Review

Some Recent Advances on Germanium Recovery from Various Resources

Francisco Jose Alguacil * and Jose Ignacio Robla *

Posted Date: 18 April 2024

doi: 10.20944/preprints202404.1197.v1

Keywords: germanium; recovery; leaching; liquid-liquid extraction; adsorption; ion exchange

Preprints.org (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 April 2024 doi:10.20944/preprints202404.1197.v1

Review

Some Recent Advances on Germanium Recovery from Various Resources

Francisco Jose Alguacil * and Jose Ignacio Robla *

Centro Nacional de Investigaciones Metalurgicas (CSIC). Avda. Gregorio del Amo 8. 28040 Madrid, Spain; fjalgua@cenim.csic.es (F.J.A.); jrobla@cenim.csic.es (J.I.R.)

Abstract: Though nowadays germanium do not reach the range of popularity than other metals, i.e. rare earth elements, its utility in target industries makes of it also a strategic metal. Though germanium can be find in a series of raw materials, the principal source for its recovery is from secondary wastes of the zinc industry, and also, the recycle of germanium-bearing waste materials is becoming of interest. In this recovery, Hydrometallurgy is performing a key role to the successful achievement of this goal. The present work reviews the most recent applications (2023 and 2024 years) of hydrometallurgical operations on the recovery of germanium from different solid and liquid sources.

Keywords: germanium; recovery; leaching; liquid-liquid extraction; adsorption; ion exchange

1. Introduction

Germanium is an element with has not any significant biological role, and it is being used as a semiconductor, component of alloys, phosphor in fluorescent lamps, and as a catalysts. Besides the recovery of this element from secondary sources, germanium can be found in sulphide deposits (USA, Mexico, Argentina, Canada, Russia) and oxidisation zones in Ge-bearing sulfide deposits (USA). As it is recently described in the literature [1], there is three large coal deposits containing germanium: Spetsugli deposit in the Russian Far East, Wulantuga deposit of Inner Mongolia (northern China) and Lincang deposit in Yunnan Province (southwestern China). Other important germanium-occurrence is in bornite materials [2], such as the carbonate hosted bornite Cu-Zn-Co(-Ge) deposit located in the Cosmos Hills (western Alaska, USA). Other Ge-bearing carbonate hosted base metal deposits are located in Africa, such the Tsumeb (Namibia), Kipushi (DRC), Khusib Springs Namibia), Kombat (Namibia), and Kabwe (Zambia) deposits.

Another potential germanium-occurrence is bitterns (residual brines produced in the solar sea-salt extraction in the Mediterranean sea region) [3], and as it is mentioned above, in subproducts of the zinc industry and in the recycling of electronic wastes [4].

At the time of writing this manuscript the price of this element is $2856.30/kg, which compares well with that of other metals, i.e. Cu ($8.49), La ($625), Nb ($45), Tb($1460), Y($30), but not with i.e. Au ($70015), Os ($14000).

Thus, there is an interest in the recovery of this relatively less known metal from these various sources, being hydrometallurgical processing widely used to reach this goal. This manuscript reviewed the most recent advances (2023-2024 years) about the use of these hydrometallurgical operations in the recovery of this valuable and strategic element.

2. The hydrometallurgical operations

2.1. Leaching

Germanium is recover from a zinc oxide dust subproduct from a Pb-Zn smelter [5]. Since germanium is found to be in different phases (oxide, sulfide, silicate and solid insoluble), the behavior of these phases in the leaching process is investigated. A waste electrolyte of 43.3 g/l Zn, 22.5 g/L Mg, 4.8 g/L N, 0.3 g/L Cl and 160 g/L sulphuric acid is use to leach the zinc oxide dust containing 1320 g/t germanium. The metal presented in the oxide and sulfide phases dissolve without much difficult; however, this is not the case of the silicate and solid insoluble phases. The structure of the aluminate phase is destroy in a leaching operation using 40 g/L HF, whereas dusts containing Fe and Si produced a negative effect in the leaching rate of germanium.

The recovery of germanium from a zinc oxide dust is also investigate in the next reference [6]. In this dust, germanium is find to be as oxidised and germanates species, being the metal dissolution dependent on the leaching time, due to that longer operation times produced the precipitation of $Fe_4Ge_3O_{12}$ species. Best experimental conditions to produce the highest germanium recovery rate (84%) are fixed as: liquid/solid ratio of 5, temperature of 85º C, leachant (sulphuric acid) concentration of 120 g/L and operation time of 30 min. The addition of sodium sulphite in the leaching process increases the germanium recovery rate until 89%, due to the inhibition of the iron(II) oxidation to iron(III), avoiding the further precipitation of the Fe-Ge mixed oxide.

As it is mentioned in the Introduction section, coal deposits are a source to germanium recovery, thus, in the next reference coal fly ash (CFA), produced in coal-fired power plants, is used as a source material for the recovery of germanium and other metals (vanadium and lithium) [7]. A spent-medium bioleaching process, with *Pseudomonas putida* and *Pseudomonas koreensis*, is use to produce organic acids (Table 1), which dissolved these metals. Previously to this leaching step, the starting material is roast in the presence of sodium carbonate. Best leaching results (83% germanium recovery) are obtain when *Ps. putida* is used to produce the organic acids. This recovery rate compares well with the value (58%) obtained when the roasted material is chemically leached with the same organic acids, being this behavior attributable to that other metabolites, like amino acids and undetermined organic acids, may be involved in the leaching process.

Table 1. Some organic acids produced as consequence of using *Ps. putida* and *Ps. koreensis*.

Acid	Ps. putida	Ps. koreensis
Citric	7.23 mM	6.97 mM
Gluconic	65.76 mM	55.06 mM
Oxalic	11.66 mM	0.78 mM

From [7].

Using also a zinc oxide dust, the recovery of germanium utilizing sulphuric acid and sonication is investigated [8]. The use of ultrasonic (270 W) allows to the recovery of 95% of the initial germanium content (661 g/t) of the starting material, being the other parameters fixed as: 78º C , 131 g/L of sulphuric acid, 22 min of reaction time liquid/solid ratio of 7.6 and a 0.71% addition of iron powder. It is concluded that sonication destroyed dust particles, inhibited its agglomeration and favored the dissolution of germanates and germanium sulphides species.

