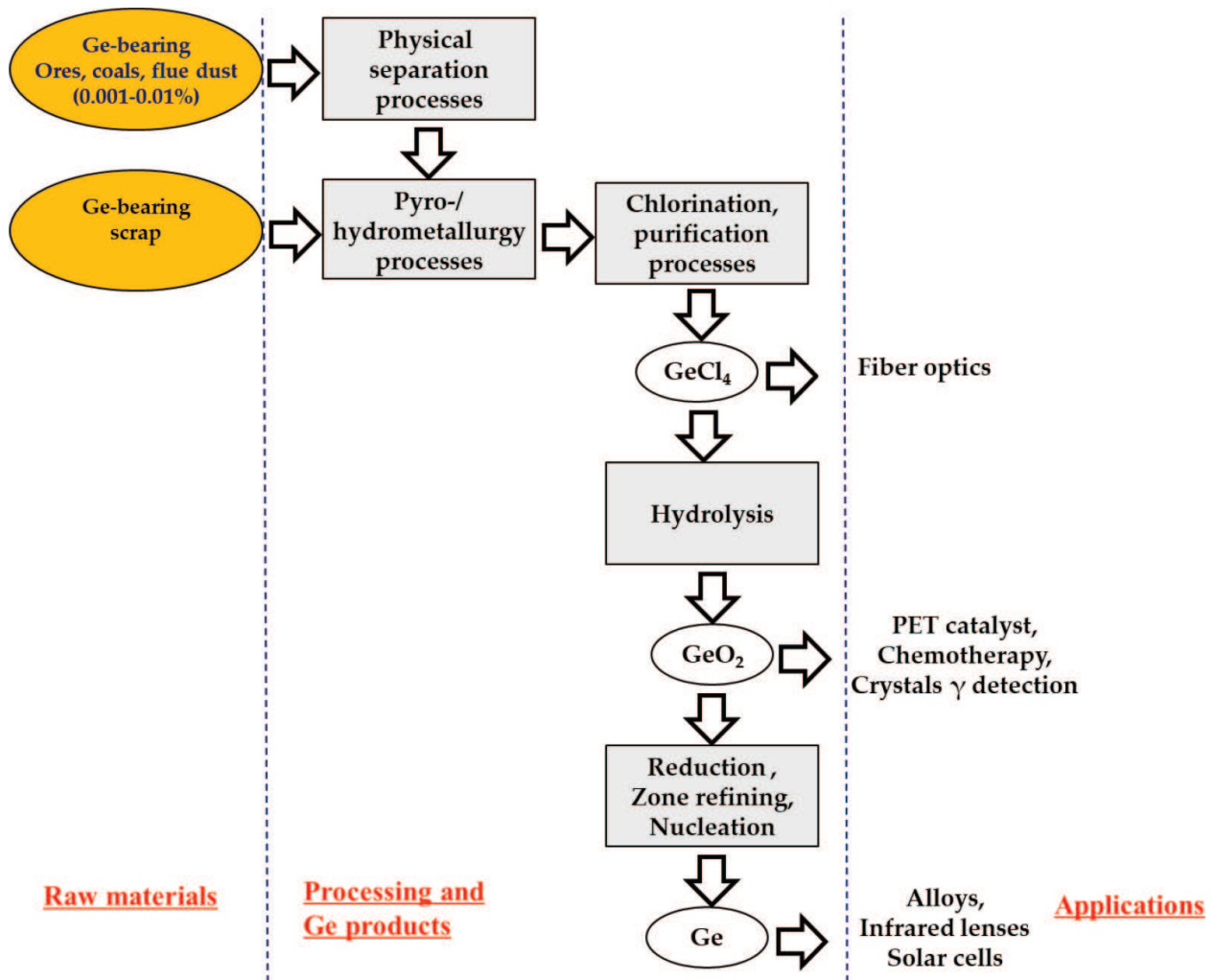


Figure 1. Germanium processing pathway, modified from Melcher and Buchholz [3].

produce GeO_2 , which is used in the manufacture of certain types of optical lenses and as a catalyst in the production of PET resin. Germanium metal powder is produced through the reduction of GeO_2 with hydrogen.

In 2017, the worldwide production of Ge was estimated to be about 134,000 kg that is mainly recovered from Zn concentrates, coal deposits, coal fly ashes, and recycled materials [20]. While several authors have reported an increase (~30%) of the Ge production in the last decade, it is known that Ge reserve is scarce and it is estimated to be 8600 tons [9, 28, 34, 35]. The contradiction between the increasing consumption and the scarce reserve of Ge is becoming more notorious and has been contributed to a strong recycling process for Ge. In 2016, about 30% of the total Ge consumed was supplied from scrap (recycled materials), e.g., from windows in decommissioned tanks and military vehicles. In special, recycling rates for fiber-optic scrap are reported as high as 80%. As a consequence, about 50% of the Ge metal used for electronic and optic are recycled in short cycle [36, 37].

