

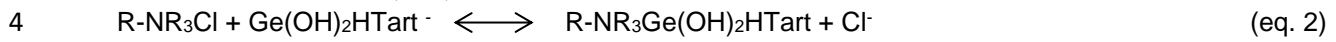
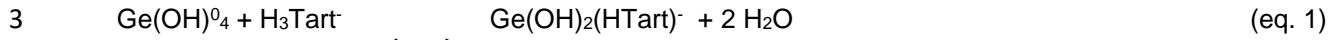
1 complexes with di- and tri-carboxylic acids. For instance, the adsorption of Ge from aqueous solutions on
2 activated carbon impregnated with tartaric, oxalic, and citric acids has been reported in several papers (Kogan
3 and Evdokimov, 1966; Evdokimov and Kogan, 1970), as well as the adsorption of the Ge-catechol complex
4 onto activated carbon (Marco et al, 2006; 2007). Solvent extraction of catechol-, oxalic acid- or tartaric acid-Ge
5 complexes have been reported (Menendez et al, 1989; Arroyo et al, 2008; Liang et al, 2012; Kuroiwa et al,
6 2014; Kamram et al, 2018a). Also, tartaric acid-germanium complexes sorbed onto chelating resins from
7 alkaline solutions have been reported by Chirkst et al. (2008). Recently, the possibility of selective recovery of
8 Ge studying the transport of the Ge-tartaric acid complex from synthetic solutions through supported liquid
9 membranes has been studied by Kamram et al (2018a, 2018b).

10 Another process widely used for Ge recovery from aqueous solutions is precipitation. For instance, Hollness
11 published in 1954 the precipitation of germanium by tannin addition from oxalate solutions, McCroy-Joy (1985)
12 reported the GeO_2 precipitation from oxalate solutions by a electrolytic procedure, Menendez et al (1989)
13 reported the precipitation of polygermanate after a solvent extraction process from tartaric acid solutions and
14 Liang et al (2008) obtained a germanium precipitate by tannin addition from synthetic solutions similar to those
15 obtained in Zn metallurgy processes. Thus, germanium can be precipitated from oxalate solutions adding tannic
16 acid, which forms large floccules easy to filter. In contrast, this precipitate drags some impurities (Schoeller,
17 1932; Holness, 1948). Hilbert (1982) has reported the Ge recovery from Zn bearing solutions by means of tannic
18 acid precipitation in an industrial plant of Bleiberger Bergwerk-Union. According to Liang et al. (2008) in China
19 Ge is produced almost exclusively as by-product of the Zn industry and most of the hydrometallurgical plants
20 are based on the Ge complexation-precipitation with tannic acid. The most recent literature concerning recovery
21 of Ge from secondary sources is addressed to one of the stages of the process here described, such as leaching
22 (Gonzalez et al, 2016; Wei and Lei, 2011) or the following removal or concentration stages (Nusen et al, 2014;
23 Kamram et al, 2018a; Chen et al, 2012, Liu et al, 2010). Also references exist describing a global Ge recovery
24 process (Chen et al, 2017; Liu et al 2017).

25 In previous research works (Arroyo and Fernandez-Pereira, 2010; Arroyo et al, 2011), the germanium retention
26 onto conventional anionic resins was tested from standard solutions and real leachate solutions after previous
27 complexation with catechol. The papers demonstrated the possibility of achieving a selective retention of
28 germanium using conventional anionic resins from aqueous fly ash leachates by adding catechol. However, the
29 proposed procedure has two drawbacks: 1) the catechol amount consumed is high and due to its price, the
30 process could not be commercially competitive, and 2) the amount of process water used (especially in the
31 leaching stage) is also very high, and it could be a handicap for the implementation of the process at an industrial
32 scale. The present study addresses these two problems, replacing catechol by a more accessible and cheaper
33 reagent, such as tartaric acid and studying the possibility of the reintroduction of the raffinate in the process as
34 leaching solution instead of fresh water.

35 Regarding the leaching stage, it must be borne in mind that Ge in fly ash is in the form of germanium oxides
36 and sulphides (Font, 2007) and that, on the other hand, these forms increase their solubility significantly in the
37 presence of citric, oxalic, or tartaric acids (Pokrovski and Schott, 1998). Therefore, the addition of citric, oxalic
38 or tartaric acid to the leaching solution is supposed to increase the Ge leaching efficiency. In the ion exchange

1 (IX) stage, it was considered that Ge in solution and tartaric acid form an anionic complex at pH < 3 according
 2 to equation 1 (Pokrovski and Schott, 1998) and the complex may be retained by anionic resins (eq. 2).



5 Based on this background the present study focused on the evaluation of a global process of Ge recovery from
 6 IGCC FA. For this purpose, each of the stages that comprise the hydrometallurgical process has been studied
 7 within the global process. Firstly, the leaching procedure was evaluated comparing the Ge extraction yield using
 8 tartaric acid solutions and the IX raffinates as leaching agents. In a second stage, the possibility of recovery the
 9 Germanium-tartaric complex from the leachates employing commercial anionic resin was evaluated, and finally,
 10 the precipitation of a germanium bearing solid was tested using tannic acid as precipitation agent.

11

12 **2. Experimental**

13 **2.1. Materials**

14 All reagents were analytically pure and used without further purification. IRA-900 in chloride form (from Rohm-
 15 Haas) was chosen according to a previous published work (Arroyo et al, 2010). IRA-900 is a macroreticular
 16 strongly basic quaternary ammonium resin, with a total exchange capacity of 1 eq L⁻¹. Particle size is in the
 17 range 16-50 mesh (US std screens) and pore sizes are sufficiently large to absorb the germanium-tartaric acid
 18 complex.

