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Demonstration Plant Equipment Design and Scale-Up from Pilot Plant of a Leaching and Solvent Extraction Process

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Abstract: Germanium recovery from coal fly ash by hydrometallurgical procedures was studied at the pilot scale (5 kg of fly ash/h). Results were used to design the equipment of a demonstration-sized plant (200 kg of fly ash/h). The process is based on hydrometallurgical operations: firstly a germanium extraction from fly ash by leaching and a consequent Ge separation from the other elements present in the solution by solvent extraction procedures. Based on the experimental results, mass balances and McCabe-Thiele diagrams were applied to determine the number of steps of the solvent extraction stage. Different arrangements have been studied and a countercurrent process with three steps in extraction and six steps in elution was defined. A residence time of 5 min was fixed in both the extraction and elution stages. Volumetric ratios in extraction and stripping were: aqueous phase/organic phase = 5 and organic phase/stripping phase = 5, so a concentration factor of 25 is achieved. Mixers and decanters were completely defined. The maximum extracted and eluted germanium was estimated and a global efficiency of 94% was achieved. The cost-effectiveness of the equipment was estimated using the Lang factors.

Keywords: germanium; fly ash; pilot plant; design; scale up; hydrometallurgy

1. Introduction

Germanium is not very abundant in the Earth's crust, occurring only at a concentration of 1 to 7 ppm [1]. It is widely dispersed in nature, sometimes as a pure metal in association with more abundant elements (such as Zn and its minerals) and as germanium oxide. By far, the most important application of germanium is in the manufacturing of semiconductors, but innovative uses for germanium in new and high technological industrial applications have led to an increase in its price, so it is currently more attractive to process raw materials with low contents of germanium (sometimes only a few ppm) and considerable quantities of other elements.

Worldwide, about 30% of the total germanium consumed comes from recycled materials. With regard to "new" germanium production, the main sources are the zinc and copper ores, from which germanium is obtained as a byproduct. Nevertheless, due to the uses for germanium in new and high technological industrial applications, germanium metal and oxide have increased in price (1800 $/kg of germanium metal in September 2013) [2], and alternative sources such as combustion [3] and gasification [4] coal fly ashes. When the coal is gasified under proper conditions the fly ash (FA) can reach germanium contents ten times higher than the germanium content in the original coal [5].

Fly ash valorization poses a significant economic and environmental burden, but can also be viewed as a resource of huge potential. There are a few approaches nowadays for FA valorization aside from building purposes since it has a potential role as a value-added product in material preparation (e.g., ceramics), recovery of materials (e.g., metals) and agricultural applications (e.g., as bioremediation). Nevertheless, in most cases, reported work to date in this area has been of theoretical research or laboratory scale and further development work is needed.

Germanium occurs in relatively high contents in the fly ash (FA) produced in the Puertollano (Spain) Integrated Gasification Combined Cycle (IGCC) power plant. Nowadays, the 335 MW (ISO) Puertollano IGCC plant is the largest worldwide gasification plant in operation. In this plant, a 50:50 local coal/pet-coke blend is gasified with 2%–4% w/w of limestone (fluxing agent), in a pressurized entrained flow gasifier, at 1600 °C and 25 bars. The Puertollano coal is a high volatile bituminous coal, rich in a number of metals [6], while pet-coke, supplied by an oil refinery is generally a C-rich material with high concentrations of S, V and Ni [7]. The high slag/FA ratio (90:10 or 85:15) produced in the Puertollano IGCC plant is the opposite with respect to that of conventional pulverized coal combustion plants (20:80). Germanium is completely volatilized during gasification and subsequently condenses during gas cooling to form sulphides and oxide species [8]. The complete volatilization of these elements is caused by the organic occurrence of Ge and the main sulphide affinity of Pb, Ga and Bi in the Puertollano coal [8]. The high calcophile affinity of these elements in reducing conditions account for the formation of sulphide species, such as galena for Pb, GeS and GeS_2 for Ge or substituting for Zn in spharelite/wurtzite lattices for Ga, and the subsequent high retention of these elements in fly ash [8] (Table 1).

Germanium occurs in FA mainly (up to 91% w/w) as water-soluble hexagonal-GeO_2 and GeS_2 (solubility: 4.5 g/L) and GeS (solubility: 2.4 g/L). Minor proportions (up to 20%) of Ge may occur as low soluble species (tetragonal-GeO_2 or GeO_4 tetrahedral).
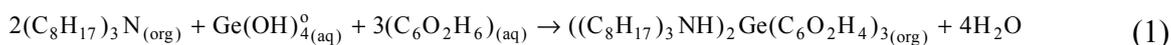
Many conventional techniques have been developed to separate germanium from other elements contained in leachates, including precipitation with tannin, distillation of $GeCl_4$ [9], flotation of a Ge

complex [10,11] adsorption onto activated carbon [12], precipitation [13], solvent extraction [14,15] and sorption onto chelating exchange resins [16,17].

