Suggested Citation format for this article:

Arroyo, F., Fernández-Pereira, C., Coca, P., 2010, Precipitation of Germanium from Coal Fly Ash Leachates. *Coal Combustion and Gasification Products* 2, 28-34, doi: 10.4177/CCGP-D-09-00021.1

Precipitation of Germanium from Coal Fly Ash Leachates

Fátima Arroyo[1], Constantino Fernández-Pereira[1,*], Pilar Coca[2]

[1] University of Seville, School of Engineering, Chemical and Environmental Engineering Department, Camino de los Descubrimientos, Seville (Spain), phone: 011-034-95-448-1379, fax: 011-034-95-448-6082, E-mail: pereira@esi.us.es
[2] ELCOGAS S.A., 13500 Puertollano, Ciudad Real, Spain

A B S T R A C T

The valorization of a coal gasification fly ash was studied by leaching the fly ash using different aqueous solutions followed by the subsequent precipitation of the germanium solubilized from the ash. Experimental investigations were focused on the precipitation of a germanium−catechol (CAT) complex with cetyl trimethyl ammonium bromide (CTAB). The influences of pH and amounts of CTAB and CAT on the precipitation yield were investigated. To this aim, a central composite rotatable design and ANOVA Design Expert 7.0.3 Wiley software were employed for experimental design and analysis of the results. Thus, the independent and combined effects of pH, CAT/Ge and CTAB/Ge molar ratios were investigated and optimized using a quadratic mathematical model. The optimum values of these factors were found to be 10, 12, and 4, respectively (in this case, the germanium precipitation yield was 98.8% for water leachates). The precipitation of germanium as a complex compound with CAT and CTAB was found to be selective towards germanium and this element can be effectively separated from As, Mo, Sb, V, or Zn. Total organic carbon in solution was measured to estimate the amounts of CAT and CTAB precipitated with germanium and with the interferences present in aqueous leachates. In addition, thermogravimetric analyses have been performed on the germanium-complex solids as a result of which 600°C was determined as the minimum temperature to completely remove the organic content of the precipitate.

1. Introduction

Germanium is a semiconductor, hard, and crystalline element. Germanium is found in the earth's crust in an abundance of 1–7 ppm and concentrated in very few minerals such as argyrodite, germanite, or renierite. Some Ag, Sn, Cu, Fe, and especially Zn ores, contain germanium and small traces of the metal can also be found in many silicates. Germanium is not extracted from any specific mineral, but the majority is obtained as a byproduct of Zn metal (Adams, 1992; Moslalyk, 2004).

Germanium is mainly used in fiber optics, optical infrared polymerization catalysts for the manufacture of polyethylene terephthalate, solar panels, and different electronics. As a result of its important uses, demand for Ge (and its price) has been growing every year. Nowadays, secondary sources of Ge are very important because 60% of the consumed Ge is used in the manufacture of electronic devices and it can be obtained by recycling (Adams, 1992; Moslalyk, 2004).

Coal and coal combustion/gasification by-products may be an attractive source of germanium (Seredin and Danilcheva, 2001; Seredin et al., 2006; Qi et al., 2007). For instance, the element occurs in relatively high concentrations in a number of coal basins (Banks et al., 1962; Swaine, 1990; Wang, 1999; Alastuey et al., 2001; Hower et al., 2002; Yudovich, 2003; Seredin et al., 2006; Zhuang et al., 2006; Du et al., 2008) because coal seams are favorable for Ge mineralization (Hu et al., 2009) and it is usually concentrated in coal combustion/gasification fly ashes that can

Corresponding author. Tel.: 011-034-95-448-1379. *E-mail*: pereira@esi.us.es

reach germanium contents 10 times higher than in coal (Clarke, 1991; Meij, 1994; Querol et al., 1995; Font et al., 2005a). Commercial Ge-end products are mainly Ge metal and GeO_2, with different purity depending upon producers. The industrial recovery of Ge is usually based on hydrometallurgical processes with high economic and environmental costs. Most of the industrial processes for the recovery of Ge involve the generation of a Ge-bearing solution by acid leaching of raw materials followed by production of Ge end products.

