Industrial Equipment Design for the Recovery of Germanium from Coal Fly Ash Leachates by Solvent Extraction

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ABSTRACT

Germanium recovery from coal fly ash (FA) leachates by solvent extraction procedures was studied. Tests at pilot plant scale were performed in order to design industrial equipment.

Based on the experimental results, mass balances and McCabe-Thiele diagrams were applied to determine the number of steps of the SX stage.

Different arrangements have been studied and a countercurrent process with 3 steps in extraction and 6 steps in elution was defined. A residence time of 5 minutes was fixed in both extraction and elution stages. Volumetric ratios in extraction and stripping were: Aqueous phase (AP)/Organic phase (OP) = 5 and OP/Stripping phase (SP) = 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.

LIST OF ACRONYMS

Area: A
Aqueous extract: AE
Aqueous phase: AP
Blades length: l_{blades}
Blades width: b_w
Catechol: CAT
Diameter of the impeller of the agitator d_{imp}
Estimated cost of main individual equipment: C_i

Factors to estimate direct costs: f_{dir}
Factors to estimate indirect costs: f_{ind}
Fly ash: FA
Flow: Q
Height to which the deflectors are placed over the reactor bottom: b_a
Height to which the impeller is placed over the reactor bottom: h_{imp}
Kerosene: KER
Leachate: L
Lang factor: F_{lang}
Maximum rotational speed: N_{max}
Organic extract: OE
Organic phase: OP
Raffinate: R
Reactor Diameter: D
Reactor Height: H
Reactor Length: Le
Residual Organic phase: ROP
Rotational speed: N
Separation of the baffles from the reactor wall: b_c
Solvent extraction: SX
Stripping phase: SP
Total cost of main equipment: I_b
Total investment: I_{total}
Trioctylamine: TOA

1. INTRODUCTION

Germanium is not very abundant in the Earth's crust, occurring only at a ratio 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 manufacture of semiconductors, but innovative uses for germanium in new and high technological industrial applications have led to anincrease 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 industries, 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 (1400 $/kg of germanium metal in December 2008),[2] and alternative sources have started to emerge; mainly the combustion[3] and gasification[4] of coal fly ashes. When the coal is burned/gasified under proper conditions the fly ash can reach germanium contents ten times higher than the germanium content in the original coal.

Many conventional techniques have been developed to separate germanium from other elements contained in leachates, including precipitation with tannin,[5] distillation of $GeCl_4$,[6] flotation,[7,8] adsorption onto activated carbon,[9] precipitation,[10] solvent extraction[11,12] and sorption onto chelating exchange resins.[13,14]

The SX method for the recovery of germanium from fly ash is based on the germanium-catechol ($C_6O_2H_6$) chelate and the subsequent extraction of the complex using tri-n-octylamine ($(C_8H_{17})_3N$) and stripping with alkaline solutions. The equilibrium extraction and stripping are given by the following equations respectively:

$$2(C_8H_{17})_3N_{(org)} + Ge(OH)^0_{4(aq)} + 3(C_6O_2H_6)_{(aq)} \text{ ¡ê } ((C_8H_{17})_3NH)_2Ge(C_6O_2H_4)_{3(org)} + 4H_2O_{(aq)} \tag{1}$$

$$((C_8H_{17})_3NH)_2Ge(C_6O_2H_4)_{3(org)} + 2OH\ _{(aq)} \text{ ¡ê } 2(C_8H_{17})_3N_{(org)} + Ge(C_6O_2H_6)_{3(aq)} + 2H_2O_{(aq)} \tag{2}$$

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 discover possible operational problems in a future industrial plant. The main points related to equipment design and assembly of the pilot plant were continuity and versatility, taking into account the scaling up from the pilot scale to an industrial level.

This paper shows the design of an industrial scale plant from experiments carried out at pilot scale.