Table 1. Production date, limestone dosage (%), coal/pet-coke ratio and Ge content (mg/kg) in fly ash samples selected for Ge and Ga extraction tests [8].

| Fly Ash	Date	Limestone (%)	Coal/Pet-Coke Dose	Ge Content (mg/kg)
FA#2	11/09/1999	4.1	50:50	347
FA#7	24/10/2000	2.6	50:50	244
FA#10	--/11/2002	2.2	50:50	356
FA#13	20/10/2005	2.5	50:50	319
FA#15	03/06/2008	2.7	50:50	235
FA#16	30/06/2008	2.8	50:50	268
FA#17	02/07/2008	2.8	50:50	228
FA#18	19/09/2008	2.4	50:50	174

The solvent extraction (SX) method for the recovery of germanium from fly ash is based on the germanium-1, 2-dihydroxybenzene (catechol, CAT) ($C_6O_2H_6$) chelate and the subsequent extraction of the complex using tri-*n*-octylamine (TOA) ((C_8H_{17})$_3$N) and stripping with alkaline solutions. The equilibrium extraction and stripping are given by the following equations respectively:

$$2(C_8H_{17})_3N_{(org)} + Ge(OH)^0_{4(aq)} + 3(C_6O_2H_6)_{(aq)} \rightarrow ((C_8H_{17})_3NH)_2Ge(C_6O_2H_4)_{3(org)} + 4H_2O \tag{1}$$

Once the Ge is in the organic phase, two stripping possibilities are apparently possible, because the ternary complex is not stable in strong acidic or alkaline solutions [18]. Alkaline stripping is shown in Equation (2).

$$((C_8H_{17})_3NH)_2Ge(C_6O_2H_4)_{3(org)} + 2OH^-_{(aq)} \rightarrow 2(C_8H_{17})_3N_{(org)} + Ge(C_6O_2H_6)_{3(aq)} + 2H_2O \tag{2}$$

The last step of a hydrometallurgy process for the recovery of germanium from FA consisted in precipitation processes for germanium from the Ge-bearing solutions. A possible precipitation is based on precipitating Ge with cetyltrimethylammonium bromide (CTAB) and catechol [19]. The Ge-CAT complex has a high solubility in water probably due to its polarity, but when CTAB is added to an aqueous solution that contains the Ge-CAT complex, the CTA$^+$ cation and the Ge-CAT complex form a heavy ion pair that precipitates. The ion-pair could be formed as follows if the stoichiometric ratio of reagents is Ge:CAT:CTAB 1:3:2 [19,20].

$$2C_{19}H_{42}NBr + [Ge(C_6H_4O_2)_3]^{2-} \rightarrow (C_{19}H_{42}N)_2Ge(C_6H_4O_2)_3 + 2Br^+ \tag{3}$$
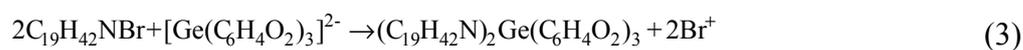
The Ge precipitate can be roasted (at temperature >600 °C) rendering an end product in the form of germanium dioxide. The mechanism for the decomposition of the germanium-complex has been published previously [19,20].

A pilot plant operation is usually needed to generate information about the behavior of the system to be used in the design of larger facilities; therefore, a pilot plant was designed to test this hydrometallurgical method and to obtain operating conditions and some data necessary for a future larger plant design. The main points related to equipment design of the pilot plant were continuity and versatility [20], taking into account the scaling up from the pilot scale to a demonstration level.

This paper shows the design of a demonstration plant from experiments carried out at the pilot scale regarding leaching and SX process.

2. Process and Pilot Plant

The pilot plant design was based on the results obtained at laboratory scale [13,14,21] and it was operated in a continuous mode. A schematic arrangement of the flow configuration is illustrated in Figure 1, and pilot plant design and experimentation have been previously published [22]. The pilot plant comprised two main stages: germanium extraction from FA (leaching with water) and separation of germanium from other elements dissolved in the leachate (L) (interferences). After water leaching, wet fly ash and leachate are separated in a vacuum filter. Catechol is added to leachate and the pregnant solution (leachate + CAT + H_2SO_4) is contacted in a mixer-settler unit with an organic phase carrying an extracting agent for Ge. After extraction, the aqueous phase (AP) and organic phase (OP) are allowed to separate in the settler. The organic solution from the extraction stage feeds the stripping mixer-settler where it is contacted with an alkaline stripping solution (SP), which reverses the extraction process.
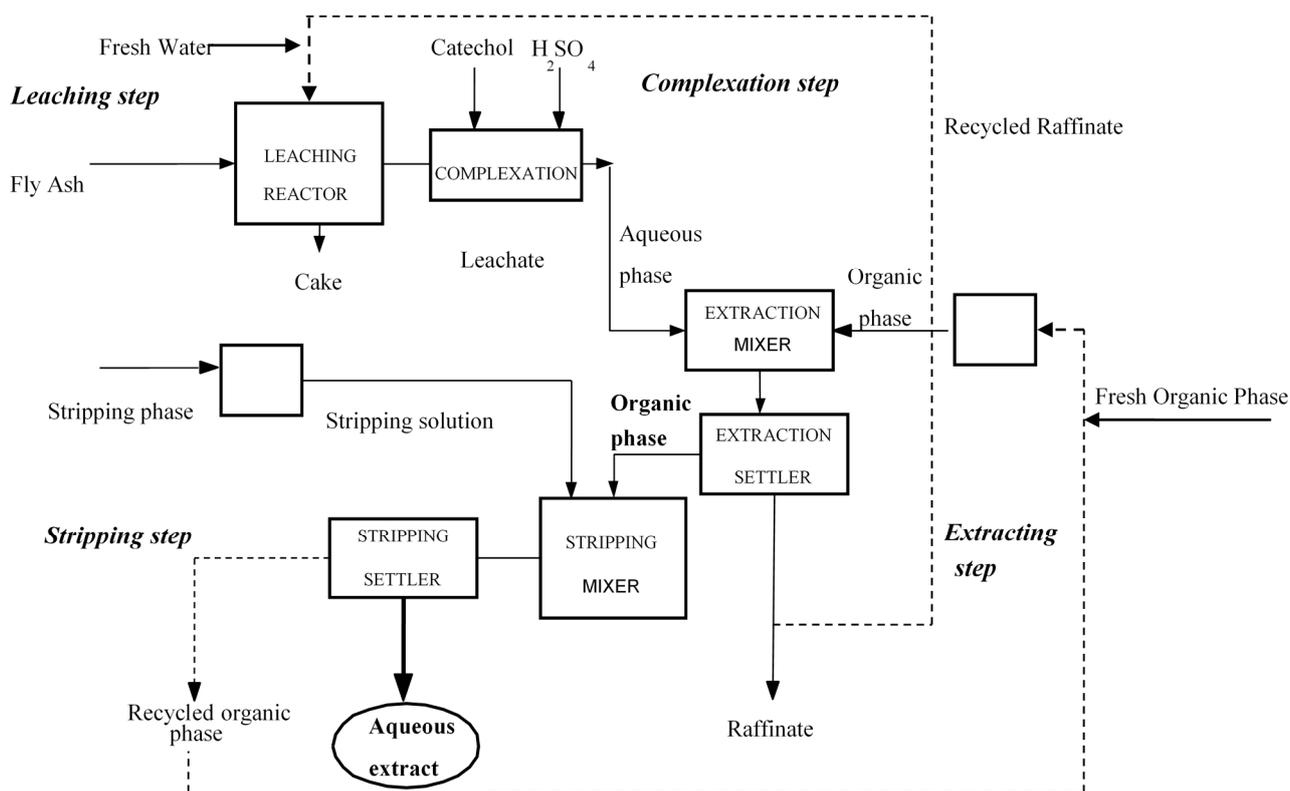