The recovery of germanium using zinc powder replacement residue (ZPRR) in a two-stage acid leaching process is investigated [9]. In the first stage, the dissolution uses a solution of 15 g/L sulphuric acid, whereas in the second stage, the material is leach by means of a 150 g/L sulphuric acid solution. The increase of temperature produces an increase of the metal leaching rate, however, at 120º C, this leaching rate decreases due to the precipitation of germanium in the presence of SiO_2. This precipitation can be avoid by combining temperature, strong magnetic field and sonication. Within optimal condition the rate of germanium leaching reached 97%.

A three steps procedure (leaching-roasting and leaching) of a zinc oxide dust to recover germanium is investigated [10]. Firstly, the dust is leach under sonication and oxidation (potassium permanganate) conditions in order to improve the solubilization of sulphide phases. Further, the residue of the previous operation is roast in the presence of sodium carbonate and magnesium nitrate, which promoted the reaction between the insoluble tetrahedral germanium dioxide and complex forms of germanium-containing compounds. In the third operation, germanium in the roasting slag is recover by conventional leaching. The recovery of this strategic metal increases up to 40% with respect to previous results.

By combination of atmospheric pressure leaching and oxygen pressure leaching methodologies, the dissolution of indium and germanium from a complex matrix formed by oxides, sulfides, germanates, ferrites, silicates is investigated [11]. The results show that both indium and germanium solubilizes from oxides and germanates matrices under atmospheric pressure leaching conditions (80º C, three hours, and 180 g/L sulphuric acid). Refractory compounds can be leached under conditions of pressure leaching (120º C, three hours, 0.25 MPa and 180 g/L sulphuric acid). Under these two operations the leaching rate reached more than 95% each for indium. germanium, copper and zinc. Apparently, authors do not include information about the separation of the different metals from the leaching solution.

Acidic leaching process was used in the dissolution of germanium from low germanium bearing silica residue (GRS) with high silicon content [12]. In comparison with non-pressure procedure, the leaching of the germanium-bearing material at high pressure yielded higher germanium leaching rate, i.e. at 240º C this rate reached 74%, value being 3.5 times higher than that obtained from the conventional acid leaching process. Moreover, the increase of the temperature from 120º C to 240º C increased the germanium leaching rate, since at the higher temperature the depolymerization and polycondensation reaction of polysilicic acid is increased, resulting in the conversion of silicon into dense oligomeric silica with a low specific surface area. Within this conversion, the encapsulation (adsorption) of germanium on silicon is inhibited, favoring the metal leaching.

Problems in relation of the presence of tannin in zinc electrolysis, neutralization and precipitation-leaching procedure was investigated in order to replace Ge precipitated by tannin to enrich Ge [13]. The leaching solution of zinc oxide dust was used as raw materials and industrial zinc oxide dust was used as neutralizing agent. Under conditions of neutralization-precipitation at 45º C, 2 hours, and pH 5.0-5.2 (first stage) and 45º C, 1.5 hours, oxygen dosage 60 L/h and pH 5.0-5.2, the precipitation rates were of 99% (Ge), 27% (Fe), 99% (As) and 95% (Si). The neutralizing sediment contains 1.1% Ge in the first stage, and a germanium concentration in the second stage solution of near 2 mg/L. The leaching residue after oxidative pressure leaching is leached under atmospheric pressure, increasing the leaching rate of germanium increases to 96%. Tough the procedure resulted in the simultaneous germanium enrichment and impurity removal, no data is included in the work about how separate germanium from undesirable impurities.

The leaching of zinc and germanium from a zinc oxide dust by combination of ultrasonic and hydrazine sulphate was investigated [14]. It was established that best results necessitates the reduction of both Ce(IV) and Fe(III) to Ge(II) and Fe(II), respectively. The final mixed controlled model is determined to control the whole leaching reaction. Under the best conditions of initial acidity of 140 g/L, liquid/solid ratio of 7 L/kg, dosage of the reducing agent of 1/3 of the molar mass of Fe in zinc oxide dust, ultrasonic intensity of 300 W, 1 hour and 60º C, the leaching rates are 97% (Zn) and 95 % (Ge). In comparison with the results under conventional leaching, the leaching rates increased by 6 % (Zn) and 11% (Ge). Again, no data about the separation of these metals are included in the work.

To resolve some problems arising in the treatment of germanium-zinc leaching residue, the next investigation used a two-stage countercurrent pressurized acid leaching technique [15], which consisted of i) iron-controlled low-acid pressure leaching and ii) deep high-acid pressure leaching. Experimental data indicated that the increase of temperature, the reaction time and the oxygen partial pressure enhanced the dissociation of zinc-loaded and germanium ferrite ($MeFe_2O_4$) complex phases as well as facilitate the occurrence of Fe(III) hydrolysis and precipitation. Under the optimized conditions of 150º C, initial acidity of 100 g/L, reaction time of three hours, oxygen partial pressure of 0.4 MPa, the leaching rates of zinc and germanium are near 92% and 61%, respectively. No data about the separation of the metals are included in the work.

The results derived from the investigations about germanium recovery from these different germanium-bearing materials are summarize in Table 2.

doi:10.20944/preprints202404.1197.v1

Table 2. Germanium recoveries from some several secondary materials.

Material	Ge content, g/t	Leachant	% Ge recovery	Ref.
ZOD	1320	Waste electrolyte	80	[5]
ZOD	418	Sulphuric acid	84	[6]
CFA	250	Organic acids	83	[7]
ZOD	661	Sulphuric acid[a]	95	[8]
ZPRR	1500	Sulphuric acid[b]	97	[9]
ZOD	2000	Sulphuric acid[c]	95	[10]
GRS	2.8	Sulphuric acid[d]	74	[12]
ZOD	510	Sulphuric acid[e]	95	[14]

ZOD: zinc oxide dust. CFA: coal fly ash. ZPRR: zinc powder replacement residue. GRS: germanium silica residue. [a]Acid and sonication. [b]Two steps. [c]Three steps: acidic leaching, roasting and acidic leaching. [d]Acid plus temperature and high pressure. [e]Acid and reduction.