2. PROCESS AND PILOT PLANT

The pilot plant design was based on the results obtained at laboratory scale[15]. A schematic arrangement of the flow configuration is illustrated in Figure 1. 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 (interferences). CAT is added to leachate and the pregnant solution (leachate + CAT) is contacted in a mixer–settler unit with an organic phase carrying an extractant for germanium. After extraction the AP and 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.

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).

The pilot plant is fed with 5 kg/h of FA and it consists of a leaching reactor unit (100L), a complexation tank (30 L), two mixer-settler units, for extraction (mixer: 10L - settler: 2L with 120 cm^2 of settling area) and stripping (mixer: 3.5L - settler: 0.8L with 100 cm^2 of settling area) three auxiliary reactors for raffinate discharge and storage (30L), organic phase preparation (25L) and germanium-rich final solution storage (10L), all constructed of stainless steel. Auxiliary dosifiers, tanks, pumps, valves and control devices were also integrated into the process.[16]

Concerning the solvent extraction method, previous results show that the extraction yields achieve 95% when the residence time in the extraction mixer is 5 minutes and AP/OP =5. Regarding the stripping stage, the germanium stripping yields achieve 98% with a sodium hydroxide solution when an OP/SP = 5 is used in 5 minutes.[16]

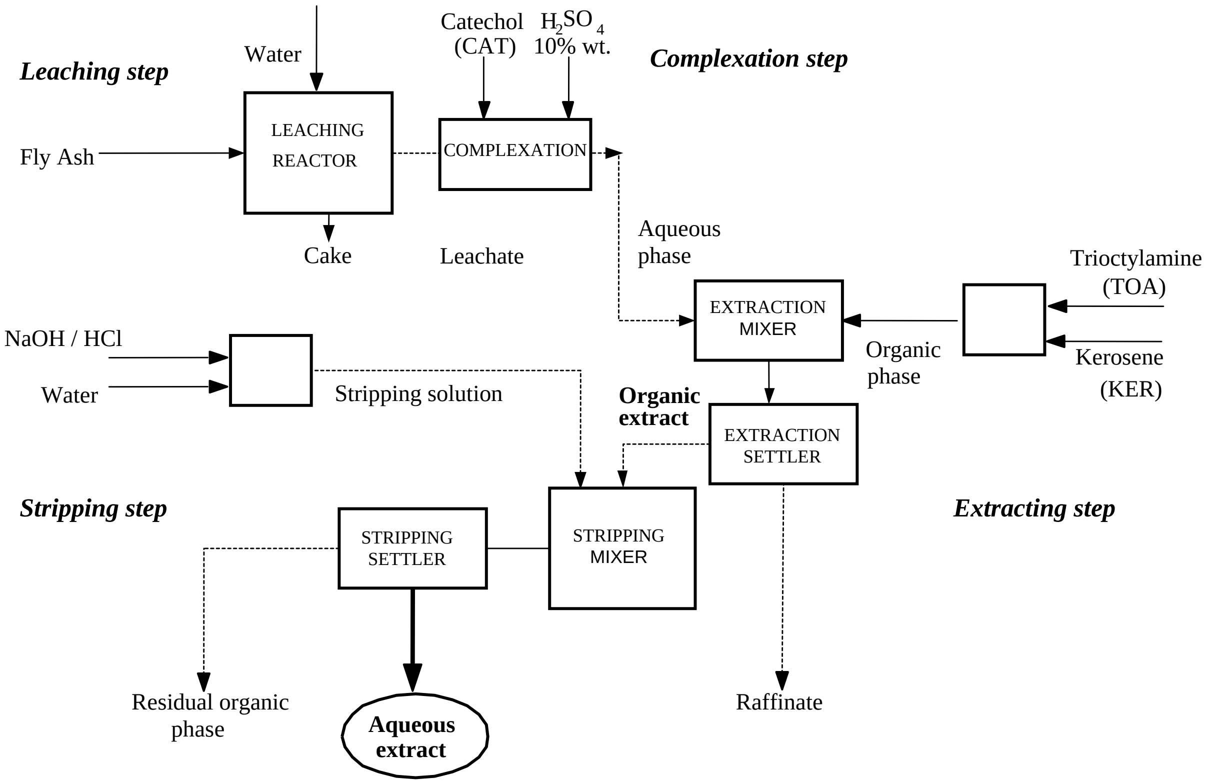

Figure 1. Pilot Plant Flow Sheet Scheme

3. PRELIMINARY MASS BALANCE

The design considered a semi-industrial plant capacity of 200 kg/h of fly ash with a Ge content of 300-400 ppm. In Table 1 the pilot plant and industrial plant preliminary mass balances are shown.