Figure 1. Pilot plant flow sheet scheme.

The pilot plant mass balance was performed with a feedstock of 5 kg/h of fly ash, with a theoretical recovery of germanium of 1.3 g/h (as GeO_2) [22].

The pilot plant is fed with 5 kg/h of FA and it consists of a leaching reactor unit (100 L), a complex formation tank (30 L), two mixer-settler units, for extraction (mixer: 10 L—settler: 2 L with 120 cm^2 of settling area) and stripping (mixer: 3.5 L—settler: 0.8 L with 100 cm^2 of settling area) three auxiliary reactors for raffinate discharge and storage (30 L), organic phase preparation (25 L) and germanium-rich

final solution storage (10 L), all constructed of stainless steel. Auxiliary dosifiers, tanks, pumps, valves and control devices were also integrated into the process [22].

One fundamental stage of the process was the germanium leaching performed in a reactor with water and FA continuous additions. Some leaching tests with three different L/S ratios (3, 5 and 7) were carried out at laboratory and pilot plant scale [13,14]. At leaching times <6 h, a small increase of germanium extraction was observed with increasing L/S ratio. But taking into account other aspects such as the fluency of the fly ash-water mixture, worse for L/S = 3, or the quantity of liquid residues, higher in the case of L/S = 7, tests performed in the pilot plant confirmed L/S = 5 as the optimum relation in agreement with the laboratory results [13,14]. After the leaching, wet FA and leachate were separated by a vacuum rotary filter [22]. Concerning the SX method, previous results show that the extraction yields achieve 95% after 5 min of residence time when AP/OP = 5 is used [13,14]. Regarding the stripping stage, the germanium stripping yields achieve 98% with a sodium hydroxide solution in 5 min (residence time) for OP/SP = 5 [13,14].

The reutilization of raffinate as leaching solution was studied, and results show the best option in terms of leaching yield. Tests were performed and results are shown in Table 2. A larger amount of raffinate in the leaching solution increased the germanium content in leachate, but if the pH of the leaching solution is very low, the puzzolanity of the fly ash can change, avoiding its reutilization after germanium extraction in many of their current applications [4,21]. Fly ash would also be a residue instead of a by-product so a leaching solution constituted by 75% of raffinate from SX process and 25% of fresh water (Table 2) was selected. With this reutilization, the Ge extraction yield can increase up to 25% compared with the leaching with water due to the low pH and the amount of catechol, so leachates with Ge contents of 50 mg/L can be achieved. Residence time decreased due to catechol and acid effect to 2 h (from 24 h with water leaching).

Table 2. Leaching tests with different raffinate/water ratios and residence times.

Leaching Solution	Leaching Time (h)	Ge in Leachate (mg/L)
65% raffinate 35% water	1.5	30
	2	45
	6	40
75% raffinate 25% water	1.5	32
	2	53
	6	46
85% raffinate 15% water	1.5	43
	2	52
	6	49

The return of the organic phase in the SX stage was also studied in the pilot plant trials and results shown that TOA remained in the OP after stripping, so reutilization of OP is possible and extraction yields remained almost constant [21]. Some fresh organic phase diluent and TOA has to be introduced in the system due to evaporation and entrainments in the raffinate losses.

3. Preliminary Mass Balance

The actual FA production of ELCOGAS IGCC Power Plant (Puertollano, Spain) is 2000 kg/h. The demonstration plant was designed for 10% of actual FA production because, for a new process, a conservative scaling factor of 10 is recommended by some authors [23]. The design considered a demonstration plant capacity of 200 kg/h fly ash (10% of 2000 kg/h) with a Ge content of 300–400 ppm (Table 1). In Table 3, the pilot plant and demonstration plant preliminary mass balances are shown.

Table 3. Pilot plant and demonstration plant preliminary mass balance. Ge mass balance.