19 Fly ash was produced in Puertollano IGCC power plant in 2009. An exhaustive characterization of IGCC fly ash
 20 has been carried out and the results have been published elsewhere (Font et al, 2001; Font et al, 2005; Aineto
 21 et al, 2006) in which the main chemical characteristics, granulometry and mineral composition by XRF-diffraction
 22 and scanning electronic microscopy using energy dispersive X-ray analyser (SEM-EDX) of the fly ash used in
 23 this study are shown. Main chemical components of the fly ash used in the present study (wt %) are: SiO₂ (59.3),
 24 Al₂O₃ (20.6), Fe₂O₃ (4.2), K₂O (3.5), CaO (3.2), SO₃ (2.4), and MnO (0.04). Ge content in this fly ash is 420 mg
 25 kg⁻¹. The content of fly ash in other minor components contents are shown in Table 1.

26

27 Table 1. Minor components of FA (mg kg⁻¹)

As	955	Co	53	Ga	320	Pb	4796	Sn	67
Ba	433	Cr	155	Mo	135	Sb	381	V	6256
Cd	24	Cu	392	Ni	2296	Se	19	Zn	7230

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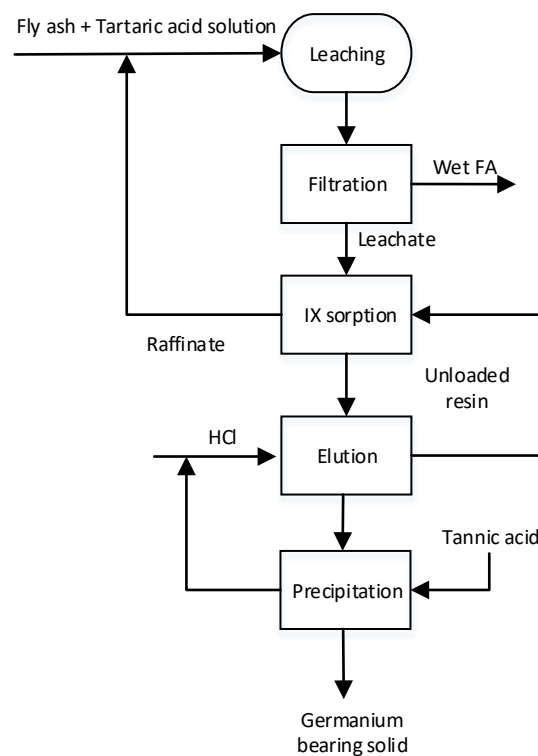
29 **2.2. Process**

1 The process proposed consists of four stages: leaching, sorption, elution and precipitation (Figure 1). Because
2 the two first stages (leaching and sorption-IX) are interdependent, firstly, the possibility of retaining the
3 germanium tartaric acid complex by conventional anionic ion exchange resins was confirmed from standard
4 solutions. A parametric study was performed to optimize the Ge retention onto the resins. Once optimal
5 conditions were determined, the possibility of eluting Ge from resin was investigated. In a second phase the
6 possibility of leaching fly ash using the raffinate from the IX step was checked. After checking each phase
7 separately, the global process was performed.

8 2.3. Leaching Procedure

9 Leachates were obtained by contacting coal fly ash with different leaching solutions at room temperature. The
10 leaching procedure was performed in 500 mL agitated flasks at 20°C. The liquid/solid ratio was chosen to be 5
11 and contact time was varied throughout the study. The leaching agent was aqueous solutions containing tartaric
12 acid and raffinate from the ion exchange step. Tartaric acid content and pH were varied through the study. pH
13 adjustment were performed adding 1M H₂SO₄ to solutions. After the required contact time, fly ash and leachates
14 were separated by filtration through a membrane filter (0.45 μm), and the filtrates were analysed for element
15 contents by inductively coupled plasma-mass spectrometry (ICP-MS), model VG PLASMAQUAD PQ2.

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20 2.4. Ion-Exchange Procedure

21 All experimental tests were performed using a batch technique. In each experiment, 50 mL of pregnant solutions
22 (containing [Ge]₀ = 70 mg L⁻¹) were placed in 100 mL flasks and maintained in contact with the resins for 24h at

1 25°C using a rotary shaker. Different fertile solution/resin ratios were used throughout the study. When
 2 necessary, pH adjustments were performed adding 1M HCl to solutions. After the contact, the pregnant resin
 3 and solution (raffinate) were separated by filtration through a membrane filter (0.45 µm). Raffinate was analysed
 4 for Ge content. A mass balance gave the germanium retained in resin, and from it the Ge retention efficiency
 5 (E, in %) and the loading capacity (Q, in mg g⁻¹) were calculated according to eq. 3 and eq. 4 respectively. The
 6 resins were washed with doubly distilled water before the eluting stage in which pregnant resins and eluting
 7 solution were contacted as in the sorption stage. Different volume ratios were studied for the selected desorption
 8 solution. A mass balance was performed to obtain the eluted metal. The efficiency of eluting (S, in %) is defined
 9 in eq. 5.

$$E(\%) = \frac{(C_o - C_e)}{C_o} \cdot 100 \quad (\text{eq. 3})$$

$$Q \left(\frac{\text{mg}}{\text{g}}\right) = \frac{(C_o - C_e) \cdot V}{W} \quad (\text{eq. 4})$$

$$S(\%) = \frac{C_s}{C_s^*} \cdot 100 \quad (\text{eq. 5})$$

13 In the above equations Co and Ce (mg L⁻¹) are the initial and equilibrium germanium concentrations in the
 14 leachate and raffinate, respectively; Cs is the germanium content of eluting solution (mg L⁻¹); C*s is the
 15 equivalent germanium content of resin (calculated by mass balance in retention step); V (L) is the volume of
 16 solution and W (g) is the resin mass.