The above Table indicates that these recent investigations used secondary materials as the initial source for germanium recovery, and that in all the cases acceptable, to say the less, rate recoveries with most of the proposed different leaching system are obtain. However, no one of the references, included in this Table, indicate what to do with the germanium-bearing solution or how this strategic metal can be recover from the different leachates.

2.2. Liquid-liquid extraction

Ionic liquids are a group of chemicals that due to its properties are broadly consider as *green solvents*. This reference reviews the use, on germanium extraction, of one specific type of these extractants based on the phosphonium ion (R_4P^+), where R represented various carbon-based chains. The counter anion for this phosphonium moiety can be of inorganic or organic nature. The review concluded that phosphonium-based ionic liquids, extracted germanium *via* an anion exchange mechanism and that due to its specific properties: good selectivity, high thermal stability and low volatility, this type of extractants presented promising characteristics for its use in the recovery of this valuable metal.

Germanium is recover from a solution (49 mg/L Ge, 48 g/L Zn, 0.19 g/L Fe, 1.07 g/L As and 0.33 g/L Cd) coming back from the treatment of a secondary zinc oxide with a 75 g/L sulphuric acid solution [17]. In this investigation, the organic phase contains the amine and tributyl phosphate (TBP), as phase modifier, dissolved in sulfonated kerosene; to this organic phase, different concentrations of hydroxycitric acid (HCH) are add. With the metal equilibrium extraction reached after six minutes, germanium is extracted (80- 99%) preferably to the other metals, present in the solution, in the equilibrium pH range of 0.1-2.5. As it is mention above, TBP is need in order to avoid third phase (or secondary organic phase) formation (Figure 1). Best germanium extraction results is reached under the conditions: equilibrium pH of 1, 20% v/v amine, 5% v/v TBP and a molar ratio of CHA/Ge of 5. The system is also investigate on simulated solutions derived from the treatment of copper cake, coal fly ash and biomass. A 0.5 M NaOH solution is an effective strippant for germanium (and arsenic). No data is provide in the reference about how these two elements can be separate from the stripping solution.

Figure 1. Undesirable third phase formation (left) in liquid-liquid extraction *versus* ordinary two phases systems (right). (Picture by F.J.Alguacil).

Using simulated sulphuric acid solutions, the extraction of germanium using the tertiary amine N235 (R_3N, R= C_8H_{17}) in the bisulphate cycle dissolved in sulfonated kerosene is investigated [18]. The addition, to the organic phase, of trioctyl phosphate (TOP) and L(+)-tartaric acid (H_2L) is also considered. TOP avoids the formation of a third phase after equilibration of the phase, and participates in the formation of extraction complexes through hydrogen bonds in the form of Ge–OH···O[dbnd]P but does not co-extract germanium with the amine. In fact, it is described that the metals is extracted into the organic phase *via* an anion exchange mechanism, with formation in the organic phase of $Ge(OH)(HL)_2L{\cdot}HNR_3$ and $Ge(OH)(HL)L_2{\cdot}(HNR_3)_2$ species. This work does not provide data about the stripping operation, thus, the usefulness of its utility be must put into quarantine. Also, it is strange that the authors use as extractant a tertiary amine in the bisulphate cycle ($R_3NH^+HSO_4^-$), when the known rule that tertiary amines are most effective (and broadly used) as extractants of metals in the chloride system ($R_3NH^+Cl^-$).

Liquid-liquid extraction of germanium, from a leaching solution of 0.53 g/L Ge, 93 g/L Zn, 7.6 g/L Fe, 1.5 g/L Cu, 0.64 g/L Cl, 0.66 g/L F and 67 g/L sulphuric acid, with organic phases containing hydroxamic acid (YW100), di(2-ethylhexyl) phosphoric acid (D2EHPA) and the tertiary amine (N235) is investigated [19]. Kerosene is use as diluent of the organic phase. Though the authors claim that formation of a third phase is avoid with the use of the amine, in the opinion of these reviewers, and after looking at the Fig. 2 of the published manuscript, this third phase is not avoid completely, and thus, the data presented here are useless, and the manuscript should never have been published.

This reference investigates the extraction of germanium from wet zinc refining solutions using the mixture of the amine N325 and the phosphorus esther tributylphosphate (TBP) [20]. This last chemical is used as modifier to prevent the formation of a third phase. The extraction mechanism responded to an anion Exchange process in which ($Ge(C_4H_4O_6)_2^{3-}$) species formed part of the extracted complex. The system is selective with respect of the presence of As^{3+}, Fe^{2+} and Zn^{2+} in the feed solution, Germanium can be stripped from the organic solution by the use of 2.5 M NaOH solutions. Note the major mistake done by the authors when As(III) is considered a cation, since this element is never find as cation in aqueous solutions.

This manuscript, very similar to the previous reference, investigates the extraction of germanium(IV) by the same system amine N235 and TBP, but using different metal-coordinated complexes [21]. The coordination abilities follow the next sequence: tartaric acid>oxalic acid>citric acid>maleic acid>salicylic acid. Again here authors committed a major fault by considering germanium(IV) as the cation Ge^{4+}.

2.3. Precipitation

The next reference investigates about the indium-germanium separation from a leaching solution containing, among others, 2.45 g/L In, 0.11 g/L Ge and 37 g/L sulphuric acid. The procedure consisted of two steps. In the first step, indium is separate from germanium by liquid-liquid extraction with an organic phase of 15% v/v DEHPA in kerosene, in the second step the germanium-bearing raffinate, from this liquid-liquid extraction operation, is neutralized with ZnO dust until pH values in the 3.5–4.0 range, and then mixed with tannin. By this procedure, germanium is selectively and quantitatively (99%) precipitated as a tannin-germanium complex, this solid is baked at 500 °C during 3 hours to yield a germanium concentrate.