The occurrence of Ge as water soluble species (GeS_2, GeS, and hexagonal-GeO_2) in the 335 MW IGCC power plant of ELCOGAS in Puertollano (Spain), fed with a 50:50 blend of a local metal-rich bituminous coal and pet coke (Moreno, 2002), may help to find a low cost and environmentally acceptable germanium recovery process from fly ashes, resulting in a commercial Ge end product. The research on the water germanium extraction from the Puertollano IGCC fly ash revealed that relatively high extraction yields (up to 86%) were obtained using pure water (Font et al., 2005b; 2006).

This article focuses on evaluating the feasibility of a recovery process based on precipitating Ge with cetyl-trimethyl-ammonium bromide (CTAB) and catechol (CAT) from diluted solutions from fly ash aqueous leaching.

The complex germanium-catechol was first described by Antikainen and Malkonen (1959) with a structure of chelate and a Ge/ligand proportion of 1/3 (Figure 1).

Pokrovski and Schott (1998) have investigated the stability of the complexes formed by Ge with aqueous carboxylic acids and phenols and they reported that the level of coordination of Ge in the presence of catechol depends on the pH of the solution (Pokrovski et al., 2000). In the pH range 1–2, Ge is in the form $Ge(OH)_4^0$ and at pH$>$ 4 an octahedral complex is generated, whose formation mechanism proposed would be as follows:

$$Ge(OH)_4^0 + 3C_6H_4(OH)_2 \leftrightarrow Ge(C_6H_4O_2)_3^{2-} + 2H^+ + 4H_2O \quad (1)$$
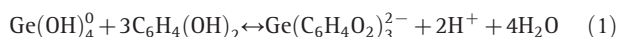
Cetyl-trimethyl-ammonium bromide is a quaternary ammonium salt, soluble in water, with a long alkyl group, whose chemical formula is $C_{19}H_{42}NBr$. CTAB is a surfactant with a hydrophobic group (the long-chain hydrocarbon) and a hydrophilic group (quaternary ammonium). Probably due to its polarity, the complex Ge-CAT is very soluble in water. When CTAB is added to a solution with the complex Ge-CAT, the CTA^+ and the chelate form a large ion pair (molar mass = 964.6) which precipitates. The ion-pair could be formed as follows if the stoichiometric ratio of reagents is Ge: CAT: CTAB 1:3:2:

$$2C_{19}H_{42}NBr + \left[Ge(C_6H_4O_2)_3\right]^{2-} \leftrightarrow (C_{19}H_{42}N)_2Ge(C_6H_4O_2)_3 + 2Br^- \quad (2)$$
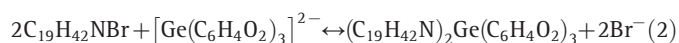
This mechanism agrees with that proposed by Scott et al. (2003) for complex Sn-CAT-CTA and by Barreto et al. (2006) for complex CAT-CTA-Fe.

The recovery of the germanium-catechol complex from aqueous solutions has been accomplished by activated carbon (Marco et al., 2006; Marco-Lozar et al., 2007), flocculation (Linares Solano et al., 2009), ion-flotation (Hernández-Expósito et al., 2006), solvent extraction (Arroyo and Pereira, 2008), and by two different precipitation methods carried out on germanium-bearing solutions as a last step of a hydrometallurgical process for the recovery of Ge from the Puertollano IGCC fly ash (Arroyo et al., 2009). One of these methods, the precipitation with CAT and CTAB, now applied
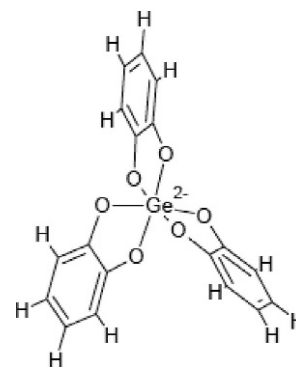

Fig. 1. Complex structure of germanium-catechol.

directly to the IGCC fly ash leachate, has been optimized and the main results are presented in this paper.