Main Compounds		Flow	Units	Concentration (mg/L)	Flow	Units	Ge Total (g)
Fly ash	FA	5.0	kg/h	350	200	kg/h	70.0
Leaching solution (W/FA = 5)	Fresh water (FW)	6.3	L/h	0	250	L/h	0.0
	R recycled (RR)	18.8	L/h	4	750	L/h	3.0
	Total	25.0	L/h	-	1000	L/h	3.0
Leachate/Aqueous phase	AP	22.4	L/h	53	896	L/h	46.8
Cake	C (FA)	5.0	kg/h	-	200	kg/h	20.7
	C (leachate)	2.6	L/h	53	104	L/h	5.5
	Total (Wet FA)	7.5	-	-	300	-	26.2
Organic phase (AP/OP = 5)	Fresh OP (FOP)	0.4	L/h	0	17.9	L/h	0.0
	ROP (recycled)	4.0	L/h	20	161.3	L/h	3.2
	Total	4.5	L/h	-	179.2	L/h	3.2
Organic extract	OE	4.3	L/h	259	170.2	L/h	44.0
	Losses	0.2	L/h	259	9.0	L/h	2.4
	Total	4.5	L/h	-	180	L/h	-
Raffinate	Residual raffinate	3.7	L/h	4	146	L/h	0.6
	For recycling (RR)	18.8	L/h	4	750	L/h	3.0
	Total Raffinate	22.4	L/h	4	896	L/h	3.6
Stripping phase (OE/SP = 5)	SP	0.9	L/h	0	34.0	L/h	0.0
Aqueous extract	AE	0.9	L/h	1243.2	34.0	L/h	42.3
Residual organic phase	ROP	4.0	L/h	20	161.3	L/h	3.2
	Losses	0.2	L/h	20	9.0	L/h	0.2

A total of 83.9% of recovered raffinate was reintroduced in the process as leaching agent, and 95% of the organic phase was reintroduced in the process too.

A germanium balance is included, and 61 g/h of GeO_2 (equivalent) could be recovered from the 200 kg/h of FA.

4. Demonstration Equipment Design

In the case of the demonstration plant, geometric similitude with pilot plant equipment was maintained. The criteria for the pilot plant equipment design was the simplest as possible, because a hydrometallurgical process for a residue valorization (with a low content of germanium) only can be profitable if both equipment and operational costs are low.

4.1. Leaching Equipment

Leaching solution comes into contact with the coal fly ash in the leaching reactor to dissolve the germanium content. The leaching reactor is a stirred tank, and the basic design parameters are: geometry, construction material, design and location of baffles and, design of agitator [24].

Maintaining the pilot plant equipment geometry, the leaching reactor is made up of vertical cylindrical jacketed stainless steel AISI 316 vessel with a tori-spherical bottom and up heads and a central agitator to avoid vortex. It is an up charging reactor with a bottom discharge valve (Figure 2).
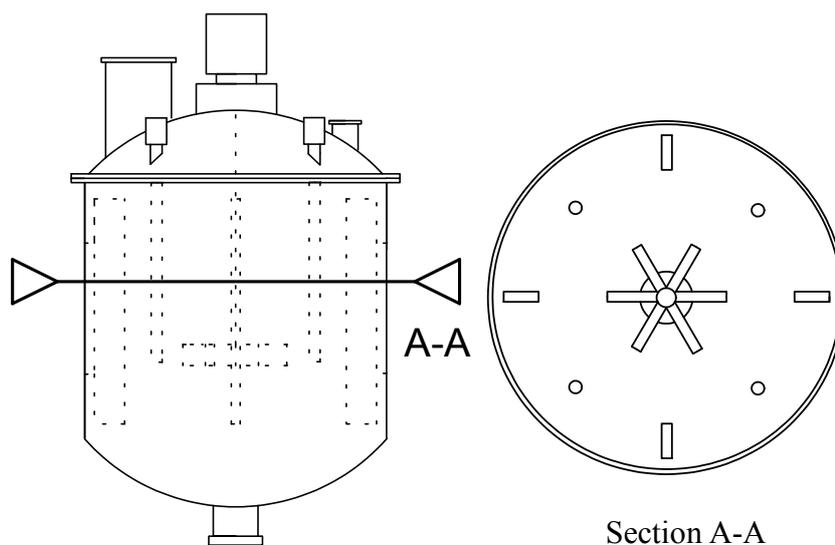

Section A-A

Figure 2. Leaching reactor scheme.

Accordingly with the mass balance (Table 2) 1000 L/h of water/leachate and 200 kg/h of fly ash are discharged. If the residence time is 2 h and a filling factor of 80% was selected, the required volume of the leaching reactor is 2.73 m³. The volume is defined as the sum of the cylindrical volume and the volume of the heads (Equation (4)).

$$V_{\text{reactor}} = V_{\text{cylinder}} + 2 \cdot V_{\text{head}} = \frac{\pi}{4} \cdot D^2 \cdot H + 2 \cdot 0.0809 \cdot D^3 \tag{4}$$

Where V_{reactor} is the volume of the reactor, V_{cylinder} is the volume of the cylindrical part, V_{head} is the volume of the tori-spherical bottom and head of the reactor, and D and H are the reactor diameter and height respectively. For agitated reactors, a diameter similar to height is preferred [25], so the diameter and height of the leaching reactor have been determined as 1450 and 1400 mm respectively (Figure 2).

Stirring tanks should have baffles to prevent the formation of vortices and promote the contact between phases. Baffle shapes depend on the solution viscosity. For the slurry (FA and water) the deflectors are standard and they should maintain determined ratios approximately (Equations (5)–(7)) [25].

$$b_w = \frac{D}{10} \tag{5}$$

$$b_c = 0.15 \cdot b_w \tag{6}$$

$$b_a = \frac{1}{2} \cdot b_w \tag{7}$$

Where D is the reactor diameter, b_w is the baffle width (150 mm), b_c is the separation of the baffles from the reactor wall (23 mm), and b_a is the height to which the deflectors are placed over the reactor bottom (75 mm). Four stainless steel AISI 316 baffles have been distributed along the perimeter of the tank (cross form), and b_w = 150 mm, b_c = 23 mm and b_a = 75 mm were calculated using Equations (6) and (7).