2.4. Ion exchange resins

In this reference [23], the anion exchange resin D201×7 (strongly basic styrene-based anion exchange resin with quaternary ammonium group ($R_3R'\text{-}N^+$ being R= CH_3 and R′= Cl) and chloride as counter-anion) has been used to separate germanium from a sulfuric solution using tartaric acid as a complexing agent. In the sulfuric acid system, $Ge(OH)_4$ was converted to an anionic complex $[GeO_2(OH)_2C_4H_4O_4]^{2-}$ at a 1:1 tartaric acid to metal molar ratio, and thus, the resin uptakes this anionic complex. The anionic exchange process fits the pseudo-second-order kinetic and the Langmuir isotherm models. Maximum metal loading onto the resin is estimate as 214 mg/g. At pH 2 and using single metal solutions, the rate of germanium loading onto the resin is better than that of iron(III), but using mixed Ge(IV)-Fe(III) solutions, this situation is reversed and iron(III) is loaded preferably to germanium(IV). Elution of germanium from loaded resin is best accomplish with the use of 1 M NaOH solutions. Moreover, selective germanium uptake and purification are enhance in column operation. The results show that with an enrichment factor of 74.7, the concentration of germanium in the eluate reached 36.6 g/L.

2.5. Adsorption

This reference investigated the mechanism of germanium adsorption onto lead sulfate, and uses ultrasonication to inhibit this adsorption [24]. Results concluded that the adsorption process fits the pseudo-second-order kinetic and Langmuir isotherm models. Germanium adsorption onto lead sulfate consists of three steps: fast, slow, and equilibrium. The adsorption at 25–55º C is a spontaneous, endothermic, and entropy increasing process, while at 55–85º C it is a spontaneous, exothermic, and entropy decreasing process. Increasing of the ultrasonic power in the 0-22.5 W increases germanium uptake onto lead sulphate, though a further increase of the ultrasonication up to 70 W decreases the metal uptake, and thus, the adsorption of germanium onto lead sulphate is inhibited. (Table 3).

Table 3. Equilibrium germanium uptakes *versus* ultrasonic power.

Ultrasonic power, W	$[Ge]_{eq}$, mg/g
0	10<x<10.5
15	13.5<x<14
22.5	14<x<14,5
30	11.5<x<12
45	9<x<9.5
75	7.5

Initial germanium concentration: 3.4 g/L. Lead dosage: 3 g. Temperature: 85º C. From [24].

In the next investigation [25], a microwave-based synthesis method is used for functionalize polystyrenic bead with catechol (A-Cat), nitro-catechol (A-Cat-N), and pyrogallol (A-Py). These adsorbents have been used in the selective removal of germanium from dilute acidic solutions under various experimental conditions. The metal adsorption fits the Langmuir isotherm with uptakes, at pH 3, of 29.76 mg/g, 39.14 mg/g, and 37.13 mg/g, for A-Cat, A-Cat-N, and A-Py, respectively. The adsorption mechanism responds to surface complexation of germanium with the ligand (i.e. catechol):

$$\mathbf{Ge(OH)_4 + 3H_2L = (L_3Ge)^{2+} + 2H^+ + 4H_2O} \tag{1}$$

The adsorbents were highly selective for germanium against other elements at pH 1–3, showing no adsorption for many competitive ions (Be(II), Mg(II), Al(III), Sc(III), Mn(II), Fe(III), Cu(II), Zn(II), Ga(III), As(V), Cd(II), La(III), Yb(III), Pb(II), Th(IV) and U(VI)) at pH 1–2. The A-Cat was more selective than A-Cat-N and A-Py. The adsorbents fit the pseudo-second-order kinetic equation. Using A-CAT desorption is best perform with 2 M sulphuric acid solutions.

Catechol-functionalized chitosan (C-Cat) has been synthesized and use to recover germanium from dilute acidic solutions [26]. With maximum metal uptake in the 4-11 pH range, the adsorption fits the Langmuir isotherm and the pseudo-second order kinetic models. Maximum loading capacity reached 22.7 mg/g, which compares bad with the value of 79.7 mg/g resulting with the use of Purolite S108 (N-methylglucamine-based commercial adsorbent), though C-Cat presented a highly selectivity for germanium against the presence of other competing ions in the solution. Experimental results show that germanium is adsorbed preferably to Al(III), Cu(II), Zn(II) and Pb(II) (no adsorption of these), with limited adsorption of Fe(III), Ga(III), and As(V). Best desorption results are obtained with the use of 1 M HCl (72%) after 24 hours, whereas in the case of 1 M sulphuric acid the rate is 65% within the same reaction time. There is a decrease in germanium uptake capacity with consecutive adsorption-desorption cycles, i.e. 20 mg/g in the first cycle and 12 mg/g in the third cycle.

An adsorbent for recovery of germanium is prepared by grafting D-anhydrous glucose onto UiO-66-NH_2, resulting in DG-UiO-66 adsorbent [27]. Under the optimum experimental conditions of 25º C and pH 10, the grafted adsorbent presents a removal rate of 90%, which compares well with that of the pristine adsorbent (80%). The maximum adsorption loading onto the adsorbent is almost 217 mg/g. Similarly to previous references, the adsorption of Ge(IV) fits to the pseudo-secondary kinetic and Langmuir isotherm models, being the adsorption mechanism described by the intraparticle diffusion model. The thermodynamic results show that the higher the temperature (25-45º C range), the stronger the adsorption capacity of Ge(IV), and the reaction is spontaneous. The presence of anions in the feed solution decreases the rate of germanium adsorption (Table 4). Desorption is carried out with a solution of 10% thiourea and 1% sulphuric acid.

Table 4. Germanium adsorption in the presence of anions.

Anion	Concentration	% Ge adsorption
Sulphate	0.1 M	80
	0.5 M	77
	1 M	70
Chloride	0.1 M	87
	0.5 M	84
	1 M	82

From [27].