Table 1. Pilot plant and industrial plant preliminary mass balance

Main compounds	Pilot Plant	Industrial Plant
Fly ash	FA: 5 kg·h^{-1}	FA: 200 kg·h^{-1}
Water (W/FA = 5)	W: 25 L·h^{-1}	W: 1000 L·h^{-1}
Leachate	L: 22.4 L·h^{-1}	L: 900 L·h^{-1}
Cake	FA: 5 kg·h^{-1} L: 2.6 L·h^{-1}	FA: 200 kg·h^{-1} L: 100 L·h^{-1}
Aqueous phase	AP: 22.4 L·h^{-1}	AP: 900 L·h^{-1}
Organic phase (AP/OP = 5)	KER: 4.5 L·h^{-1} TOA: 41 mL·h^{-1}	KER: 180 L·h^{-1} TOA: 1.64 L·h^{-1}

Organic extract	KER: 4.5 L·h^{-1}	KER: 180 L·h^{-1}
Raffinate	L: 22.4 L·h^{-1}	L: 900 L·h^{-1}
Stripping phase(OE/SP = 5)	0.9 L·h^{-1}	36 L·h^{-1}
Aqueous extract	0.9 L·h^{-1}	36 L·h^{-1}
Residual organic phase	KER: 4.5 L·h^{-1}	OP: 180 L·h^{-1}

4. EQUIPMENT DESIGN

4.1. EXTRACTION EQUIPMENT

The fertile solution is contacted with the organic phase in the extraction equipment. A mixer-settler cascade was chosen as extraction equipment.[17]

A. Number of stages

The number of stages has been determined graphically from the McCabe-Thiele diagram which 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 germanium 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. The required stages are 3, and the extraction yield achieved is 98%.