2. Experimental

2.1. Materials

Prior to the precipitation tests, leaching of fly ash in was performed. Two different leaching reagents were used: pure water and 0.016M catechol solution. Fly ash was produced in Puertollano IGCC power plant under the following conditions: 50:50 coal/pet coke blend and 2.5% limestone addition as fluxing agent. An exhaustive characterization of IGCC fly ash has been carried out and the results have been published elsewhere (Font, 2007; Arroyo and Pereira, 2008) in which the main chemical characteristics of the fly ash used in the present study are shown. A special two-step sample digestion method for the analysis of potentially volatile elements devised by Querol et al. (1993) was used to dissolve the fly ash prior to the analysis. Different characteristics of fly ash such as granulometry or mineral composition by X-ray diffraction (XRD) and scanning electronic microscopy using energy dispersive X-ray analyser (SEM-EDX) have been published elsewhere (Font et al., 2001; Font et al., 2005a; 2005b; Aineto et al., 2006).

The leachates were obtained for a L/S ratio of five (L/kg) at room temperature for 24 hours with mechanical agitation. Precipitation reagents (CAT, CTAB and NaOH for pH adjustment) were added to this leachate for the germanium precipitation.

2.2. Design of experiments

The design of experiments is a practical tool that reduces the number of experiments to conduct a study for a number of variables and allows a more efficient approach using only a portion of the possible combinations to estimate the main effects of all factors (Montgomery, 2005). In this work, a multilevel analysis with three variables has been chosen (Figure 2). The total number of experiments is 20 (eight Hadamard points in the cube vertices, six central points, and six star points on a line crossing the centers of the cube faces and at distance of $1.682 \cdot$ cube side size from cube center).

Three variables affecting the precipitation of the germanium contained in leachates were included in the optimization study: the molar ratios of CAT/Ge (C) and CTAB/Ge (T) and the final pH of the solution (P): two of these variables are reagents needed for the germanium precipitation through the complexation mechanisms described in the previous section, while the third variable refers to the medium in which the precipitation occurs.
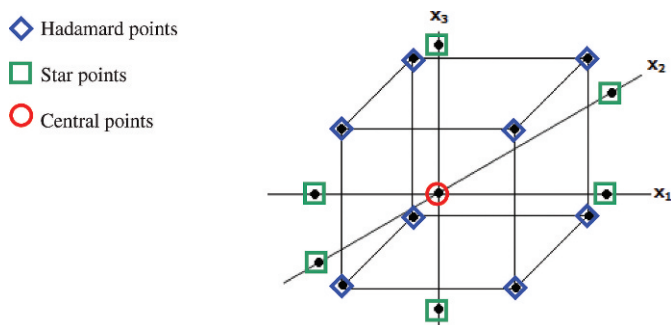
Fig. 2. Coded points for a three variables multilevel design.

To design the experiments, it is first necessary to code the variables, which can be described in the following steps:

1. Define the space of interest for the experiment (see Table 1).
2. Express each test in coded terms (see Figure 2 and Table 1).
3. Scale tests to obtain the actual values with the following expressions:

$$A = 0.5 \cdot \frac{x_2 - x_1}{1.682} \qquad (3)$$

where x_2 is the value of higher value and x_1 is the lower value of the range

$$A_{actual} = A_{coded} + 0.5 \cdot (x_2 + x_1) \qquad (4)$$

With the results, the surface response can be calculated. The ranges of variability of each variable were obtained from previous works (Arroyo, 2007; Arroyo and Pereira, 2008) and real and coded values of variables are shown in Table 1.