As shown in **Figure 2**, the worldwide production of Ge is led by China (65.7%) followed by Russia (5%) and other countries such as Canada, Belgium, and Germany (30%) [20]. In China, Ge use in fiber optics increased substantially from 2012 to 2016 which supposed the highest consumption growth of Ge. Moreover, countries such as the USA and China treat Ge a strategic reserve, due to important value for the high-tech industry for civilian and military purposes [38]. Several authors indicate that reliable information about global Ge prices for public domain is very little published [1, 38, 39]. From the point of view of the authors, the last statements have partially contributed to the extremely global Ge price fluctuations, exceeding in last year 1300 US \$/kg for Ge metal only in the USA [20].

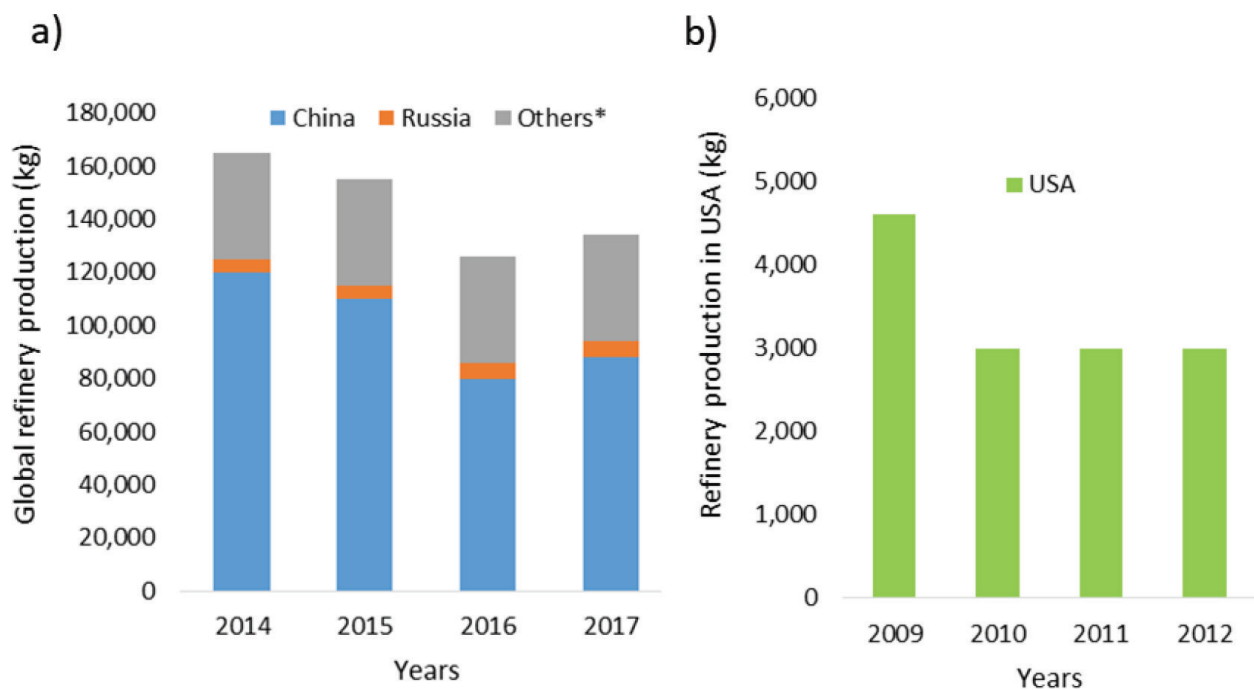


Figure 2. Germanium refinery production of (a) global main producers between 2014 and 2017 excluding the USA—* includes Belgium, Canada, Germany and others [20, 29, 30, 34]—And (b) of USA between 2009 and 2012.

4. Current and novel recovery processes for germanium

Several processes have been recommended for Ge recovering based on its content, chemical species, and mineral phases that are present in by-products from Zn, Cu, and Pb ores processing and from coal combustion and gasification. In general, hydrometallurgical processes are favored, because almost all Ge extracted is mainly concentrated by processes based on mass transfer operations. Nevertheless, it is difficult to find extractants which meet the following characteristics: (i) selective, (ii) cost-effective, (iii) eco-friendly, and (iv) commercially available. In the next sections, the authors aboard main extraction methods used for the recovery of Ge from different sources and problems associated.