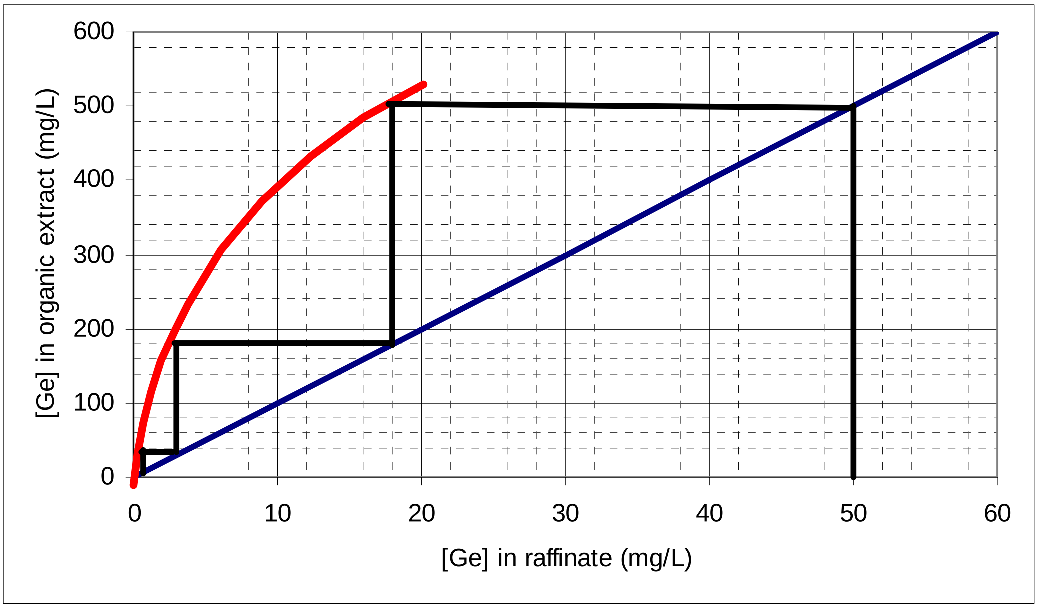

Figure 2. McCabe-Thiele diagram of the extraction system

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 torispherical bottom constructed of stainless steel AISI 316. Taking into account the flows of the aqueous and organic phases (see Table 1), the residence time (5 minutes) and the filling factor (80%), the volume in the mixer is 0.113 m^3 (eq. 3). The volume is defined as the sum of the cylindrical volume and the volume of the bottom (eq. 4). For this kind of reactor, a diameter similar to height is preferred,[18] so the diameter and height of the mixer have both been determined as 480 mm.

$$V = Flow(\frac{m^3}{h}) \cdot residencetime(h) \cdot \frac{1}{filling\ factor} \tag{3}$$

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

Stirring tanks should have baffles to prevent the formation of vortices and to contribute to the contact between phases. Four baffles have been distributed along the perimeter of the tank (cross form). Since the viscosity of the slurry is not very high, the deflectors are standard and they should maintain determined ratios (eq. 5 – 7);[18] therefore, b_w= 48 mm, b_c=8 mm and b_a=24 mm have been calculated for the extraction equipment baffles.

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

$$b_c = 0{,}15 \cdot b_w \tag{6}$$

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

To encourage contact between the two phases, turbine agitators are recommended,[18] so turbine agitators with 6 flat 45º inclined blades were chosen. The recommended geometry of the agitator chosen is:

$$\frac{d_{imp}}{D_V} = 0{,}20 - 0{,}50 \tag{8}$$

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

$$\frac{l_{blades}}{d_{imp}} = 0{,}25 \tag{10}$$

A ratio impeller diameter/tank diameter of 0.33 was selected since for the mixing of immiscible liquids small impellers at high speeds are recommended.[18] According to previous equations, the geometry of the turbine agitator is $d_{imp} = h_{imp} = 160$ mm, and $l_{blades} = 40$ mm. The maximum rotational speed of the impeller can be calculated by eq. 11, where N is expressed in $r \cdot min^{1-}$ and d_{imp} in feet. The N_{max} recommended for this agitator is 120 $r \cdot min^{-1}$. For turbine agitators, in turbulent regime, the power can be calculated as a function of the Newton factor. For the extraction mixer agitator the consumed power is 4 kW.

$$N^3 \cdot d_{impeller}^2 < 20 \qquad (11)$$

C. Settler

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.

Table 2, 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 a ratio Q/A of 4.8 $m^3/m^2 \cdot h$. 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 2. Different widths for different ratio Q/A in settler

Q/A ($m^3/m^2 \cdot h$)	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

4.2. Stripping equipment

A. Number of stages

The graphical representation of the McCabe-Thiele diagram of the stripping system is shown in Figure 4. The required stages are 6, and the stripping yield achieved is 96%. The stripping system chosen is the same as for the extraction equipment. The flow arrangement is counter-current.

B. Mixer

The SP and OP are in a vertical cylindrical mixer with a torispherical bottom constructed of stainless steel AISI 316. For a phase volume ratio of 5, the residence time in the stripping mixer (5 minutes) 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 3-4), the stripping mixer is: D = 300 mm and H = 200 mm high with 4 baffles made of the same stainless steel AISI 316, distributed along the perimeter. A 6 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 4 kW.