17 Conventional methods of experimentation do not depict the combined effect of all factors involved and do not
 18 assure the determination of optimal conditions, but these limitations can be avoided by using a properly
 19 statistical technique for designing experiments such as response surface method (RSM). In this study RSM
 20 based on a five-factor level, two-level factorial central composite rotatable design (CCRD) was employed. CCRD
 21 is a standard factorial design (2k), increased by 2k axial points (± α, 0, 0, ..., 0), (0, ± α, 0, ..., 0), (0, 0, 0, ..., ±
 22 α), and n_c centre points (0, 0, ..., 0). The software Stat-Ease Design-Expert (version 9.0.6.2) was used for
 23 experimental design and response surface design and analysis of IX results. The general design of the trials to
 24 be conducted is expressed in coded terms for statistical calculations. To analyse the interaction between the
 25 parameters, a 1-replicate 5 factor level and 3 factors central composite rotatable design (CCRD) with 20
 26 experiments was employed for optimization of germanium retention with respect to pH, fresh tartaric acid
 27 dosages (TA) and resin dosages (R).

28 The space of interest was defined by pH (0.5 – 2.5), fresh TA dosages (1 – 4 g L⁻¹) and resin dosages (0.8 – 5
 29 g L⁻¹) that were tested on standard solutions. Resin and TA lowest values of the ranges are based on
 30 stoichiometric ratios and the highest values are based on preliminary experiments and manufacturer
 31 recommendations. The lowest pH value was selected according to the results published by Menendez et al
 32 (1989) that reported the highest stability of tartaric acid-Ge complex occurring at pH near 1. The highest limit
 33 was set considering that the Ge-tartaric complex is formed stably at pH < 3 (eq. 1; Pokvroski and Schott, 1998).
 34 The pHs of the IGCC FA leachates obtained with different TA-containing aqueous solutions as leaching agents
 35 were measured and they were in the range of pH = 1-3.

36 The experimental data obtained in the tests were fitted by a polynomial equation. The predicted responses in
 37 the model are retention and capacity. Description of both is analogous. The quality of the fit polynomial model

1 was expressed by R^2 and its statistical significance was examined by the F-test. The models obtained from the
 2 RSM methodology predicted the optimum Ge retention conditions. To make predictions or determine the relative
 3 impact of factors in the response value, the equation in coded terms is preferred, and it is easier to handle
 4 mathematically, as it works in the same range $[-\alpha, \alpha]$ for all the factors. Table 2 shows the design matrix in which
 5 the variables, the coded levels used and the actual values are given. The general design of the trials to be
 6 conducted is expressed in coded terms for statistical calculations (equations 6-8).

$$7 \quad \text{pH}_{\text{cod}} = \frac{\text{pH}_{\text{actual}} - \frac{(2.5+0.5)}{2}}{0.5946} \quad (\text{eq. 6})$$

$$8 \quad \text{TA}_{\text{cod}} = \frac{\text{TA}_{\text{actual}} (\text{g L}^{-1}) - \frac{(4+1)}{2}}{0.8919} \quad (\text{eq. 7})$$

$$9 \quad \text{R}_{\text{cod}} = \frac{\text{R}_{\text{actual}} (\text{g L}^{-1}) - \frac{5+0.8}{2}}{1.2487} \quad (\text{eq. 8})$$

10
11
12
13

Table 2. Design Matrix Evaluation for Response Surface Model

Designed experiments							Experimental results	
Test	pH coded	TA coded	R coded	pH actual	TA actual (g L ⁻¹)	R actual (g L ⁻¹)	E (%)	Q (mg g ⁻¹)
1	1	1	1	2.1	3.4	4.1	99.2	1.7
2	1	1	-1	2.1	3.4	1.7	89.4	3.7
3	1	-1	1	2.1	1.6	4.1	99.3	1.7
4	-1	1	1	0.9	3.4	4.1	62.5	1.1
5	1	-1	-1	2.1	1.6	1.7	90.9	3.7
6	-1	-1	1	0.9	1.6	4.1	73.3	1.3
7	-1	1	-1	0.9	3.4	1.7	60.0	2.5
8	-1	-1	-1	0.9	1.6	1.7	58.7	2.4
9	1.6818	0	0	2.5	2.5	2.9	98.1	2.4
10	0	1.6818	0	1.5	4.0	2.9	88.5	2.1
11	0	0	1.6818	1.5	2.5	5.0	96.3	1.3
12	-1.68188	0	0	0.5	2.5	2.9	64.1	1.5
13	0	-1.6818	0	1.5	1.0	2.9	95.9	2.3
14	0	0	-1.6818	1.5	2.5	0.8	57.1	5.1
15	0	0	0	1.5	2.5	2.9	97.6	2.4
16	0	0	0	1.5	2.5	2.9	95.1	2.3
17	0	0	0	1.5	2.5	2.9	95.1	2.3
18	0	0	0	1.5	2.5	2.9	97.7	2.4
19	0	0	0	1.5	2.5	2.9	97.6	2.4
20	0	0	0	1.5	2.5	2.9	97.9	2.4

14

1 **3. Results and discussion**

2 **3.1. Germanium retention from standard solutions by IX**

3 The experimental efficiencies and loading capacities of Ge retention onto IRA-900 (E_{Ge} in % and Q_{Ge} in $mg\ g^{-1}$,
 4 respectively) are given in Table 2. It is worth noting that high Ge retention efficiencies were achieved in all tests,
 5 being most of them > 90%. Therefore, this method is suitable to recover Ge from dilute standard solutions.
 6 Design-expert software computed the terms of the models that correlate each response surface with pH, tartaric
 7 acid dosage and used resin in coded and actual terms. The statistical significance of models was checked by
 8 an F-test and the analysis of variance (ANOVA) and it is summarized in Table 3. The efficiency model F-value
 9 of 15.24 implies the model obtained for E_{Ge} is significant; and there is less than 0.01% chance that an F-value
 10 this large could occur to uncontrollable variations from the inputs. The same can be said for the model obtained
 11 for Q_{Ge} (F-value of 38.03 and 0.07% in the case of Q_{Ge} model). The complete mathematical models (in coded
 12 terms) are shown in equations 9 and 10 (terms in grey in Table 3 were not significant).