4.1. Recovery of germanium from Zn ore processing

Nowadays, Zn ore processing is the main source of Ge as Zn ores have large and recoverable quantities of Ge. Zinc refinery residues, which are the typical by-products of hydrometallurgical zinc processes, usually contain between 0.2–0.5 wt% Ge and 0.3–0.4 wt% Ga with Zn, SiO₂, Cu, Fe, and Pb as the main components [39, 40]. However, on a global scale, as little as 3% of the Ge contained in Zn concentrates is recovered since it can also have a negative impact on Zn recovery, detracting from the core business for refineries [20, 41]. As a consequence, except the Chinese refineries, only two Zn refineries currently extract Ge as part of their operations [36].

Several studies have been conducted on the behavior of Ge for the effectiveness of its recovering from by-products and residues of Zn processing [23, 42–45]. In 1987, a reductive SO₂ leaching process as an alternative for Ga and Ge recovery from Zn leaching residue was investigated [42]. Only 57% of Ge was extracted, which was mainly attributed to the formation of silica-germanium gel; H₄GeO₄ and H₄SiO₄ were shown to hydrolyze the mixed polymers [46–48]. A higher yield for Ge was observed with an alkaline process used to treat Zn refinery residues. However, the authors also detected that Si, Pb, and Al hinder the recovery and purification of Ge [44, 49]. Recovery of Ge from zinc refinery residues has more frequently been carried out by leaching with H₂SO₄ being the resulting solution treated with solvent extraction (SX). Currently, synergistic SX (SSX) has been proved to increase the yield of Ge recovery and purification. Some of SX and SSX processes for Ge recovery studied are summarized in **Table 3** [50–58].

Chelating extractant Kelex 100 was primarily used for the separation of Ge⁴⁺ from Zn, reaching Ge extraction 98% in a solution of 156 g/L H₂SO₄ [50]. However, slow-phase disengagement and a high concentration of NaOH were required to strip the Ge⁴⁺ from the loaded organic solution.

Moreover, two studies achieved a good separation of Ge from Cu, Ni, As, Cl, and Fe²⁺ with a H₂SO₄ solution of 100 g/L by the use of LIX 63 [51, 52]. In 1984, a SX system, consisting of LIX 63 and LIX 26, was used for the extraction of Ge from a solution containing Ge⁴⁺ (3.5 g/L), arsenite (0.8 g/L), and Fe³⁺ (1.5 g/L) [53]. Over 99% of Ge⁴⁺ was extracted with 99% (v/v) LIX 63 and 1% (v/v) LIX 26 in four stages at lower acidity (50 g/L H₂SO₄) compared with using LIX 63 alone (>90 g/L H₂SO₄).

Extractant	Main issues of process	Reference
	Solvent extraction (SX)	
Kelex 100	<ul style="list-style-type: none"> • Good separation of Ge from Zn, Cd, Ni, Co, and As • Poor phase separation in stripping • High concentration of NaOH required for stripping 	[50]
LIX 63	<ul style="list-style-type: none"> • Good separation of Ge from Zn, Cu, Ni, As, Fe(II), and Cl • Low extraction efficiency • Slow extraction kinetics 	[52, 53]
H106	<ul style="list-style-type: none"> • Ga and Ge co-extraction • Selective stripping • H106 is not commercially available 	[55]
G315	<ul style="list-style-type: none"> • 95% Ge extraction efficiency at a low acidity • G315 is not commercially available 	[56]
	Synergistic solvent extraction (SSX)	
D2EHPA + TBP	<ul style="list-style-type: none"> • TBP improves extraction efficiency and phase separation • High concentration of NaOH for stripping 	[57]
LIX 63 + LIX 26	<ul style="list-style-type: none"> • Increased Ge extraction by addition of LIX 26 	[53]
LIX 63 + O.P	<ul style="list-style-type: none"> • Good selective Ge extraction and high efficiency • Fast degradation of LIX 63 by the acidity of O.P acid 	[58]

O.P: organophosphoric acid.

Adapted from [43].

Table 3. Summary of investigated SX or SSX systems for Ge recovery.

Other SX systems consisting of LIX 63 and D2EHPA, M2EHPA, and OPAP were also developed to recover Ge⁴⁺ from H₂SO₄ solutions (75 g/L) containing Zn²⁺, arsenate, Cd²⁺, Sb (V), In³⁺, Cu²⁺, and Fe²⁺ using a multistage counter-current process. In this case, over 95% of Ge⁴⁺ was extracted using a mixture of 25% LIX 63 and 75% D2EHPA [52].