A metal–organic framework adsorbent (Ma-Zr-MOF) is synthesized using mucic acid and used to recover germanium from aqueous solutions [28]. The maximum adsorption capacity of germanium by Ma-Zr-MOF is 82 mg/g at 22º C and pH 6, and again, the adsorption of germanium onto Ma-Zr-MOF responded to the pseudo-second-order kinetic and Langmuir isotherm models. Thermodynamic calculations yield that the adsorption process is endothermic and spontaneous with an increase of the adsorption capacity with the increase of the temperature in the 25-45ª C range. Experimental results concluded that ortho-hydroxyl group plays a key role in the removal of germanium from the solution and that the adsorption mechanism included chelation and ion exchange processes. Similarly to the previous reference, the adsorption of germanium decreases in the presence of different anions (chloride, sulphate, phosphate, silicate or carbonate), though in this case this interference occurs at anion concentrations as low as 0.1 mM. Germanium is adsorbed preferably to Mn(II), As(III), Zn(II) and Si(IV). Alkaline (NaOH) solutions are not useful to desorb germanium from the loaded adsorbent, against the above, the use of nitric acid allows the recovery of germanium from the adsorbent, but there is a continuous decrease in the adsorption capacity with continuous use, i.e. 89% in the first cycle *versus* 66% in the fifth cycle.

Poly-dopamine (PDA) coated magnetic nano-Fe_3O_4 particle composites (Fe_3O_4@PDA) are prepared by a dopamine self-assembly method [29]. Further Fe_3O_4@PDA-PEI composite materials are synthesized through poly-ethylenimine (PEI) modification reaction. This Fe3O4@PDA-PEI is used to adsorb germanium at various pH values, being pH 6 the most adequate to the efficient removal of the metal, being this removal well fitted to the pseudo-second kinetic model. Against all the above adsorbents, germanium uptake onto this material fits to the Sips model, thus, the adsorption is between single layer and multilayer, and chemisorption plays a role in it. It is also concluded that complexation coordination is the dominant mechanism of adsorption, with the phenolic hydroxyl and amino groups on the surface of the material playing a determinant role in germanium adsorption.

This reference described the performance of a tartaric acid functionalized chitosan (TA-CS) material as an adsorbent for Ge from a zinc residue leachate [30]. The introduction of tartaric acid onto chitosan results in abundant protonable hydroxyl and carboxyl groups, which provides to the material with a buffering capacity under acidic conditions. Adsorption kinetics and isotherms showed an adsorption capacity of 57.28 mg/g for Ge(IV). In binary systems, Ge(IV) was preferentially adsorbed over Zn(II), a major coexisting ion, with a separation factor of 3.22. The immobilization of germanium on tartaric acid is the result of a combination of electrostatic adsorption, complexation, hydrogen bonding and ion exchange. Again, the presence of anions (up to 10 mM) in the solution decreases the rate of germanium removal, being this effect more notorious in the case of SiO_3^{2-} that in the case of SO_4^{2-}, phosphate and carbonate, while the presence of chloride only slightly influences the removal of the metal from the solution. The usefulness of the adsorbent is also proved in the recovery of germanium from a leaching solution (10.2 g/L Zn, 8.3 g/L Cu, 1.8 g8L Fe(III). 0.24 g/L Ge at initial pH of 0.17) coming from the treatment of a sampled native zinc residue. With a dosage of 15 g/L TA-CS, the rate of germanium adsorption reached 80%. Desorption is investigated using 0.5 M nitric acid of 0.5 M NaOH solutions, giving the acidic medium the best desorption results , though using both type of solutions, there is a decrease in the adsorption capacity after continuous cycles of adsorption-desorption.

Three chitosan-based adsorbents are designed by grafting chitosan with p-hydroxybenzoic acid (HBA-CS), 3,4-dihydroxybenzoic acid (DBA-CS), and 3,4,5-trihydroxybenzoic acid (TBA-CS), and used on the germanium recovery from solutions [31]. Metal recovery performance is correlated with the arrangement of the active adsorption sites and follows the order TBA-CS > DBA-CS > HBA-CS, being this order attributable to that the steric effect of TBA-CS is more ideal than that of the other materials due to the presence of more o-phenolic hydroxyl groups, which enhanced its affinity toward germanium. The adsorption behavior of DBA-CS and TBA-CS fit to the pseudo-second-order kinetic and Langmuir isotherm models, indicating that it is a single layer and chemisorption process. As in previous cases, the presence of anions (10 mM) decreases the performance of the adsorbent in the order; silicate>phosphate>carbonate>sulphate>fluoride>chloride. At 1:1 germanium:iron(III) ratio, iron(III) is adsorbed preferably to germanium, however as the ratio decreases in the 1:2, 1:5 and 1:10, the rate of germanium adsorption is greater than that of iron(III). Copper and zinc are worst adsorbed than germanium at every germanium:metal ratios (from 1:1 to 1:10). Nitric acid medium is useful to desorb germanium, but at a cost of a sharp reduction of the adsorption efficiency: near 60% in the first cycle, to less than 40% in the fifth cycle. Against to the title indicates, the investigation is not performed on a zinc residue leachate but on a synthetic solutions.

The removal of Trace Elements (TEs: B, Co, Ga and Ge) from solar saltworks brines using commercial N-methylglucamine chelating sorbents (S108, CRB03, CRB05) is investigated [32]. The three sorbents revealed a good efficiency in the removal of the four elements. Both B and Ge exhibited the fastest sorption kinetics, reaching equilibrium (>90 %) in less than an hour, except for S108, which required 2 h. Elution of the adsorbed metals can be performed by the use of 1 M HCl solutions. No data are included in the manuscript about the separation of the metals from the eluate.

The chelating compund DIAION CRBO2 anionite, containing hydroxyl and amine groups, had been investigated in the removal of Ge(IV) and Cu(II) from chloride solutions [33]. It is demonstrated that the hydroxyl and amino groups of anionite interacted with germanate and copper(II) ions, forming the corresponding metal-anionite complexes. Germanium(IV) is removed from the solution by the adsorption of germanate acid H_2GeO_3 molecular, as well as metagermanate $HGeO_3^-$ and germanate GeO_3^{2-} anions. Whereas copper can be desorbed with 2.5% HCl solutions, germanium is desorbed with 2.5% NaOH solutions.