13 $E_{Ge} (\%) = 96.93 + 13.23 \cdot pH_{act} - 1.71 \cdot TA_{act} + 7.65 \cdot R_{act} - 6.37 \cdot pH_{act}^2 - 2.45 \cdot TA_{act}^2 - 7.86 \cdot R_{act}^2 + 0.97 \cdot pH_{act}$
 14 $\cdot TA_{act} + 0.14 \cdot pH_{act} \cdot R_{act} - 1.38 \cdot TA_{act} \cdot R_{act}$ (eq. 9)

15 $Q_{Ge} (\%) = 2.37 + 0.37 \cdot pH_{act} - 0.032 \cdot TA_{act} - 0.94 \cdot R_{act} - 0.19 \cdot pH_{act}^2 + 0.25 \cdot R_{act}^2 - 0.1 \cdot TA_{act}^2 + 0.013 \cdot pH_{act} \cdot TA_{act} -$
 16 $0.19 \cdot pH_{act} \cdot R_{act} - 0.037 \cdot TA_{act} \cdot R_{act}$ (eq. 10)

17

18 Table 3. Statistical significance of model (F-test), Analysis of variance (ANOVA), Coded terms and Effect of
 19 each factor

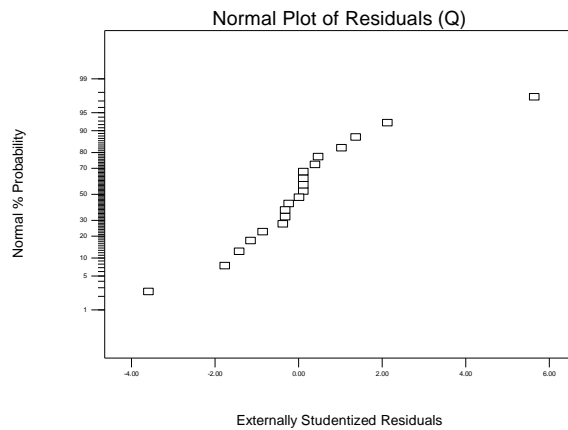
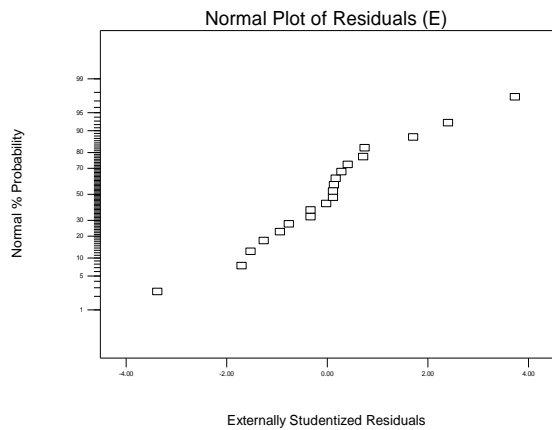
Model of E_{Ge}	Sum of Squares	df	Mean Square	F Value	p-value (Prob > F)
	4571.40	9	507.93	15.24	0.0001
pH	2415.90	1	2415.90	72.48	< 0.0001
TA	40.51	1	40.51	1.22	0.2961
R	764.26	1	764.26	22.93	0.0007
pH·TA	7.80	1	7.80	0.23	0.6390
pH·R	0.15	1	0.15	$4.538 \cdot 10^{-3}$	0.9476
TA·R	14.31	1	14.31	0.43	0.5271
pH²	588.34	1	588.34	17.65	0.0018
TA²	86.86	1	86.86	2.61	0.1375
R²	863.62	1	863.62	25.91	0.0005
Residual	333.33	10	33.33		
Lack of Fit	324.25	5	64.85	35.74	0.0006
Pure Error	9.07	5	1.81	15.24	
Std. Dev.	5.77	Mean	85.72	Adeq. Precision	11.503
R-Squared	0.9320	Adj. R-Squared	0.8709	Pred. R-Squared	0.4771
Model of Q_{Ge}	Sum of Squares	df	Mean Square	F Value	p-value (Prob > F)
	16.18	9	1.80	38.03	< 0.0001

pH	1.84	1	1.84	39.02	< 0.0001
TA	0.014	1	0.014	0.29	0.6001
R	12.24	1	12.24	259.04	< 0.0001
pH-TA	$1.25 \cdot 10^{-3}$	1	$1.25 \cdot 10^{-3}$	0.026	0.8740
pH-R	0.28	1	0.28	5.95	0.0349
TA-R	0.011	1	0.011	0.24	0.6361
pH²	0.49	1	0.49	10.28	0.0094
TA²	0.13	1	0.13	2.75	0.1282
R²	0.96	1	0.96	20.32	0.0011
Residual	0.47	10	0.047		
Lack of Fit	0.46	5	0.092	34.45	0.0007
Pure Error	0.013	5	$2.667 \cdot 10^{-3}$		
	16.65	19			
Std. Dev.	0.22	Mean	2.35	Adeq. Precision	23.455
R-Squared	0.9716	Adj. R-Squared	0.9461	Pred. R-Squared	0.7823