A technology for In³⁺, Ge⁴⁺, and Ga³⁺ recovery from a H₂SO₄ leach solutions of Zn residue was also proposed [54]. Indium was first separated from the solution using SX with 30% D2EHPA in kerosene, while Ge (97%) and Ga (95%) were co-extracted with the SSX system consisting of 20% D2EHPA and 1% YW100 in kerosene at low pH values. However, the authors found that YW100 is not commercially available and the process is not eco-friendly.

The D2EHPA extractant was also developed for selective extraction of In³⁺ and Fe³⁺ and used H106 for co-extraction of Ga³⁺ and Ge⁴⁺ from a solution from H₂SO₄ leach solutions of a cementation residue in a mini pilot plant scale. Recoveries of 91%, 94%, and 93% for In, Ga, and Ge, respectively, were achieved [55].

The extractant G315 was tested to recover Ga and Ge from solutions containing Zn²⁺ (22.7 g/L), Ge⁴⁺ (0.1 g/L), Ga³⁺ (0.3 g/L), and Fe³⁺ (2.2 g/L), in 40 g/L H₂SO₄ at an aqueous/organic (A/O) phase ratio of 1:2. The extraction of Ge achieved 94.6%, but the structure or type of the extractant was not disclosed [56].

For the separation of Ge^{4+} from Zn^{2+} , Ga^{3+} , and Fe^{3+} in solutions with a high acidity (80 g/L H_2SO_4), a SSX system was also used [57]. The process consisted of 30% (v/v) D2EHPA and 15% (v/v) TBP. The extraction efficiency was 94.3% in two stages, and the strip efficiency was almost 100% using 250 g/L NaOH at an A/O phase ratio of 1:2.

A single contact system consisting of 10% LIX 63 and 2% Ionquest 801 to recover Ge from a synthetic leach solution of Zn refinery cementation residues was used [43]. Over 68% Ge^{4+} was extracted at a low pH at an A/O ratio of 1:1 and 40°C. Almost 73% Ge^{4+} was stripped with 0.5 M NaOH and 1.0 M Na_2SO_4 .

A common disadvantage of the above SX or SSX processes for Ge^{4+} extraction is the use, for instance, of strong NaOH for stripping and of some reagents that are not commercially available. Therefore, more efficient and effective SX or SSX systems for the recovery of Ge are required using commercially available reagents.

4.2. Germanium from coal combustion and gasification fly ashes

Coal plays an essential role in our global energy scheme for power generation. There are 1,139,331 million tons of proven coal reserves worldwide, sufficient to meet 153 years of global production which makes coal a reliable source [59, 60]. However, coal is currently a target to accomplish with the Paris climate agreement for both countries and companies which has caused a decline in coal production and consumption. Pulverized coal combustion (PCC) is the most widely used technology for coal power generation and, in a lesser extent, integrated gasification combined cycle (IGCC). In both processes, coal with a proximate Ge content <100 ppm can either vaporize totally and then be easily adsorbed on the finest coal fly ash (FA) particles during flue gas cooling or vaporize partially and enrich in both the coal FAs and, in a lesser extent, bottom ashes or slags (**Figure 3**). FAs are normally captured in particulate control devices with a high efficiency (>90%), but a small fraction of them may reach the flue-gas desulfurization (FGD).

Although part of the FA components may dissolve in the aqueous phase of the sorbent slurry when the flue gas passes through the sprayers, remaining in the FGD, the content of Ge in the FGD by-products (water effluent and FGD-gypsum) is not significant [60, 61]. Coal FAs are regarded as the main output stream of Ge.

The current annual production of coal FA worldwide is estimated to be around 750 million tons, and this is anticipated to increase in the near future [62]. The average content of Ge in coal FA is approximately 18 mg/kg, but as some research showed, it can reach 420 mg/kg [26, 63]. Therefore, one attractive source of Ge comes from coal FAs [64–66]. Coal combustion FA is a fine powder made up of spherical high Si-Al-Ca-K-Fe-Ti-Mg vitreous particles with Fe oxides and Al-Si species and irregular unburned coal and ash particles (**Figure 4**). It is generally accepted that vitreous FA particles consist of a relatively pure Al-Si-Ca-K-Fe glass within on which mullite crystals form a network [67, 68]. Furthermore, other types of particles such as calcite (CaCO_3), lime (CaO), quartz (SiO_2), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are formed.