An agitating system is employed to promote the contact between FA and leaching solution. To encourage contact between the two phases, turbine agitators are recommended [25], so turbine agitators with 6 flat 45° inclined blades were chosen. The recommended geometry of the agitator is related to the reactor geometry (Equations (8)–(10)).

$$\frac{d_{imp}}{D} = 0.2 \text{-} 0.5 \tag{8}$$

$$\frac{h_{imp}}{D} = 0.17 \text{-} 0.34 \tag{9}$$

$$\frac{l_{blades}}{d_{imp}} = 0.25 \tag{10}$$

Where d_{imp} is the diameter of the impeller, h_{imp} is the height to which the impeller is placed over the reactor bottom, l_{blades} is the blades length, and D is the reactor diameter. A ratio impeller diameter/reactor diameter of 0.33 was selected since for the mixing of immiscible liquids small impellers at high speeds are recommended [25]. According to previous equations, the geometry of the turbine agitator was d_{imp} = 525 mm, h_{imp} = 380 mm, and l_{blades} = 93 mm.

The maximum rotational speed (N_{max}) of the impeller can be estimated using the Equation (11).

$$N_{max}{}^3 \cdot d_{imp}^2 < 20 \tag{11}$$

Where d_{imp} is the diameter of the impeller. The N_{max} recommended for this agitator is 110 r·min^{-1}.

For turbine agitators power consumption is usually expressed by the dimensionless Newton number N_P (Equation (12)) and the rotational Reynolds number Re (Equation (13)) when no vortex is present. This procedure provides a single master curve that depends only on impeller geometry and can be used to predict power requirements for any given fluid properties (density ρ and viscosity μ), impeller dimensions and rotational speed [26].

$$N_F = \frac{P}{N^3 \cdot d_{imp}^5 \cdot \rho} \tag{12}$$

$$Re = \frac{N \cdot d_{imp}^2 \cdot \rho}{\mu} \tag{13}$$

Where N_P is the Newton (or power) number, Re is the Reynolds number, d_{imp} is the diameter of the impeller (expressed in m), μ is the viscosity of the fluid (Pa·s) and ρ is the density of the fluid (kg/m^3).

In case of the leaching reactor, for the maximum recommended agitator speed, turbulent regime is achieved ($Re \approx 25,000$), so N_P is independent of Re and can be calculated graphically as 2 [25]. The required power is 0.5 kW.

4.2. Filter

According to the fly ash physical characteristics (refinement) and pilot plant vacuum filter performance, a filter press has been chosen to separate the fly ash and leachate from leaching reactor. This equipment operates discontinuously, so to maintain the continuity of the industrial plant operation, two press filters have been designed which operate alternately. Both filters are identical.

Equation (14) allows calculation of the needed filtration area. The fabric resistance has been neglected against the cake resistance [27,28].

$$Q = \frac{A_F \cdot \Delta P}{\mu \cdot \alpha \cdot C_S \cdot \dfrac{V_F}{A_F}} \tag{14}$$

Where Q is the flow (m³/h), A_F is the filtration area (m³), V_F is the volume of filtrate (m³), ΔP is the pressure drop across the filter (Pa), μ is the dynamic viscosity of the fluid (Pa·s), and C_s is the solids concentration.

For the design of filters, it is necessary to establish a filtration time (the time between filling the filter to the time at which proceeds to download the cakes). In this work, a filtration time of 2 h was proposed taking into account the leaching time (2 h) to maintain the continuity of the process. At this time, the filter must process a slurry flow rate of 896 L/h (with a solids concentration of 183 kg/m³) (Table 2), so the total filtrate volume (in a filtration cycle, it means 2 h) is 1792 L.

The maximum pressure drop for a small-medium size filter (plate size 300–1300 mm) is 16 bar. This provides the smallest filtering area required. Usually, the batch experiments performed at constant increment de P for determination of filtration parameters, are expressed as a line (Equation (15)) [28,29].

$$\frac{t_F}{V_F} = \frac{\mu \cdot \alpha \cdot C_S}{A_F{}^2 \cdot \Delta P} V_F + \frac{\mu \cdot Rm}{A_F \cdot \Delta P} = K_P \cdot V_F + K_m \tag{15}$$

where t_F is the filtration time and V_F is the cumulative filtrate volume. So, the slope of the line (K_p) was determined from tests in laboratory ($1.8 \cdot 10^{10}$). Using the definition of K_p (Equation (15)), the specific cake resistance (α) can be calculated:

$$K_p = \frac{\mu \cdot \alpha \cdot C_S}{A_F{}^2 \cdot \Delta P} \tag{16}$$

$$A_F = N_{FP} \cdot l_{FP}{}^2 \tag{17}$$

Where l_{FP} is the length of filtering plates and N_{FP} is the number of filtering plates. The calculated specific resistance of cake (Equation (16)) was 1.02×10^{12} m/kg, so the filtering area (Equation (17)) was 5.6 m². Accordingly to Equations (16) and (17), the designed filtering plate length is 500 mm, and 23 plates are required.

4.3. Extraction Equipment

The fertile solution is contacted with the organic phase in the extraction equipment. Mixer–settlers are widely used in the chemical process industry because of reliability, operating flexibility, and high capacity. These extractors are particularly economical for operations that require few stages. In this process, 5–9 stages are needed (see Sections 4.3.1 and 4.4.1). Taking into account the time or reaction (5 min), phase ratio (AP/OP = 5 and OP/SP = 5) and total throughput (<2.5 m^3/h), vertical agitated mixer-settler are recommended [30].

A mixer-settler cascade was chosen as extraction equipment.

4.3.1. Number of Stages

The number of stages has been determined graphically from the McCabe-Thiele diagram that represents the equilibrium curve and the operating line. The equilibrium curve consists of a series of experimental points, which represents the germanium content in raffinate and the Ge content in the organic extract for different volumetric ratios (AP/OP) and residence times. After contact, both phases are in equilibrium. The operating line sets the operating conditions and its slope is the ratio AP/OP.