The organic acid-functionalized TiO_2 nanoparticles were synthesized by modifying TiO_2 nanoparticles with organic acids contenting different number of hydroxyl groups, the content of these groups influenced the Ge(IV) adsorption capacity [34]. The material containing tartaric acid (dihydroxysuccinic acid) TiO_2 (TA-TiO_2-OH), having more hydroxyl functional groups (up to near 4.48 mmol/g), presented the highest metal adsorption capacity (near 122 mg/g) at pH 3. Desorption can be done by the use of 1 M HCl solutions, though a decrease in adsorption efficiency is observed after continuous use, this is attributable to the uncomplete germanium desorption after each cycle.

In the process of zinc oxide dust neutralization leaching, there is a loss of germanium caused by its adsorption on colloidal $Fe(OH)_3$. It is demonstrated [35], that the use of ultrasonicationic reduced the redox potential of the reaction system and inhibited the formation of colloidal $Fe(OH)_3$. Under the conditions of 30 g/L sulfuric acid, temperature of 80 °C, ultrasonic power of 500 W, and pH adjustment time of zinc oxide slurry within 3 min, experimental data (Table 5) showed that in conventional processing, the loss rates of the elements were higher than under ultrasonic procedure.

Table 5. Element losses (%) at different operational conditions.

Element	Conventional	Ultrasonication
Ge(IV)	25	7.7
Fe(II)	2.2	4.3
Fe(III)	46	14

From [35].

Table 6 summarizes the maximum adsorption capacity of some adsorbents used in the recovery of germanium from different solutions.

Table 6. Maximum germanium uptakes using different adsorbents.

Adsorbent	pH	[Ge], mg/g	Reference
A-Cat.N	3	39	[25]
C-Cat	4	22.7	[26]
DG-UiO-66	10	217	[27]
Ma-Zr-MOF	6	82	[28]
TBA-CS	3	28.3	[31]
TA-TiO_2-OH	3	122	[34]

It is worth to mention, that all the investigations in relation with the data presented in this Table and its respective references have been carried out on synthetic solutions. Thus, the experimental conditions, see the pH values, in which these adsorbent are useful are far to be adequate for the direct treatment of solutions coming from leaching operations (see Table 2 and related references), which generally use acidic media in excess of 100 g/L sulphuric acid.

Also, it can be seen the disparity in the maximum germanium uptake concentrations using the different adsorbents. The above joined to the general loss of loading capacity under various adsorption-desorption cycles, made extremely difficult asses about the benefit of using one or another adsorbent.

3. Miscellaneous operations

In the recovery of germanium from coal, the formation of GeO_2-SiO_2 solid solution difficulties the recovery of this metal, thus, a procedure involving the enrichment of germanium in lignite by gravity separation and low temperature sintering is investigated [36]. In this procedure, gravity separation produced a metal concentration factor in lignite of near 2, whereas the treatment of the sinter at 300-500º C produced a residual ash containing 1.8 g Ge/kg, with a concentration factor in the order of 10.6. As consequence of the above procedure, more than 90% of germanium in lignite can be recovered by chlorinated distillation.

The combustion of lignite to produce electricity generates coal ash wastes containing arsenic, germanium and tungsten, being the recovery of these elements investigated by a procedure involving sequential vacuum distillation [37]. Arsenic is first volatilized at temperatures under 550º C, further, germanium and tungsten are volatilized as sulfides by the addition of sodium sulfite. Best conditions for this removal are summarized as: 1050º C, mass ratio of 0.6, pressure of 1 Pa and two hours of reaction time. Condensed product are As_2S_3 and GeS both for coal fly and coal bottom ashes, whereas $WO_x(x<3)/WS_2$ and WO_3/WS_2 species are present in the above respective ashes.

4. Conclusions

Though there are some raw materials containing germanium, recent investigations have been developed only in the treatment of real or simulated secondary wastes. In these developments, Hydrometallurgy plays a key role offering different alternatives to recycle germanium from zinc wastes, EoL (end of life products) and OFs (spent optical fibers), contributing to sustainable resource utilization. Though bio-hydrometallurgical approaches have not been widely developed for these waste materials at present, the development of these bio-procedures is worth of future attention. Overall, the investigation of sustainable recovery technologies for germanium (and other valuable metals) from i.e. EoL or zinc oxide dusts products is determinant for ensuring a stable and reliably supply of this element for high-tech applications. Further advancements in the optimization and implementation of these recovery processes will contribute to efficient and environmentally friendly recycling of these germanium-bearing raw materials and wastes. However these advancements need to be done on the treatment of real solid or liquid materials/wastes, if not the mismatch between what the scientists proposed and the industry needs must be insurmountable.

Author Contributions: Conceptualization, F.J.A.; methodology, F.J.A.; investigation, F.J.A. and J.I.R.; resources, J.I.R..; writing—original draft preparation, F.J.A.; writing—review and editing, F.J.A. and J.I.R.; funding acquisition, J.I.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by CSIC, grant number 202250E019 and the APC was funded by Metals Editorial Office

Acknowledgments: To the CSIC (Spain) for support.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Arbuzov, S.I.; Spears, D.A.; Ilenok, S.S.; Yu Chekryzhov, I.; Ivanov, V.P. Modes of occurrence of germanium and tungsten in the Spetsugli germanium ore field, Pavlovka brown coal deposit, Russian Far East. *Ore Geol. Rev.* **2021,** *132,* 103986. DOI: 10.1016/j.oregeorev.2021.103986
2. Jones, A. Germanium occurrence in the bornite deposit, southwestern Brooks Range, Alaska. Colorado School of Mines. **2021**. https://hdl.handle.net/11124/176411
3. Randazzo S.; Vicari F.; López J.; Salem M.; Lo Brutto R.; Azzouz S.; Chamam S.; Cataldo S.; Muratore N.; Fernández de Labastida M.; Vallès V.; Pettignano A. Unlocking hidden mineral resources: Characterization and potential of bitterns as alternative sources of critical raw materials. *J. Clean. Prod.* **2024,** *436,* 140412. DOI: 10.1016/j.jclepro.2023.140412
4. Zheng, K.; Benedetti, M.F.; van Hullebusch, E.D. Recovery technologies for indium, gallium, and germanium from end-of-life products (electronic waste)–a review. *J. Environ. Manag.* **2023,** *347,* 119043. DOI: 10.1016/j.jenvman.2023.119043
5. Chen, C.; Zhen, Y.; Li, C.; Wei, C.; Li, M.; Deng, Z.; Li, X. Leaching behavior of germanium presented in different phases from zinc oxide dust under atmospheric acid leaching conditions. Int. J. Chem. React. Eng. **2023,** *21,* 1199-1210. DOI: 10.1515/ijcre-2023-0011
6. Liang, M.; Di, H.; Song, L.; Yang, K.; Zhang, Libo. Study on leaching behaviour of germanium and iron in zinc oxide dust from lead zinc smelting. *Can. Metall. Q.* **2023,** *62,* 573–580. DOI: 10.1080/00084433.2022.2114126