During coal gasification, most of the mineral matter of the coal is transformed and melted into slag. As opposed to PCC, coal gasification produce very little FA (10–15%), which is

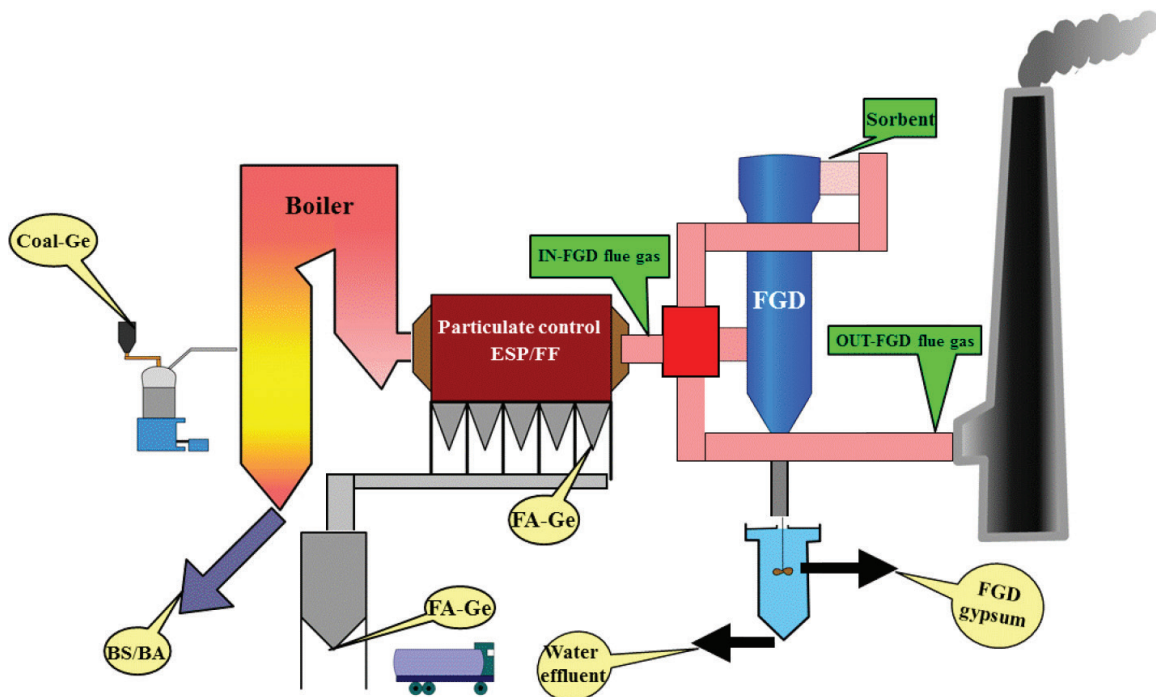


Figure 3. Configuration of a PCC power plant and partitioning of Ge.

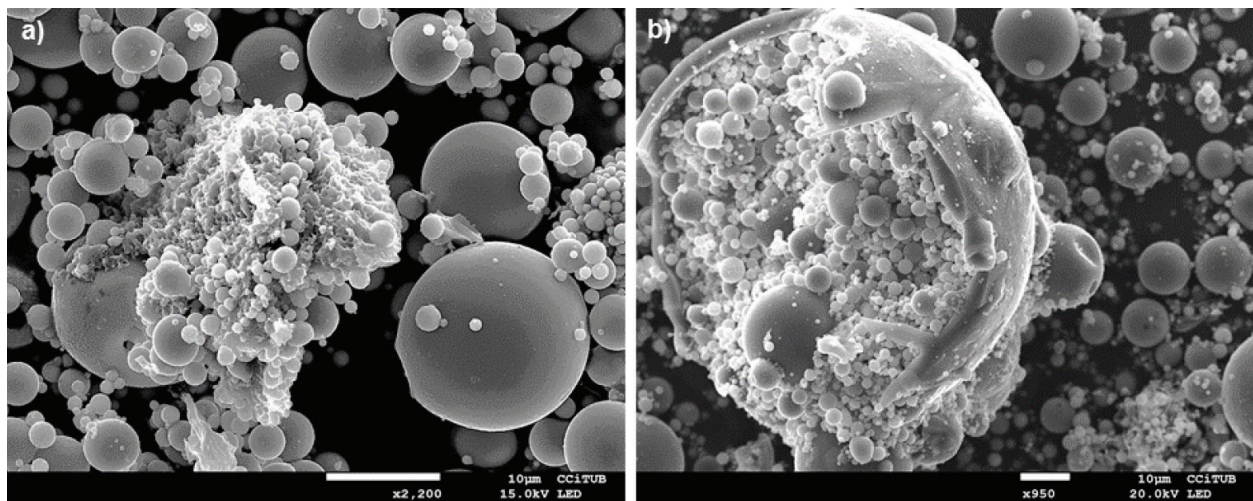


Figure 4. Scanning electron microscope photomicrographs of (a) FAs from coal and petroleum coke combustion and (b) FAs from PCC [61].

characterized by a predominant alumina-silicate glass matrix and a wide variety of crystalline-reduced species, mainly sulfides, because of the low levels of O_2 during coal gasification. Figure 5 shows the typical round morphology of IGCC FA particles [26].