2.3. Precipitation tests on water leachates

Batch experiments were focused on evaluating the selective precipitation efficiency of germanium and the optimization of the experimental parameters. The CAT and CTAB were added to the Ge-bearing solutions as complexant and precipitation agents,

respectively. The precipitation method used for the tests is described as follows: CAT is added to the aqueous solution containing Ge (fly ash leachate) with mechanical stirring until complete dissolution. Then, CTAB is added. A number of batch precipitation tests were performed by mechanically shaking the mixtures in 250 mL glass vessels at room temperature to assure a complete dissolution of both reagents (15–30 min approx.). Finally the pH is adjusted by adding the appropriate amount of 4M NaOH solution. After one hour without stirring to assure the precipitate formation, the solution is filtered through ALBET 145 filter (ash content < 0.007%) with a pore size of 7–11 μm, washed and subsequently dried at 110°C in an oven for 24 h.

The content of major and trace elements were analyzed in the solutions before and after the precipitation experiments by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).

2.4. Precipitation tests on catechol containing leachates

After the optimization of precipitation conditions carried out on fly ash water leachates, another set of experiments was performed on fly ash aqueous leachates containing catechol, with the aim of increasing the leaching yield and reducing and/or eliminating the catechol addition in the precipitation stage. The amount of catechol to be used in the leaching solutions was selected taking into account the germanium content achieved in the fly ash, according to Font et al. (2005a; 2005b) (around 400 mg/kg), and the CAT-Ge complex stoichiometry (eq. 1). In consequence, a 0.016M catechol solution was chosen as leaching agent.

Three different precipitation tests were carried out on catechol leachates: a) without adding any catechol in the precipitation stage; b) adding half the optimum CAT amount determined for water leachates (CAT/Ge molar ratio = 6), and c) adding the whole CAT amount determined as optimum (CAT/Ge = 12).

The precipitation procedure was the same as that used with water leachates, and a CTAB/Ge molar ratio of 4 and pH of 10 were fixed in all the tests.

Table 1
Coded variables and results obtained in the precipitation tests

Variable	CAT/Ge (molar)		CTAB/Ge (molar)		pH			
Range	3–12		2–6		7–13			
Test N°	C_{coded}	C_{actual}	T_{coded}	T_{actual}	P_{coded}	P_{actual}	Ge in filtrate (mg/L)	η (%)
1	1	10.18	1	5.19	1	11.78	1.3	96.3
2	1	10.18	−1	2.81	−1	8.22	2.7	92.4
3	−1	4.82	1	5.19	−1	8.22	2.8	92.1
4	−1	4.82	−1	2.81	1	11.78	5.0	86.1
5	1	10.18	1	5.19	−1	8.22	3.4	90.5
6	1	10.18	−1	2.81	1	11.78	1.8	94.9
7	−1	4.82	1	5.19	1	11.78	2.5	93.0
8	−1	4.82	−1	2.81	−1	8.22	1.0	97.1
9	1.682	12.00	0	4.00	0	10.00	0.4	98.8
10	0	7.50	1.682	6.00	0	10.00	0.7	98.1
11	0	7.50	0	4.00	1.682	13.00	1.0	97.1
12	−1.682	3.00	0	4.00	0	10.00	5.9	83.3
13	0	7.50	−1.682	2.00	0	10.00	5.2	85.5
14	0	7.50	0	4.00	−1.682	7.00	3.9	88.9
15–20	0	7.50	0	4.00	0	10.00	0.6–2.1	98.4–94.1

Table 2
Optimization of germanium precipitation minimizing reagents

Variables			Calculated variables (Stat-Ease)			
CAT/Ge	CTAB/Ge	pH	CAT/Ge*	CTAB/Ge*	pH*	η (%)
Minimization	Range [2,6]	Range [7,13]	6.3	5.2	11.4	97
Range [3,12]	Minimization	Range [7,13]	11.1	2.8	11.6	95
Minimization	Minimization	Range [7,13]	5.2	4.5	10.0	94

2.5. Total organic carbon content

The total organic carbon (TOC) present in aqueous samples was measured using a Total Organic Carbon Analyzer, high-sensitivity Shimadzu TOC-V CPH PC-controlled model with auto sampling. TOC has been used in this work as a non-specific indicator of catechol and CTAB presence in solutions.