The graphical representation of the McCabe-Thiele diagram of this system is shown in Figure 3 [21]. Three theoretical stages are required, and the extraction yield achieved is 98%.
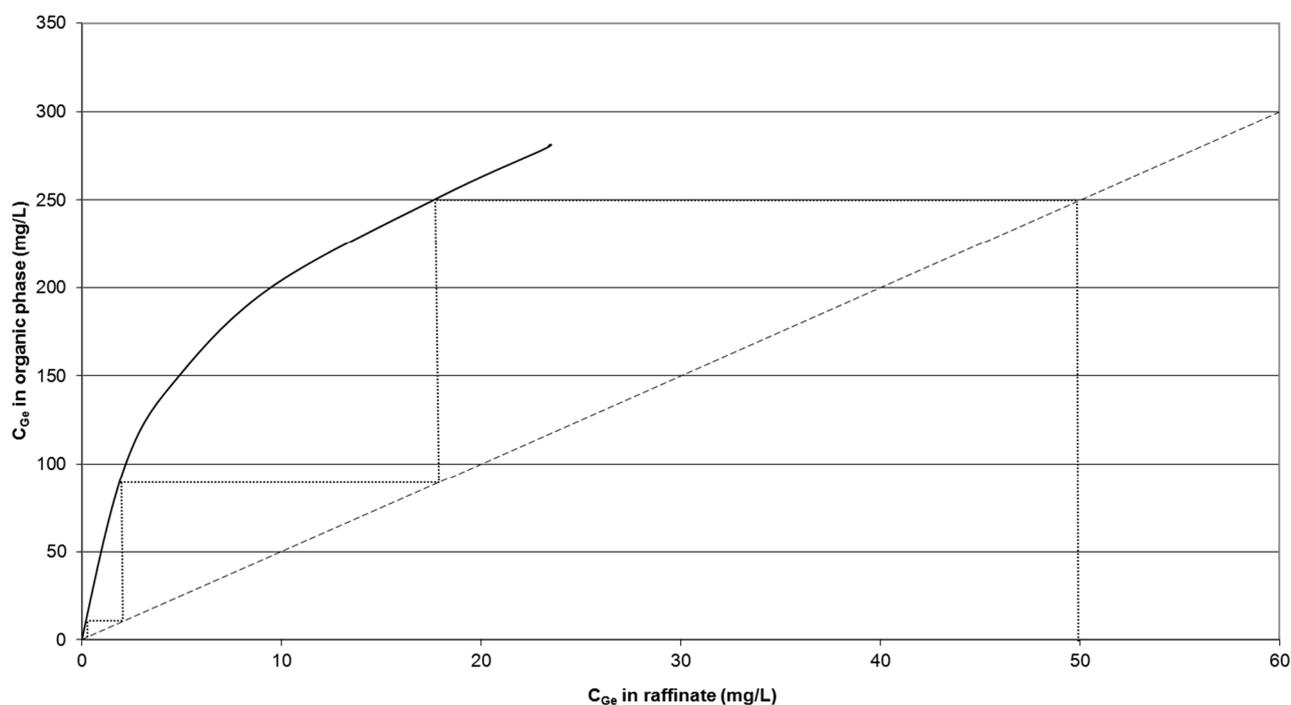

Figure 3. McCabe-Thiele diagram of extraction system.

According to Cox and Musikas [31], the number of real stages should be the theoretical number multiplied by 1.5–2. So, the real number of extraction stages should be five.

4.3.2. Mixer Geometry

The extraction equipment consists of a mixing chamber, where phases are contacted in counter-current and are mixed by the effect of agitation, and the settler consists of a settling chamber, where the phases are separated. Each extraction stage comprises one mixer and one settler.

The extraction mixer is made up of vertical cylindrical equipment with a tori-spherical bottom head constructed of stainless steel AISI 316, similar to the leaching reactor but with different size. Taking into account the flows of the aqueous and organic phases (Table 2), the residence time (5 min) and the filling factor (80%) according to results obtained in pilot plant tests [21,22], the volume in the mixer is 0.113 m^3 (Equation (3)) and the diameter and height of the mixer have both been determined as 480 mm (Equation (4)). Four baffles have been distributed along the perimeter of the tank (cross form): b_w = 48 mm, b_c = 8 mm and b_a = 24 mm (Equations (5)–(7)).

According to previous considerations, the geometry of the turbine agitator was d_{imp} = h_{imp} = 160 mm, and l_{blades} = 40 mm (Equations (8)–(10)). The N_{max} recommended for this agitator was 120 r·min^{-1} (Equation (11)) and the calculated power is 0.02 kW.

4.3.3. Settler Geometry

The settler is a parallelepiped constructed of stainless steel AISI 316. The most important aspect of this settler is the total separation of the phases, which is difficult since the ratio AP/OP is very large and OP occupies a small fraction of the volume settler. The most important design parameter of the sediment in this regard is the specific flow, which is defined as the flow per horizontal area.

In pilot plant tests, several problems with the original settler design were observed. Settling times around 15 min were needed for a complete phase separation. For typical Q/A ranging 0.06–0.1 m^3/m^2·min [25], settler lengths from 0.9 to 1.5 m were needed. In Table 4, different widths of settler are shown. A preliminary estimate of settler length is 1500 mm to ensure complete phase separation. The flow to the settler is 0.987 m^3/h. It is not recommended to exceed the maximum specific flow, so it will take an operational ratio Q/A of 4.8 m^3/m^2·h. The minimum height of the settler is 100 mm for easy separation of the phases. Therefore, the settler dimensions are: 1500 mm (length), 1100 mm (height) and 140 mm (width).

Table 4. Different options for settler design: widths, ratio Q/A (m^3/m^2·h) and settling areas.