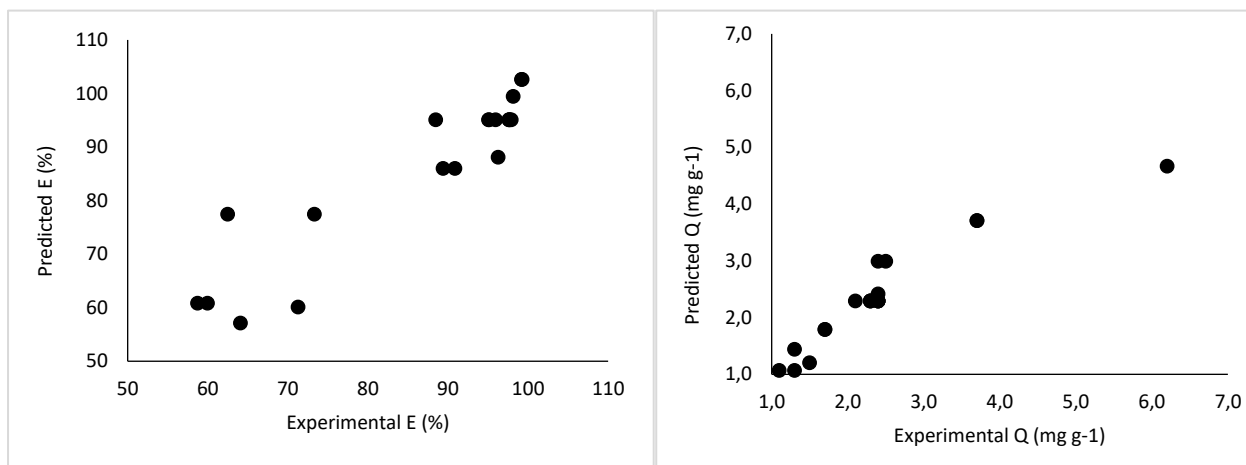
1 The adequate precision of the model measures the signal to noise ratio and the value allows quantifying the
2 range of the predicted signals relative to fluctuations that are outside experimental control. The adequate
3 precision of the model can be seen as well in the normal probability plot of the residuals (Figure 2). When a
4 normal probability of the residuals is plotted it can be seen that the relationship between the theoretical
5 percentiles and the sample percentiles is approximately linear. Therefore, the normal probability plot of the
6 residuals suggests that the error terms are indeed normally distributed.

7 The calculated ratios for the modified models (Table 3) are 11.503 (E_{Ge}) and 23.455 (Q_{Ge}) indicating an
8 adequate signal for both models. It means that the models can be used to navigate the design space. The high
9 values of correlation factors demonstrated the close agreement between the experimental factor and the
10 mathematical model but the lack of fit is significant (<0.05). A comparison between experimental and predicted
11 values for efficiency and capacity models was performed (Figure 2) and a good fit between both kind of values
12 and no bias were observed.

13



1



2

3 Figure 2. Normal plots of residuals (top) and predicted and actual values of E_{Ge} (left) and Q_{Ge} (right)

4

5 The relationship between the dependent and independent variables was studied using response surface and
 6 contour plots as shown in Figure 3 and the following conclusions can be extracted: the initial pH and resin were
 7 the most influencing variables to E_{Ge} and Q_{Ge}. The influence of both factors on E_{Ge} is positive in both cases.
 8 However, in the case of Q_{Ge} the higher resin addition, the lower loading capacity. The pH affects positively on
 9 Q_{Ge}. The effect of the tartaric addition in the studied range is not very strong for E_{Ge} neither Q_{Ge}.

10

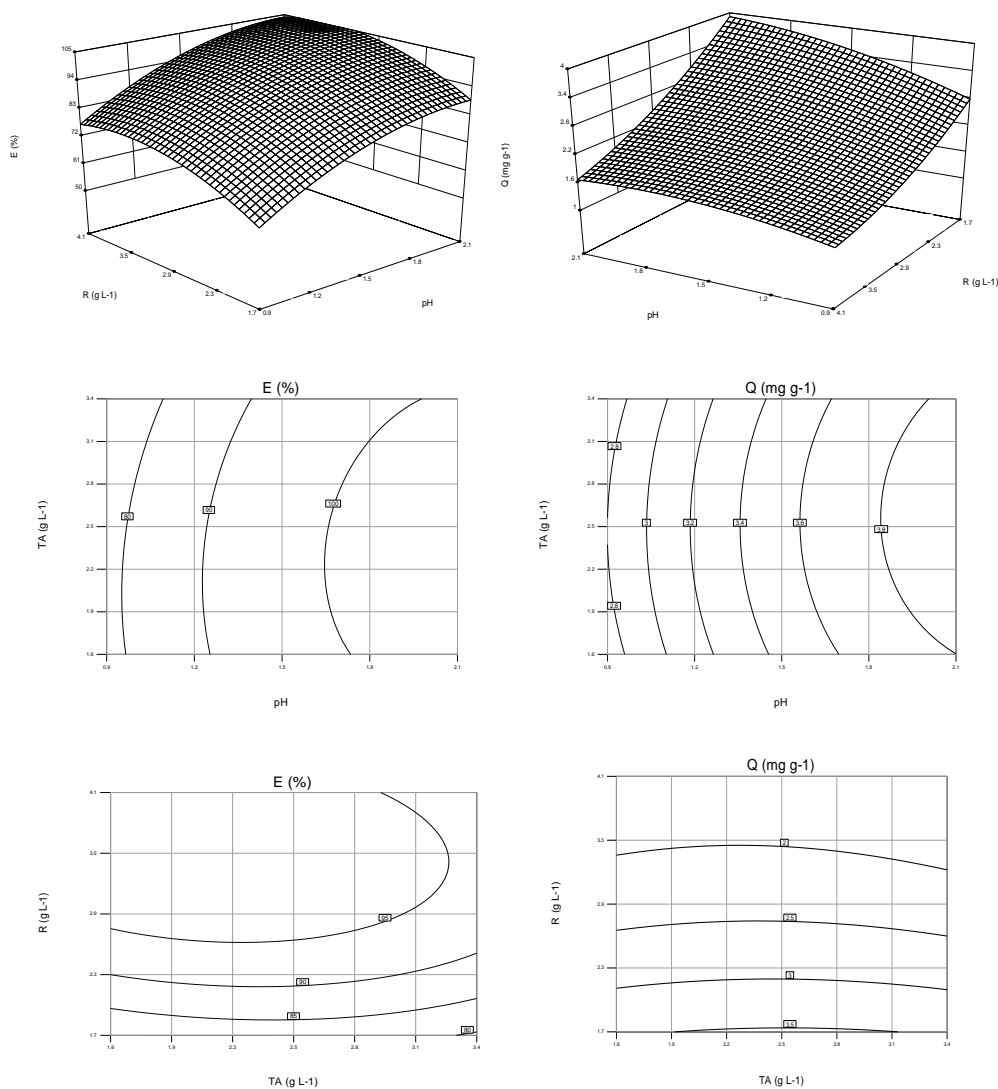


Figure 3. Response surface and contour plots for Ge retention (left) and resin capacity (right)