To measure the total carbon content (TC) concentration of the sample, the relationship between the TC concentration and peak area (calibration curve) was predetermined using a TC standard solution, to express the peak area as a ratio of the TC concentration. The TOC Analyzer measures the TC which comprises TOC and IC (Inorganic Carbon). The IC content is a combination of carbonate and bicarbonate. Subtracting the IC concentration from the TC concentration determines the TOC concentration.
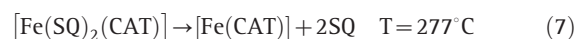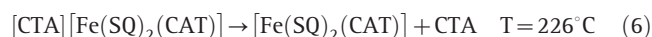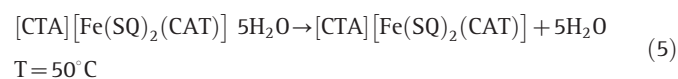
TOC content was determined in water fly ash leachates before and after the precipitation test to estimate the CAT and CTAB precipitated not only with germanium but also with other elements present in leachates. Experimental conditions were: CAT/Ge molar ratio of 5.2, CTAB/Ge molar ratio of 4.5 and pH = 10. These conditions were achieved using the Design Expert (Design-Expert© Version 6.0.10 from Stat-Ease, www.statease.com) software, for maximum precipitation yield with minimum CAT and CTAB addition.

2.6. Thermogravimetry

In thermo-gravimetric tests, the mass of a sample is measured as a function of temperature when it is heated in a controlled atmosphere. The sample is prepared in an alumina crucible, and is submitted to a heating ramp. The program measures the temperature and the weight changes produced during the process. The equipment used was a Mettler-Toledo thermo-balance, model TGA / SDTA 851.

In this study, the following heating ramp was scheduled: from 25 to 300°C in a nitrogen atmosphere with a flow of 100 mL/min and from 300 to 750°C in air atmosphere (100 mL/min), in both cases using a heating rate of 4°C/min.

According to Hernández-Expósito et al. (2006), a similar precipitate formed by Ge, CAT, and dodecylamine must be dried for 24 hours at 105°C, followed by heating in an oven at 10°C/min in an air atmosphere until constant weight is achieved at a temperature of 600°C. Barreto et al. (2006) performed a thermogravimetric study of the complex formed by iron (III), CAT, and CTAB. The thermogravimetric analysis was performed under air and nitrogen atmospheres with a heating rate of 10°C/min from 25 to 750°C, obtaining a thermal decomposition mechanism (in which SQ refers to semiquinone, a product of the CAT oxidation) that could also be applied to the mixed complex of catechol, CTAB and germanium:

$$[CTA][Fe(SQ)_2(CAT)]\,5H_2O \rightarrow [CTA][Fe(SQ)_2(CAT)] + 5H_2O \tag{5}$$
$$T = 50°C$$

$$[CTA][Fe(SQ)_2(CAT)] \rightarrow [Fe(SQ)_2(CAT)] + CTA \quad T = 226°C \tag{6}$$

$$[Fe(SQ)_2(CAT)] \rightarrow [Fe(CAT)] + 2SQ \quad T = 277°C \tag{7}$$

$$[Fe(CAT)] \rightarrow Fe_2O_3 + CAT \quad T = 297°C \tag{8}$$

$$Fe_2O_3 \text{ (residue)} \quad T > 550°C \tag{9}$$

3. Results and Discussion

3.1. Precipitation optimization

The germanium content in leachate was 35.6 mg/L. The precipitation yield (Table 2) was calculated by a mass balance between the initial content in the leachate ($Ge_{leachate}$) and in the filtrate ($Ge_{filtrate}$):

$$\eta = \frac{(Ge_{leachate} - Ge_{filtrate})}{Ge_{leachate}} \cdot 100 \tag{10}$$

In general, all the tests have had a good yield, higher than 83%, indicating that the precipitation method used is very effective. It can be seen that the highest yield was obtained for test 9 with more than 98% of Ge precipitate and all tests achieved precipitation yields.