Germanium production from coal FAs usually consists of two stages. The first step creates a concentrate and the second is the actual recovery. The first published studies on Ge recovery from coal FAs were those based on pyro-metallurgical practices [70] but at the present moment are not applied due to the high economic and environmental cost [1].

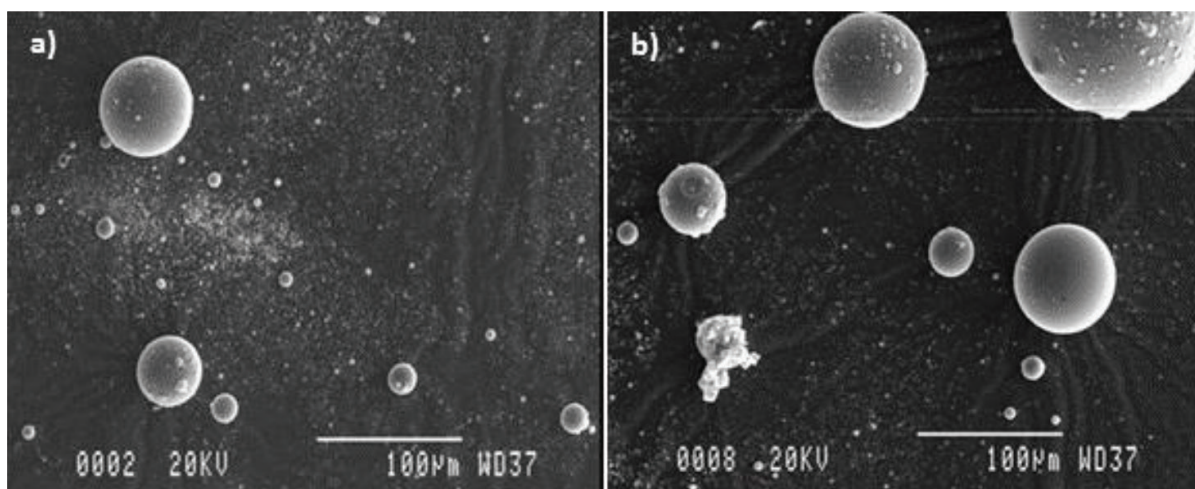


Figure 5. Scanning electron microscope photomicrographs of IGCC FAs [69].

In 1998, a hydrometallurgical procedure for extracting Ge from coal FAs based on the leaching of FA with H_2SO_4 and NaOH followed by ion flotation separation of Ge was prompted. A recovery of 100 g of Ge per ton of coal FA was achieved between 70 and 200°C [71]. Other studies implemented the ion flotation method using a mixed HCl/ HNO_3 solution and cetylpyridiniumchloride as a surfactant [72]. The authors obtained 95–100% yield of Ge after 3–5 min of flotation. A research about tannin (poly-hydroxy polyphenols) precipitation to extract Ge was proposed in 2008 [73]. The tannins were capable of forming chelates with Ge ions, resulting in low grade of precipitated tannin-germanium complex. Currently, research is aimed at developing methods for increasing FA utilization focused on reducing the concentrations of heavy metals and at the same time obtaining higher added value products.

The occurrence of Ge as water-soluble species such as GeS_2 , GeS, and hexagonal- GeO_2 , in the FAs generated in an IGCC power plant, prompted the study of Ge recovery from coal FAs using pure water in an attempt to develop an extraction process of a low cost and environmentally able to culminate in a commercial Ge end-product [26]. Results revealed high recovery efficiency (up to 86%) at 90°C, indicating that the extraction temperature was the most important parameter in the process. These results led authors to conduct research toward the study of enrichment and precipitation methods for Ge recovery such as ion flotation, adsorption on activated carbon, and/or SX. Adsorption and SX were the methods that allowed achieving Ge-bearing solutions with 256 and 1623 mg/L, respectively [74, 75].