Using the ANOVA program, the optimum Ge retention efficiency onto IRA-900 resin and loading capacity can be combined into a general function of desirability. There may be two or more maxima due to the curvature in the response surfaces and their combination in function of convenience. The set targets were: minimizing the TA and resin dosages; and maximizing pH and Ge retention efficiency. The results generated by the program indicated that the optimum ranges are: resin IRA-900 = 2-2.5 g L⁻¹, pH = 2-2.5 and TA = 1.6 – 2.0 g L⁻¹. With these conditions, the predicted efficiency and loading capacity were 90-98% and 3.0-3.5 mg g⁻¹. These conditions were considered for the real leachates experimental study.

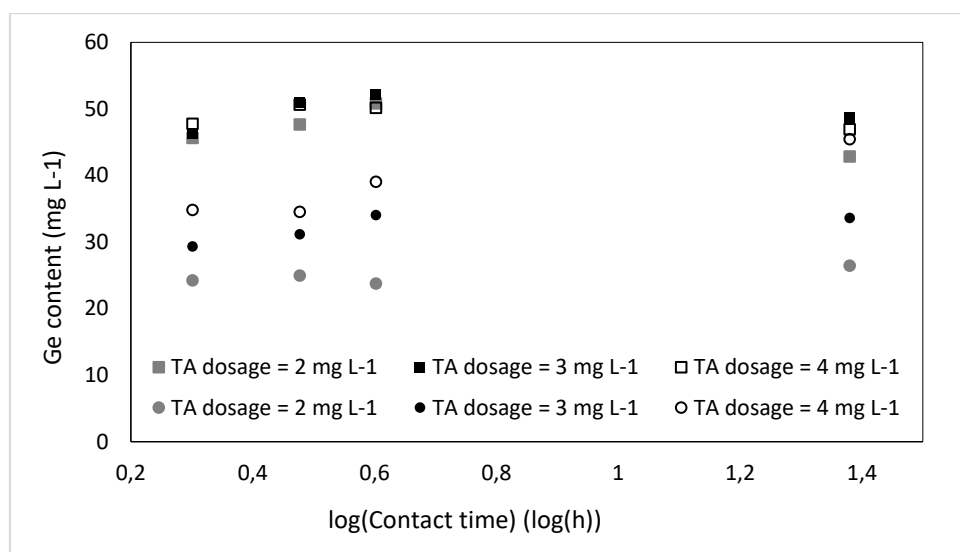
3.2. Fly ash leaching using fresh TA solutions and subsequent Ge retention onto IRA-900

In a first set of experiments, the leaching of Ge with aqueous solutions containing tartaric acid (2, 3 and 4 g L⁻¹) was investigated with acid addition (pH=1.00) and without acid addition (pH= 2.65-2.67) at different leaching times (2, 3, 4 and 24 h) (Figure 4). In the tests without pH adjustment, best leaching yields were achieved for

1 the highest tartaric acid content (4 g L^{-1}) after 24 h of contact. For $\text{pH} = 1$, leaching yields are higher and are
 2 achieved more quickly than without pH adjustment. The greatest portion of Ge was leached after 2h of contact,
 3 achieving the maximum after 3h. In this case, the effect of tartaric acid addition is negligible.

4 In a second set of leaching experiments (Table 4), three leaching experiments were performed at room
 5 temperature and $\text{L/S} = 5$. Investigated leaching solutions were TA solutions (TA dosage of 3 g L^{-1}) at different
 6 initial pH s (ranging 1-2). Contact time was 3h in the three experiments. The better performance was achieved
 7 at $\text{pH} = 1$. The pH of leachate after contact (Table 4) is close to the optimum for IX (following step in the process)
 8 determined in section 3.1.

9



10

11 Figure 4. Leaching experiments of FA with TA solutions (squares: experiments with acid addition; circles:
 12 experiments without acid addition)

13

14 Table 4. Set of leaching experiments with TA solutions at initial $\text{pH} = 1-2$ (3 h of contact and TA dosage of 3 g
 15 L^{-1})

Initial pH (leaching solution)	Final pH (leachate)	Ge content (mg L^{-1})
1.02	2.12	53.5
1.49	3.53	52.5
2.06	4.46	43.9

16

17 In addition to Ge, other potentially interfering elements that are also leached are As, Ni, Zn and Sb. The rest of
 18 elements in FA are only present in leachates in negligible amounts. Table 5 shows the content of elements
 19 present in the leachate obtained with the TA solution at initial $\text{pH} = 1.02$ (best performance experiment from
 20 those described in Table 4).

21

1 Table 5. Composition of leachate used in IX tests (Initial pH: 1.02, Ge: 53.5 mg L⁻¹)

	Content (mg L ⁻¹)		Content (mg L ⁻¹)
As	56.0	Ni	286.0
B	13.4	Sb	62.3
Co	2.4	Sn	5.4
Mo	2.2	V	80.1
Mn	4.4	Zn	562

2

3 Following the designed process, the retention of the Ge-tartaric acid complex present in FA leachates onto IRA-
 4 900 resin was investigated as described in Table 6. According to the results obtained in section 3.1, as the
 5 influence of tartaric acid addition on the retention efficiency of the complex onto the IRA-900 resin is low, no
 6 fresh tartaric acid was added in the IX step. The analysis of the influence of pH for the IX step in the case of
 7 real leachates was conducted around the optimum obtained for synthetic solutions. The best results were
 8 achieved when the pH of the pregnant solution was 2, but quite similar values were obtained for initial pH = 2.5.
 9 The results also show that the higher the value of resin dosage the higher the retention efficiency.