Figure 3 shows the level curves obtained with the Design Expert (Design-Expert© Version 6.0.10 from Stat-Ease, www.statease.com) application for optimal values of variables: CAT / Ge = 12, CTAB / Ge = 4, and pH = 10.

The equation of the germanium precipitation yield (%) obtained with the Stat Ease Design-Expert program, according to the ANOVA analysis is:

$$\eta = 59.70 + 1.62 \cdot CAT/Ge + 4.95 \cdot CTAB/Ge + 2.18 \cdot pH - 0.19 \cdot CAT/$$
$$Ge \cdot CTAB/Ge + 0.41 \cdot CAT/Ge \cdot pH + 0.73 \cdot CTAB/Ge \cdot pH -$$
$$0.26 \cdot (CAT/Ge)^2 - 1.14 \cdot (CTAB/Ge)^2 - 0.38 \cdot pH^2 \tag{11}$$
$$\text{with } R^2 = 0.7587$$

Figure 4 shows two response surfaces of the Ge precipitation yield obtained for CAT/Ge = 12 (left) and CTAB/Ge = 4 (right). When the pH is fixed at 10, the maximum Ge precipitation yield is about 95% for molar ratios CAT/Ge and CTAB/Ge of 8.40 and 5.10 respectively (Figure 5).

In the germanium precipitation yields the three variables above have influence independently and jointly. CAT/Ge, CTAB/Ge molar ratios and pH linearly increased precipitation: CTAB/Ge (4.95) > pH (2.18) > CAT/Ge (1.62). Regarding the quadratic influence, interactions with the CAT/Ge and CTAB/Ge molar ratios are negative but the effect is very small (−0.20). Moreover, the interaction of the molar ratios on the pH is positive; however, the quadratic terms of each variable are all negative. Notwithstanding,
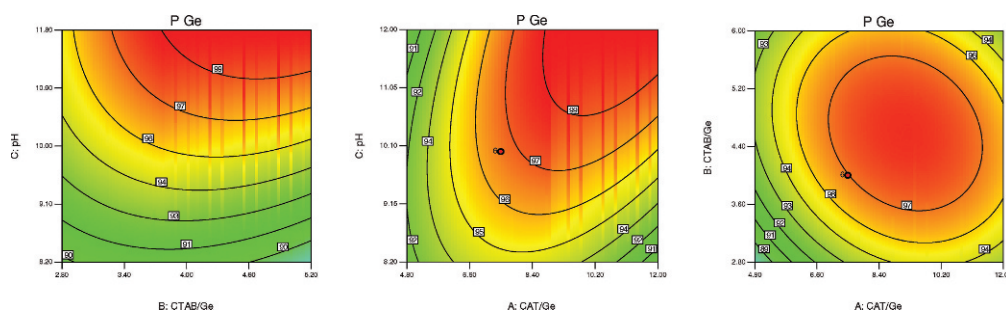
Fig. 3. Level curves of germanium precipitation with fixed CAT/Ge = 12 (left), CTAB/Ge = 4 (center) and pH = 10 (right).

the most influential terms of equation 11 are the linear ones, since the coefficients multiplying each factor are the highest.

According to equation 8, in order to maximize the germanium precipitation, it is convenient to take a high molar CAT/Ge ratio since the linear term and the interaction with the pH term are higher than the interaction with the CTAB/Ge and the quadratic terms. The CTAB/Ge molar should have an intermediate value since the quadratic term is negative. The effect of pH is similar to that of CAT/Ge ratio, a higher value is better since the linear and interactions terms are positive and higher than the quadratic term, which is negative. When the germanium precipitation yield is optimized within the range previously defined for the three variables, a 99.99% precipitation yield (practically 100%) can be achieved for CAT/Ge = 8.7, CTAB/Ge = 4.9, and pH = 11.5.