7. Rezaei, H.; Shafaei, S.Z.; Abdollahi, H.; Ghassa, S.; Boroumand, Z.; Fallah Nosratabad, A. Spent-medium leaching of germanium, vanadium and lithium from coal fly ash with biogenic carboxylic acids and comparison with chemical leaching. *Hydrometallurgy* **2023,** *217,* 106038. DOI: 10.1016/j.hydromet.2023.106038
8. Song, L.; Zeng, Y.; Liang, M.; Di, H.; Liu, J.; Yang, K.; Zhang, L. Process optimization and mechanism of high-efficiency germanium extracting from zinc oxide dust containing germanium enhanced by ultrasound. *Chem. Eng. Process.* **2023,** *191,* 109439. DOI: 10.1016/j.cep.2023.109439
9. Liang, Y.; Luo, B.; Zhao, L.; Chen, L.; Ding, B.; Shen, Z.; Zheng, T.; Guo, Y.; Li, Q.; Zhou, B.; Liu, C.Brnic, J. Strong magnetic and ultrasonic fields enhanced the leaching of Ga and Ge from zinc powder replacement residue. *Sep. Purif. Technol.* **2024,** *330,* 125572. DOI: 10.1016/j.seppur.2023.125572
10. Xu, Y.; Xia, H.; Zhang, Q.; Zhang, L. An original strategy and evaluation of a reaction mechanism for recovering valuable metals from zinc oxide dust containing intractable germanide. *J. Hazard. Mater.* **2024,** *468,* 133766. DOI: 10.1016/j.jhazmat.2024.133766
11. [11]Tan, Z.; Zhen, Y.; Jin, X.; Du, M.; Li, X.; Wei, C. Study on intensive leaching of indium and germanium from complex materials containing indium and germanium in zinc smelting. *Zhongnan Daxue Xuebao (Ziran Kexue Ban)/Journal of Central South University (Science and Technology)* **2023,** *54,* 2552-2562. DOI: 10.11817/j.issn.1672-7207.2023.07.003
12. Li, Y.; He, X.; Yang, Y.; Chen, J.; Zhang, Z. High pressure acid leaching of low germanium bearing silica residue (GRS): characterization of leach residue and mechanistic details of germanium leaching. *Hydrometallurgy* **2023,** *216,* 106015. DOI: 10.1016/j.hydromet.2022.106015
13. Wang, Z.; Deng, Z.; Chen, C.; Dai, X.; Wei, C.; Li, X.; Li, M.; Fan, G. Germanium separation and enrichment in zinc oxide leaching solution. *Zhongnan Daxue Xuebao (Ziran Kexue Ban)/Journal of Central South University (Science and Technology* **2023,** *54,* 2992-3003. DOI: 10.11817/j.issn.1672-7207.2023.08.004
14. Xu, Y.; Xia, H.; Zhang, Q.; Jiang, G.; Zhang, L.; Xin, C.; Cai, W. Ultrasonic enhanced hydrazine sulfate acid leaching of low-grade germanium dust. *Appl. Energy* **2023,** *332,* 120485. DOI: 10.1016/j.apenergy.2022.120485
15. Zhang, Z.-Y.; Li, C.-X.; Dai, X.-Z.; Liu, Q.; Zhang, M.; Zhang, Y.-Y.; Lu, Z.-Q. Enhanced dissociation and valuable metal leaching behavior of germanium-zinc leaching residue. *Zhongguo Youse Jinshu Xuebao/Chinese Journal of Nonferrous Metals* **2023,** *33,* 1659-1671. DOI: 10.11817/j.ysxb.1004.0609.2022-43189
16. Dhiman, S.; Agarwal, S.; Gupta, H. Application of phosphonium ionic liquids to separate Ga, Ge and In utilizing solvent extraction: A review. *J. Ion. Liq.* **2024,** *4,* 100080. DOI: 10.1016/j.jil.2024.100080
17. Jiang, T.; Wang, P.; Zhang, T.; Zhu, D.; Liu, Z. A novel solvent extraction system to recover germanium from H2SO4 leaching liquor of secondary zinc oxide: Extraction behavior and mechanism. *J. Clean. Prod.* **2023,** *383,* 135399. DOI: 10.1016/j.jclepro.2022.135399
18. Wang, P.; Liu, Z.; Zhang, T.; Liu, Z.; Zhu, D.; Jiang, T. Extraction mechanism of germanium in sulfate solutions using a tertiary amine (N235)-based solvent extraction system. *Sep. Purif. Technol.* **2023,** *311,* 123305. DOI: 10.1016/j.seppur.2023.123305
19. Tan, Z.; Zhen, Y.; Wei, C.; Jin, X.; Li, X.; Fan, G.; Luo, X.G. Organic phase modification of YW100 extraction system: Extraction of germanium using YW100 + D2EHPA + N235. *Sep. Purif. Technol.* **2024,** *329,* 125175. DOI: 10.1016/j.seppur.2023.125175
20. Gu, Z.-H.; Li, C.-X.; Li, C.-W.;Liu, Q.; Zhang, Y.-Y.; Zhang, Z.-Y. Extraction mechanism and selective separation behavior of germanium in hydrometallurgical zinc solution. *Zhongguo Youse Jinshu Xuebao/Chinese Journal of Nonferrous Metals* **2023,** *33,* 3476-3487. DOI: 10.11817/j.ysxb.1004.0609.2022-43738
21. Gu, Z.; Li, C.; Li, C.; Liu, Q.; Wang, Q.; Song, J.; Wang, Y. Coordination separation pattern and extraction mechanism of germanium in zinc leaching solution by wet process. *Zhongguo Youse Jinshu Xuebao/Chinese Journal of Nonferrous Metals* **2024,** *34,* 279-291. DOI: 10.11817/j.ysxb.1004.0609.2023-44155
22. Tan, Z.; Jin, X.; Zhen, Y.; Wei, C.; Li, X.; Deng, Z.; Li, M. Recovery of indium and germanium from In-Ge residue leaching solution using solvent extraction and tannin precipitation. *Sep. Purif. Technol.* **2023,** *323,* 124416. DOI: 10.1016/j.seppur.2023.124416
23. He, C.; Qi, M.; Liu, Y.; Liu, Z.; Wei, Y.; Fujita, T.; Wang, G.; Ma, S.; Yang, W.; Gan, J. Highly selective separation of germanium from sulfuric solution using an anion exchange D201 × 7 resin with tartaric acid. *Hydrometallurgy* **2024,** *224,* 106230. DOI: 10.1016/j.hydromet.2023.106230
24. Liang, M.; Song, L.; Di, H.; Hong, Y.; Dai, J.; Liu, J.; Yang, K.; Zhang, L. Research on the mechanism of lead sulfate adsorption of germanium and ultrasonic inhibition during the leaching process of zinc oxide dust containing germanium. *J. Saudi Chem. Soc.* **2023,** *27,* 101740. DOI: 10.1016/j.jscs.2023.101740
25. Patel, M.; Karamalidis, A.K. Microwave-assisted synthesis of catechol-based functionalized adsorbents for selective adsorption of critical element germanium. *Chem. Eng. J.* **2023,** *475,* 146367. DOI: 10.1016/j.cej.2023.146367
26. Patel, M.; Karamalidis, A.K. Catechol-functionalized chitosan synthesis and selective extraction of germanium (IV) from acidic solutions. *Ind. Eng. Chem. Res.* **2023,** *62,* 2892-2903. DOI: 10.1021/acs.iecr.2c03720