10

11 Table 6. Ion exchange tests with IRA-900 and real FA leachates

		pH of loaded solution		
		1.5	2.0	2.5
Resin dose	2.5 g L ⁻¹	Ge content = 18.3 mg L ⁻¹ pH of raffinate = 1.6	Ge content = 9.5 mg L ⁻¹ pH of raffinate = 2.1	Ge content = 9.2 mg L ⁻¹ pH of raffinate = 2.9
	4.1 g L ⁻¹	Ge content = 10.4 mg L ⁻¹ pH of raffinate = 1.6	Ge content = 3.7 mg L ⁻¹ pH of raffinate = 2.1	Ge content = 6.4 mg L ⁻¹ pH of raffinate = 2.9

12

13 In the retention tests of real leachates, the maximum retention of the Ge-TA complex was 93% when the pH of
 14 the pregnant solution was adjusted to 2 and 4.1 g L⁻¹ or resin was added to solutions. Under these conditions,
 15 retention yields of other elements present in high concentrations (Zn, Ni, V, Sb, As and Sb) are lesser than the
 16 Ge retention yield (Table 7). Sb retention yield is lower than 80%, V yield lower than 40% and Zn yield lower
 17 than 5%. As is not extracted at pH=2, and Ni does it only partially. Equilibrium distribution values were calculated
 18 for the retention onto IRA-900 (as defined in eq. 11) for comparative analysis of IX affinities. The highest K_D
 19 value was determined for Mo, but the content of Mo in leachate is very low, so that Mo was not considered an
 20 important interference in the proposed method. Based on the equilibrium distribution, the experimental affinities
 21 shown by Ge and main interferences for IRA 900 were: Ge >> Sb > V > Ni > As > Sn > B > Zn.

22
$$K_D = \frac{Q_e}{C_e} \quad (\text{eq. 11})$$

23

24 Table 7. Composition of raffinate composition and equilibrium distribution values after retention onto IRA-900

Ge: 3.7 mg L⁻¹, pH: 2.06; K_D = 3.28					
	Content (mg L⁻¹)	K_D		Content (mg L⁻¹)	K_D
As	47.3	0.045	Ni	209.0	0.09
B	12.5	0.018	Sb	13.0	0.93
Co	2.4	0	Sn	4.7	0.036
Mo	<0.1	5.12	V	49.8	0.15
Mn	4.4	0	Zn	548	0.006

1

2 3.3. Eluting tests

3 Equal aliquots of pregnant resin were contacted with different eluting solutions as in the sorption stage (Table
4 8). 2M, 3M and 4M HCl solutions were used to elute germanium from the resin. After the contact, stripping
5 solutions were separated of resin by filtration for subsequent analysis. Eluting Ge efficiency was calculated by
6 mass balance.

7 As can be seen, high eluting yields were obtained using 2M, 3M or 4M HCl. The lower volume of eluting solution
8 was used the higher Ge concentration was reached in the final stripping solution and the lower consumption
9 and cost of reagents. However, the yield decreased when low eluting solution/leachate volume ratios were used.

10

11 Table 8. Eluting experiments

Stripping solution/leachate ratio (vol/vol)	HCl (M)	Ge in stripping solution (mg L⁻¹)	Stripping efficiency (%)
1	4M	44.7	95
1	3M	45.1	96
2.5	2M	17.2	98
1.5	2M	28.7	96
1	2M	46.0	97
0.5	2M	89.8	97
0.25	2M	151.2	86

12

13 The stripping solution obtained with 2M HCl using a volumetric ratio of 0.5 was analyzed (Table 9) and, apart
14 from the Ge enrichment, the results also confirmed the presence of important amounts of Sb and V. On the
15 other hand, a mass balance allowed detecting that only a low percentage of the Ni retained by the resin was
16 eluted.

17

18

19 Table 9. Stripping solution composition

<i>Ge: 89.8 mg L⁻¹</i>

	Content (mg L ⁻¹)		Content (mg L ⁻¹)
As	4.4	Ni	0.2
B	1.3	Sb	84.3
Co	<0.1	Sn	<0.1
Mo	4.2	V	60.2
Mn	<0.1	Zn	0.4

1

2 3.4. Germanium precipitation

3 The possibility of achieving a selective germanium precipitation from the stripping solution was tested adding
4 different amounts of tannic acid to equal volumes of the stripping solution as described in Table 10. Precipitation
5 was performed at natural pH of stripping solution, but two different pHs were also tested: 1 and 1.26. Samples
6 were stood at room temperature overnight. Precipitates were filtered and a liquid sample was taken for analysis.
7 The germanium precipitation yield was determined by mass balance (Table 10). The lower the mass of tannic
8 acid added, the lower the precipitation yield obtained. At the natural pH of stripping solution, when 8.3 g of tannic
9 acid per g of Ge were added, 98.7% of Ge was precipitated from the stripping solution (test 4 solution in Table
10 10). 20% of V also precipitated along with Ge but the rest of elements (As, B, Sb, Mo and Zn) practically
11 remained in solution (Table 11).