Settler Design Parameters	Options						
Q/A (m^3/m^2·h)	3.6	4.0	4.4	4.8	5.2	5.6	6.0
A (m^2)	0.27	0.25	0.22	0.21	0.19	0.18	0.16
W (m)	0.18	0.16	0.15	0.14	0.13	0.12	0.11

4.4. Stripping Equipment

4.4.1. Number of Stages

The graphical representation of the McCabe-Thiele diagram of the stripping system is shown in Figure 4 (data from [21,22]). The theoretical number of required stages is six, and the stripping yield

achieved is 96%. According to Cox and Musikas [31], the number of real stages should be the theoretical number multiplied by 1.5–2. Thus, the real number of stripping stages should be nine.
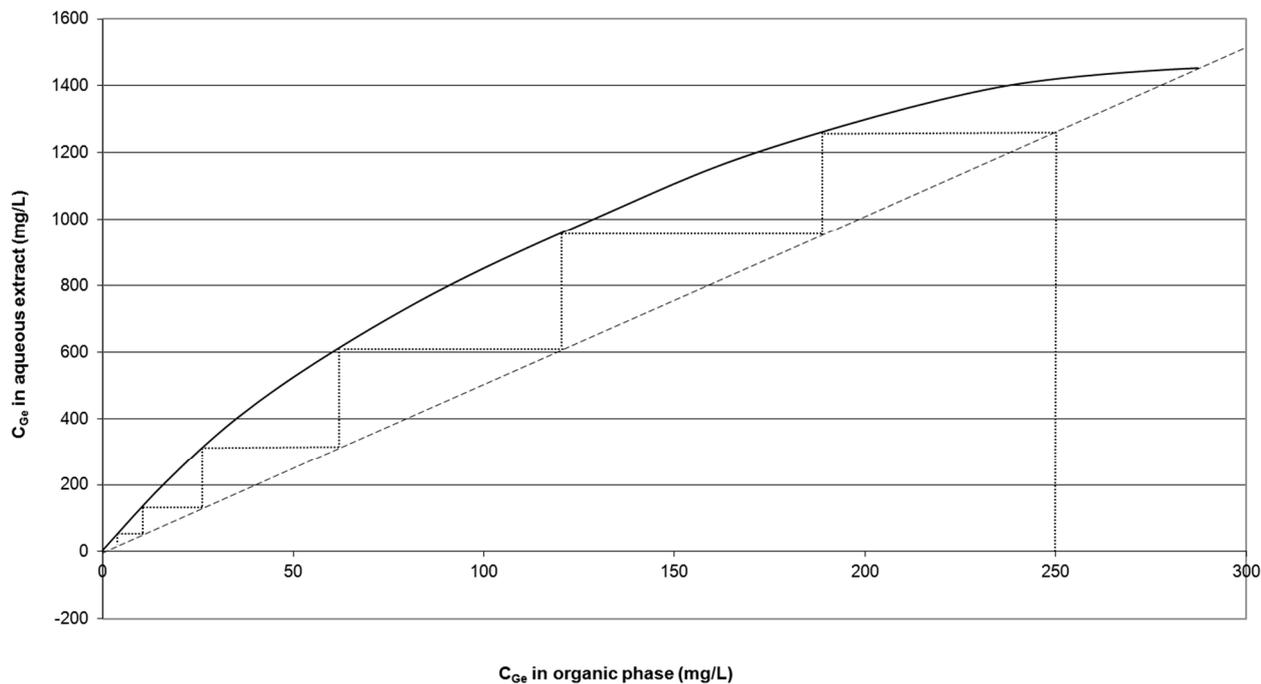

Figure 4. McCabe-Thiele diagram of stripping system.

The stripping system chosen is the same as for the extraction equipment. The flow arrangement is counter-current.

4.4.2. Mixer Geometry

The SP and OP are in a vertical cylindrical mixer with a tori-spherical bottom constructed of stainless steel AISI 316 (similar to leaching and extraction mixer reactors). For a phase volume ratio of 5 [13,14], the residence time in the stripping mixer (5 min [14]) and the filling factor (80%), the volume of the reactor is 0.023 m^3.

According to the equations considered in the design of the extraction mixer (Equations (3)–(11)), the stripping mixer is: $D = 300$ mm and $H = 200$ mm high with four baffles made of the same stainless steel AISI 316, distributed along the perimeter. A six flat-blade turbine agitator is designed with the following geometry: $b_w = 30$ mm, $b_c = 5$ mm and $b_a = 15$ mm, $d_{imp} = 100$ mm, $h_{imp} = 70$ mm and $l_{blades} = 25$ mm. The N_{max} allowed for this agitator is 195 r·min^{-1} and the power consumed by the agitator reaches 0.02 kW.

4.4.3. Settler Geometry

The settler is a parallelepiped constructed of stainless steel AISI 316. In the stripping stage, phases are easily separated [21], so a settling time of around 6 min was enough to ensure phases separation. Taking into account the same considerations as for the extraction settler, for a flow of 0.2 m^3/h and $Q/A = 3.6$ m^3/m^2·h, the settler dimensions are: 400 mm (length), 280 mm (height) and 78 mm (width).