27. Peng, Z.; Wang, S.; Wu, Y.; Liu, X.; Liu, H.; Zhang, D.; Fu, L. Synthesis of novel MOF for adsorption of germanium: Kinetics, isotherm and thermodynamics. *Micropor. Mesopor. Mat*. **2024,** *363,* 112826. DOI: 10.1016/j.micromeso.2023.112826
28. Peng, Z.; Wang, S.; Wu, Y.; Liu, X.; Zhu, M.; Li, P.; Fu, L. Novel Zr-based MOF with Ortho-hydroxyl group selectively traps germanium from aqueous media. *Sep. Purif. Technol.* **2024**, *338,* 126477. DOI: 10.1016/j.seppur.2024.126477
29. Xiang, H.; Zhao, F.; Li, X.; Min, X. Preparation and characterization of amino-containing magnetic material and its adsorption performance of Ge(IV). *Xiyou Jinshu/Chinese Journal of Rare Metals* **2023,** *47,* 252–264. DOI: 10.13373/j.cnki.cjrm.XY21060036
30. Xiang, H.; Yang, Z.; Min, X.; Liang, Y.; Peng, C.; Liu, X.; Yuan, R.; Wang, Q.; Zhao, F. Enhanced recovery of germanium(IV) from zinc residue leachate by tartaric acid functionalized chitosan: Experiments and DFT calculation. *Hydrometallurgy* **2023,** *221,* 106121. DOI: 10.1016/j.hydromet.2023.106121
31. Xiang, H.; Zhao, F.; Wu, T.; Zhang, X.; Chai, F.; Wang, Q.; Repo, E.; Min, X.; Lin, Z. Unraveling the steric hindrance roles of the phenolic hydroxyl position on the selective Ge(IV) recovery from zinc residue leachate. *Sep. Purif. Technol.* **2023,** *311,* 123338. DOI: 10.1016/j.seppur.2023.123338
32. Vallès V.; de Labastida, M. Fernández.; López J.; Cortina J.L. Selective recovery of boron, cobalt, gallium and germanium from seawater solar saltworks brines using N-methylglucamine sorbents: Column operation performance. *Sci. Tot. Environ.* **2024,** *923,* 171438. DOI: 10.1016/j.scitotenv.2024.171438
33. Jafarli M.M.; Abbasov A.D. Equilibrium conditions, adsorption, adsorption kinetics of the GeO_2-Cu(II)-NaCl system on diaion CRBO2 anionite and desorption mode from spent columns. *Chem. Prob.* **2023,** *21,* 64–71. DOI: 10.32737/2221-8688-2023-1-64-71
34. Yu, H.; Pan, Y.; Zhang, Y.; Gong, L.; Lou, Z.; Shan, W.; Xiong, Y. Surface functional group nanoarchitectonics of TiO_2 nanoparticles for enhanced adsorption Ge(IV). *J. Taiwan Inst. Chem. Eng.* **2023,** *143,* 104716. DOI: 10.1016/j.jtice.2023.104716
35. Song, L.; Liang, M.; Zeng, Y.; Dai, J.; Liu, J.; Yang, K. Zhang, L. Study on the mechanism of ultrasonic inhibition of germani-um adsorption by $Fe(OH)_3$ in the neutralization leaching section of zinc oxide dust. *Coll. Polym. Sci.* **2023,** *301,* 1185-119. DOI: 10.1007/s00396-023-05136-8
36. Bo, W.; Wu, J.; Miao, Z.; Wan, Keji. Germanium extraction from lignite using gravity separation combined with low-temperature sintering and chlorinated distillation. *Sep. Purif. Technol.* **2024,** *329,* 125215. DOI: 10.1016/j.seppur.2023.125215
37. Wang, Z.; Sun, J.; Zhang, L. Separation and recovery of arsenic, germanium and tungsten from toxic coal ash from lignite by sequential vacuum distillation with disulphide. *Environ. Poll.* **2024,** *340,* 122775. DOI: 10.1016/j.envpol.2023.122775