In 2006, a study evaluated the selectivity of the process developed by [26] for the recovery and purity of Ge by ion flotation tests on the leachates arising from the water extraction of Ge, using pyrogallol, catechol, hydroquinone, and resorb in complexing agents at a pH range of 4–7. Pyrogallol or catechol as complexing agents and dodecylamine as a surfactant showed the isolation of the Ge complex recovering 100% of Ge in 30 min [76].

A complex water leaching process consisting of Ge complexation with catechol followed by SX system, reaching an extraction yield of 95%, was published [77]. In 2014, same authors

optimized Ge and Ga recovery from coal FA using different extractants in a wide range of extraction conditions. High extraction yields of Ge (up to 90%) and Ga (up to 82%) were obtained using weak oxalic acid and sulfuric acid solution, respectively, within 1–2 h extraction period [78].

Recently, the recovery of Ge from coal FA using vacuum reduction metallurgical process was investigated [38]. Its principle is that the saturation vapor pressure of metal under the vacuum condition is lower than normal pressure to separate metals. These authors achieved a 94.6% recovery of Ge from the coal FA at a temperature of 900°C, 10 Pa, and heating time of 40 min. These studies confirm that coal FA can be explored as an alternative source of Ge and other valuable elements and minerals. The recovery of Ge from coal FA is suitable, reducing disposal costs of coal FA. However, further research is needed to develop adequate results in terms of selective recovery and purification.

4.3. Germanium recovery from copper smelting flue dust

Flue dust from Cu smelting has also been suggested as a potential source of Ge, since relatively high contents of this element may be present in Cu-sulfide ores [27]. Copper is extracted from the ore through hydrometallurgical and/or pyrometallurgical processes. The selection of the process is determined by the Cu minerals bound to ores, being Cu sulfides predominantly treated by pyrometallurgical process and Cu oxides by hydrometallurgical process. However, the pyrometallurgical process is the most commonly employed technology for Cu [79].

The processing of Cu minerals, associated to sulfides by high temperatures, produces several residues [80]. Among the residues, dust generated from physical process, flue dust and slags from smelting process, and sludge from electrowinning process are those with potential for the Ge recovering.

Although the qualitative and quantitative phase determination of dust from Cu smelting depends on the compositional characteristics of the fed into smelting furnaces, temperature and oxidative conditions inside the furnace, and equipment, the recovery of rare and precious metals such as Ge from flue dusts has not been a widely studied subject in the literature. Most of the research on flue dust composition from Cu smelting have been focused on As, Zn, and Pb since the main Cu-ores present elevated amounts of As, Zn, Cd, and Pb which are potentially hazardous to human health or the environment [27].

Font et al. (2011) evaluated for the first time the potential of Cu smelting flue dust (Cu-SFD) as a source of Ge and the possibilities to apply extraction and recovery methods similar to those patented for coal gasification FA [81]. These authors reported Ge concentrations ranging from 417 to 1375 ppm in flue dust samples with Ge extraction yields from 73 to 99%. In 2017, Chilean Cu-SFD was characterized and evaluated for the potential extraction of Li, Rb, and Ge with different chemical leaching agents [27]. The authors found high extraction yields for Ge, Li, and Rb using pure water as extractant at 25°C. Both studies suggest that Ge may occur in the form of highly soluble minerals and that Cu-SFD can be regarded as a promising source of elements with high added value such as Ge.

4.4. PhytoGerm

Phytomining is an extraction process in which metallic substances in soils or sediments are absorbed by plants [82]. With this in mind, PhytoGerm project emerged in the framework of the r³-initiative for tech metals and resource efficiency subsidy program of the German Federal Ministry of Education and Research whose goal was to find a plant species that concentrates Ge in aerial plant biomass, which grows well on poor soils and contaminated industrial sites.

The ribbon grass was selected as suitable for the PhytoGerm project. Ribbon grasses grow well on prolific siliceous soil, and due to the similar chemical properties of Ge and Si, the plant can also absorb Ge [82]. The concept of PhytoGerm project was to make use of elevated Ge levels of tailings from Zn mining sites, thus allowing the plants to accumulate sufficiently high amounts of Ge in order to achieve high yields during the extraction process [83]. The case study developed by the authors assumed that 13,636 tons/year of ribbon grass would be obtained from several cultivation areas, which is the amount needed to utilize an average 500 kW biogas plant. Along the process diagram showed in **Figure 6**, 4112 tons/year of biomass are available for Ge extraction. Once Ge is accumulated in ribbon grass plants, the solid biomass is at first dried and thermally processed in a biomass power plant. The residuals of the combustion process are ashes and FAs, enriched with Ge, with an annual output of approximately 280 tons. The investigated process route ends with producing 3.9 kg of powdery GeO₂ per year.