5. Demonstration Plant Scheme

In Figure 5, a basic scheme of the process is shown. Fly ash is stored (S1) from where it is fed into the leaching reactor (R1) through the conveyor T1. The feed flow is 200 kg/h of FA.
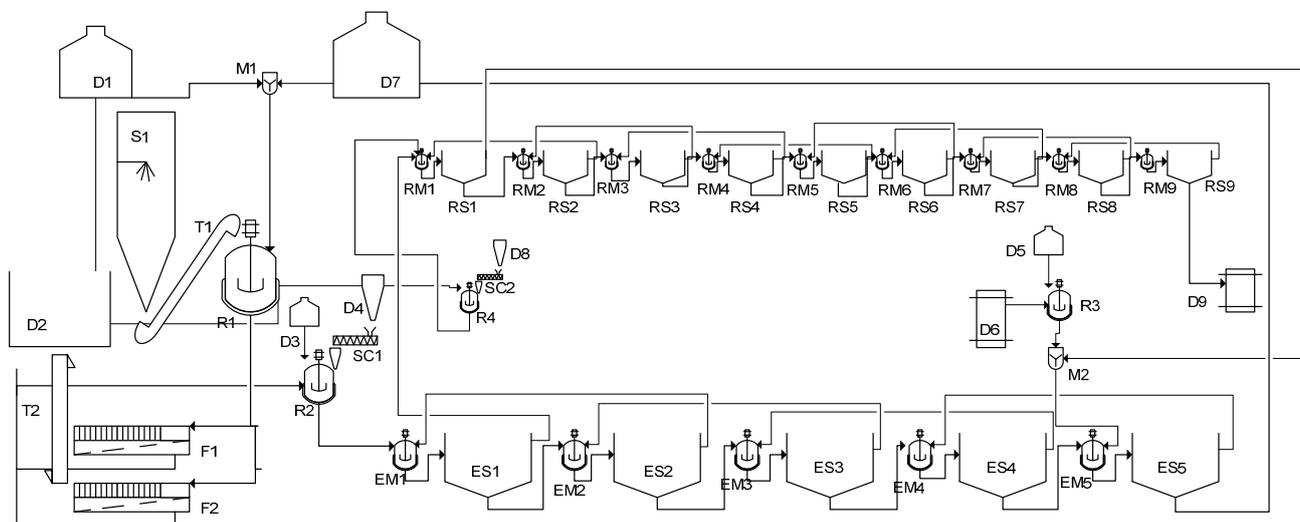

Figure 5. Demonstration plant scheme.

The plant has a water storage tank D1 for a day of plant operation in case of failure. Most of the leaching solution quantity is reintroduced from the process (raffinate from solvent extraction stage).

The slurry from the leaching reactor R1 is pumped to one of the filter press (F1 or F2). Two press filters have been installed so that one can filter while the other is discharged and cleaned. Wet fly ash with 35% moisture (approx.) is stored until reutilization (D2).

Leachate collected from the filter is pumped to the mixer (R2) where extracting solution is prepared by addition of catechol and sulfuric acid. CAT is stored in solid state (D4) and transported to the R2 with a screw (SC1). Sulfuric acid is stored in the tank D3 and pumped to R2. The OP prepared in the reactor R3 consists of kerosene and trioctylamine. Kerosene is stored in D6 and pumped to R3. Similarly, TOA is stored in D5 and pumped to R3.

The AP and OP are introduced in the first and last stages of SX equipment respectively. Each stage is made up of a mixer-settler (ER1-ER5/SR1-SR5).

Raffinate is stored in the tank D7 until its reintroduction in the R1 (leaching stage).

The pregnant OP is introduced in stripping equipment, where it is in contact with sodium hydroxide 3 M coming from R4, which receive sodium hydroxide in solid form from the silo D8 and tank water D1. The stripping equipment is named RE1-RE9/RS1-RS9.

After stripping, the pregnant and concentrated solution of germanium is stored in the tank D9 designed for that purpose. The organic waste is stored in D10 until the returned to the extraction stage.

6. Cost Estimation

This section provides factored cost estimation (Lang methodology) based on the ratio of main plant equipment (mixers and settlers). This estimate has an accuracy of 30%. The Lang methodology for cost estimation consists of two steps:

Step 1: Estimated cost of main equipment. The total cost of main equipment is the sum of the estimated costs of main individual equipment (Table 5).

Table 5. Factors for global investment estimation.

Equipment	Cost (€)
Extraction equipment	-
Mixers	75,000
Settlers	25,000
Stripping equipment	-
Mixers	70,000
Settlers	30,000
Auxiliary reactors	50,000
Pumps	30,000
Liquid store	70,000
Total	360,000

Step 2: Corrections. The cost calculated in Step 1 has to be corrected to consider additional costs such as direct and indirect costs. This correction factor is called a global factor of Lang and it is a function of the type of plant. The global cost can be calculated as shown in Equation (18) [32].

$$I_{\text{TOTAL}} = (I_b) \cdot (\Sigma f_{\text{dir}} \cdot f_{\text{Ind}} \cdot f_{\text{fix}}) = F_{\text{Lang}} \cdot I_b \tag{18}$$

Where I_{total} is the total investment, F_{lang} is the Lang factor and I_b is the total cost of main equipment, f_{dir} includes the factors to estimate direct costs and find includes the factors to estimate indirect costs (Table 5).

The estimated investment for the demonstration plant implantation is: 375,000 × 4.8 = 1,800,000 €.

7. Conclusions

The conceptual process design of a demonstration plant has been performed, including the evaluation of process, the identification of equipment options and early investment analysis.

The mass balance of the demonstration plant (200 kg/h) has been performed using the experimental results obtained at pilot plant scale (5 kg/h).

Main equipment (leaching reactor, filters, and extraction and stripping equipment were designed and data for the preliminary design was obtained in tests at laboratory and pilot plant scale.

Almost 61 g/h of GeO_2 (equivalent) could be recovered from a 200 kg/h of industrial residue such as fly ash.

The estimated investment for the demonstration plant (direct and indirect costs) is 1,800,000 euros.

Author Contributions

Fátima Arroyo performed some calculations and wrote the paper, Constantino Fernández-Pereira revised the paper, and Pilar Bermejo performed some of the calculations.

Conflicts of Interest

The authors declare no conflict of interest.

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