12

13 Table 10. Precipitation experiments

Test	Tannic acid mass (mg) per 100 mL of stripping solution	pH	Ge precipitation yield %
1	125	1.26	-
2	125	1	1.0
3	125	Natural (< 0)	99.3
4	75	Natural (< 0)	98.7
5	25	Natural (< 0)	65.5
6	15	Natural (< 0)	31.6

14

15 Table 11. Composition of stripping solution after precipitation with tannic acid (from test 4 shown in Table 10)

<i>Ge: 0.6 mg L⁻¹</i>			
	Content (mg L ⁻¹)		Content (mg L ⁻¹)
As	2.0	Ni	0.2
B	1.3	Sb	84.5
Co	<0.1	Sn	<0.1
Mo	4.0	V	48.2
Mn	<0.1	Zn	0.4

16

1 **3.5. Recycling IX raffinate**

2 The reuse of raffinates from the IX stage has two objectives: reducing the necessity of water in the process and
3 costs of wastewater treatment and reintroducing in the process the not-retained Ge and the tartaric acid
4 remaining in solution. Six different leaching solutions were obtained mixing the raffinate described in Table 7
5 and fresh 3 g L⁻¹ tartaric acid solutions in different proportions (Table 12). The used raffinate contained 3.7 mg
6 L⁻¹ of Ge and its pH was 2.06. After mixing the raffinate and fresh TA solutions, the pH was adjusted to 1 (the
7 optimum pH determined in section 3.2) with H₂SO₄. Leaching tests were performed as explained in section 2.1
8 at room temperature, with L/S = 5 and contact time = 3h.

9 The use of raffinate improves the Ge recovery as compared to the use of a fresh TA solution because the former
10 contains the Ge not retained in the IX stage. Moreover, the reason could also be related to the presence of a
11 certain amount of chloride in raffinate coming from the HCl addition employed to adjust the pH before the IX
12 step and the release of Cl produced by the resin exchange. According to the literature (Thomas, 2001; Wang
13 et al, 2011) chloride can play a role favouring the solubilization of the Ge oxides and sulphides present in fly
14 ash. In practical operation a portion of raffinate is retained by fly ash, so that a certain amount of fresh leaching
15 solution has to be added. In tests of Ge recovery carried out at pilot plant scale (Arroyo, 2010), the average
16 amount of leachate impregnating FA which was purged from the system after the leaching stage was estimated
17 in 15%.

18

19 Table 12. Leaching tests using raffinate

Ratio raffinate/fresh TA solution	Leachate pH	Ge contents in leachate (after recirculation) (mg L ⁻¹)
100/0 (pure raffinate)	1.85	72.8
90/10	1.79	68.7
80/20	1.81	62.5
70/30	1.76	63.9
0/100 (fresh TA solution)	1.65	54.6

20

21 **4. Conclusions**

22 The global process designed for the Ge recovery from IGCC fly ash comprised the following steps:

23 **Leaching**

24 Germanium can be recovered from fly ash putting in contact the solid with a pH = 1 leaching solution containing
25 tartaric acid (L/S = 5) for 3h at room temperature in an agitated vessel. Raffinate from IX retention stage can be
26 recycled as leaching solution. A leachate with a Ge content of 72 mg L⁻¹ can be recovered (86%).

27 Reuse of raffinate from IX has two objectives: reducing the necessity of water in the process and therefore
28 decreasing costs of wastewater treatment, and also making economies by reintroducing the not-retained Ge
29 and any tartaric acid present in solution. In addition to Ge, other elements potentially interfering that are also
30 leached are As, Ni, Zn and Sb. Other elements in FA are not released in significant amounts. The pH of leachate

1 was close to the optimal for the subsequent IX stage, so that minimal pH adjustment would be necessary in the
2 IX stage.

3 **Ion-exchange**

4 In this step, the most influencing variable is pH. For achieving an optimum Ge retention pH should be 2-2.5.
5 Addition of fresh tartaric acid is not necessary in this step. When Ge standard solutions were used almost 100%
6 of the Ge-tartaric complex was retained by IRA-900, but when real leachates were tested, maximum retention
7 was 93% due to the competitive effect of interferences. The experimental affinities shown by IRA-900 for Ge
8 and main interferences were: Ge >> Sb > V > Ni > As > Sn > B > Zn.

9 When 2M, 3M or 4M HCl solutions were used eluting yields higher than 95% were obtained, for eluting
10 solution/pregnant solution ratios equal or higher than 1. The lower the volume of eluting solution used the higher
11 the Ge concentration reached in the final stripping solution and the lower consumption and cost of reagents.
12 However, the yield decreased by using low volumes of eluting solution. The final (stripping) solution is enriched
13 in Ge, but also contains significant amounts of Sb and V. On the other hand, it has been demonstrated that a
14 high percentage of Ni is retained in the resin and has not been eluted.

15 **Precipitation**

16 Although there are many precipitation systems available for Ge precipitation, in this case, tannic acid was
17 studied, achieving a Ge precipitation yield of 98.7% (for natural pH of stripping solution and 8.3 g of tannic acid
18 per g of Ge). Practically the rest of elements remained in solution with the exception of V, for which a 20% was
19 precipitated. Vanadium can be removed from wastewaters using methods such as precipitation, adsorption or
20 solvent extraction (Guan et al, 2014; Leiviska et al, 2017; Wang et al, 2016; Cadaval et al, 2016; Su et al, 2018;
21 Shi et al, 2017). Some of them must be tested before precipitation to avoid the contamination of the final Ge
22 solid concentrate.

23 Further research includes improving the purity of the final Ge product mainly decreasing its vanadium content
24 through a previous removal step, optimizing the consumption of water and reagents in the process by means
25 of the raffinate recycling in the leaching stage and finally considering the treatment of the wastewater produced,
26 with the aim of minimizing the global environmental impact of the process.

27 In conclusion, the experimental findings of this research indicate that germanium can be selectively recovered
28 from IGCC-fly ash using an integrated process with a low environmental impact achieving a theoretical global
29 yield of 70%. A complete Ge recovery process as the one described in this paper, from coal fly ash to a solid
30 Ge concentrate, in which the leaching of the ash is carried out a room temperature without using any organic
31 solvent and in which the IX raffinates is used as leaching agent, has interest and can contribute to the
32 development of the production of Ge from secondary sources.

33

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