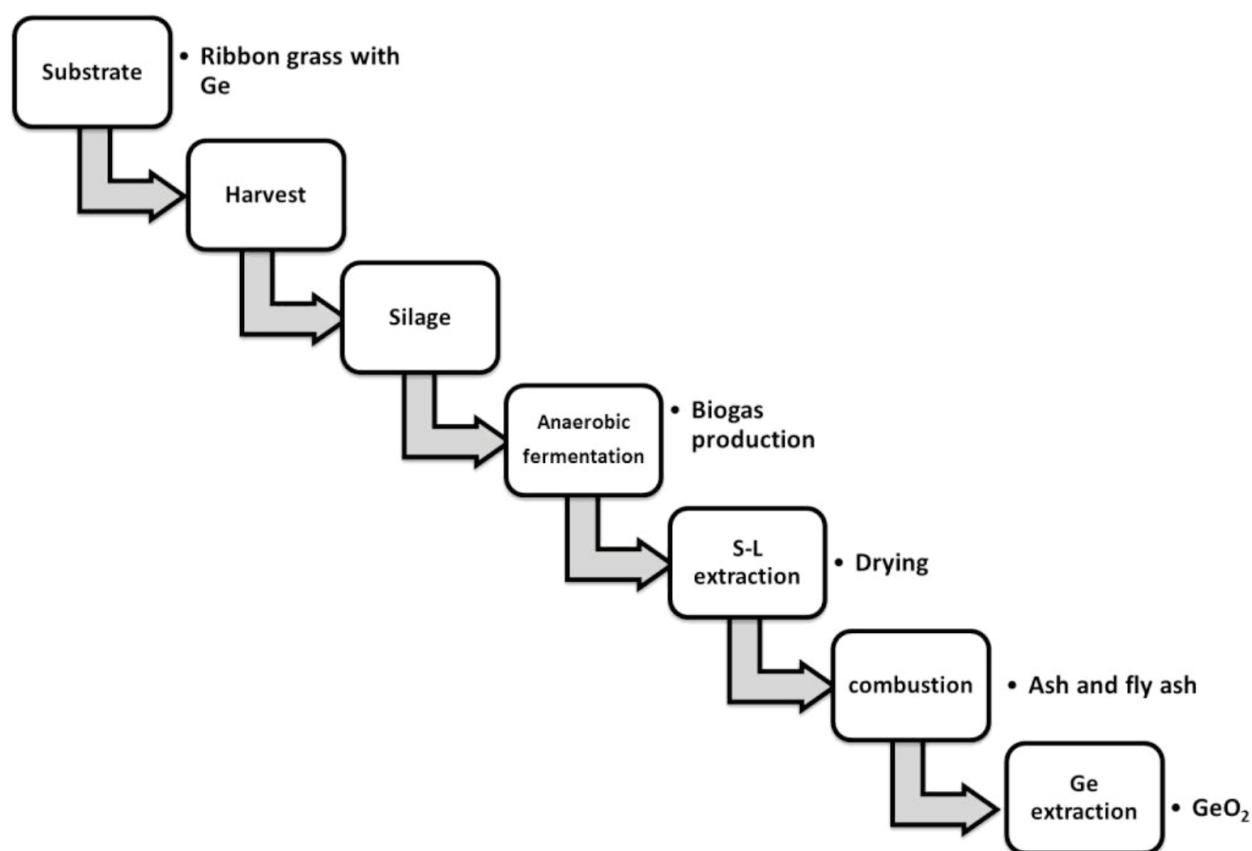


Figure 6. PhytoGerm process diagram. Adapted from [82].

5. Conclusion(s)

Nowadays, germanium is considered a critical element and also a strategic reserve for high-tech industrial applications in several countries. Germanium is used in solar cells, fiber optics, metallurgy, chemotherapy, and polymerization catalysis. Mainly sources of Ge are associated to sulfide ores (e.g., Zn, Pb, and Cu), coal deposits, and also residues from the processing of these ores and coals. Indeed, about one third of global germanium produced come from recycling processes. While the recovery of Ge from sulfide ores presents disadvantages related to the hazardous nature of organic extractants and high acidity of extractant solutions, the occurrence of Ge as water-soluble chemical species in coal gasification and copper smelting fly ashes allows the application of novel extraction methods with water at temperatures <math><100^{\circ}\text{C}</math>. This approach appears to be a feasible recovery and less harmful novel extraction method for environment, which suggests that both residues are promising sources for Ge. PhytoGerm which is based on absorption of Ge with ribbon grass on soils contaminated with Zn refinery residues results in an energy-efficient and eco-friendly recovery process for Ge.

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