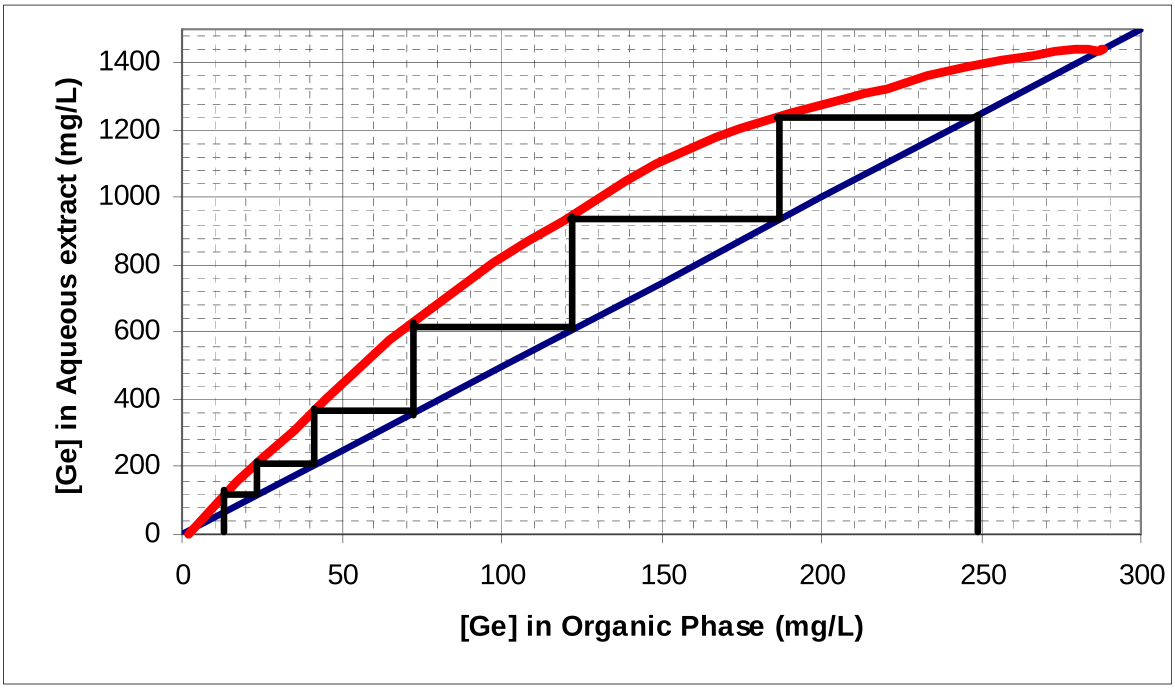

Figure 4. Number of stages of stripping stage

C. Settler

The settler is a parallelepiped constructed of stainless steel AISI 316. Taking into account the same considerations as for the extraction settler, for a flow of 0.2 m^3/h and Q/A of 3.6 m^3/m^2·h, the settler dimensions are: 400 mm (length), 280 mm (height) and 78 mm (width).

5. 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 (I_b) is the sum of the main individual equipment (c_i).

Step 2: Corrections. The cost calculated in step 1 has to be corrected to consider additional costs such as direct and indirect costs. This correcting 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 12.

$$I_{TOTAL} = F_{LANG} \cdot I_b \tag{12}$$

5.1. Estimated cost of main individual equipment. Step 1.

Table 3. Estimated main equipment cost

Equipment	Cost (€)
Extraction equipment	
Mixers	60,000
Settlers	25,000
Stripping equipment	
Mixers	50,000
Settlers	30,000
Ancillary reactors	50,000
Pumps	20,000
Liquid store	70,000
Total	315,000

5.2. Corrections. Step 2

The estimated total investment of the process would be defined as:

$$I_{TOTAL} = (I_b) \cdot (\Sigma f_{dir} \cdot f_{Ind} \cdot f_{fix}) = F_{Lang} \cdot I_b \tag{13}$$

Table 4. Factors for global investment estimation

Direct costs: purchase cost, equipment installation, instrumentation and control devices, pipes, electrical installations, buildings, utilities,...	$f_{dir} = 2.9$
Indirect costs: engineering and supervision, construction costs, legal, expenses, contractors and contingencies	$f_{Ind} = 1.1$
Working Capital	0.8
Total Inversion	$F_{LANG} = 4.8$

So the estimated investment for the semi-industrial implantation is:

315,000·4.8 = 1,512,000 €

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