However, when the precipitation yield is maximized, minimizing at the same time the amount of reagents consumed (as the optimal precipitation supposes a high amount of catechol), lower yields are obtained (Table 2). When the CAT/Ge molar ratio is minimized, the Ge precipitation yield was 95%, whereas for the minimum CTAB/Ge ratio the value reached 97%. When both molar ratios were minimized the germanium precipitation fell around 92%.

3.2. Precipitation of interferences

The elements in the fly ash leachate that can interfere in the germanium precipitation process are Sb, As, Mo, Ni, V, and Zn. The content of those elements in the leachate and filtrates, as well as the precipitation yields obtained in some selected precipitation tests are shown in Table 3.

As can be seen, precipitation of As, an element with similar properties to Ge, was low. The content of Ni in the leachate is virtually the same as Ge (37.7 mg/L for Ni and 35.6 mg/L for Ge) and the precipitation yields were high in all tests, so it could

become an important interference in the precipitate. Sb precipitated with intermediate yields, but its concentration in the leachate was 19.1 mg/L, so that for a maximum precipitation yield of 42%, it was an interference with little importance. The contents of Mo, V and Zn in the fly ash leachate (0.43, 0.33 and 2.04 mg/L) make them low significant interferences in the precipitation process.

3.3. Precipitation tests on catechol leachates

The catechol leachates contain a little less Ge (25 mg/L) than the water leachates. The interferences (Table 4) are almost the same as those present in water leachates (As, Mg, Ni, Sb, V, and Zn), but As, Sb, and Zn contents are slightly higher in catechol leachates. Results show that the precipitation of germanium without adding fresh catechol was possible with a high yield (87%). The precipitation yield increased when some catechol was added, reaching 90% when half the optimum amount was added and 92% when the whole catechol optimum amount was added.

Regarding the interferences, As does not precipitate in any test, whereas 25.8% Mg, 24.5% Sb, 60.2% V, and 94.2% Zn can precipitate in certain tests. However, as the leachate contents of these elements were not very high, they do not imply a serious interference. The only elements possibly interfering in the precipitation method are Ni and Sb. The precipitation yield of impurities decreases when the CAT addition increases, so it would be interesting to add some amount of CAT to reduce interferences in precipitates.

3.4. TOC content

Germanium content in water leachates was 30 mg/L while TOC was 1.32 mg/L. This value was taken as the origin (zero) of TOC measurements. The organic carbon present in leachates after CAT and CTAB addition was 579 mg/L. In consequence, as TOC content
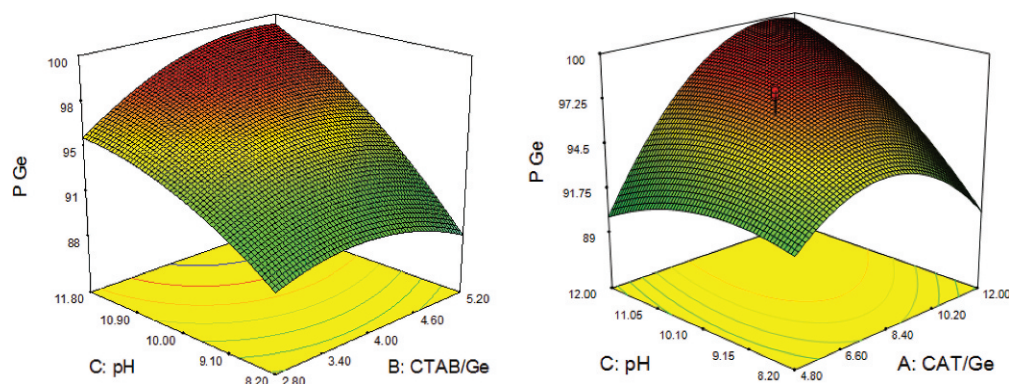

Fig. 4. Response surfaces of the precipitation with CAT/Ge = 12 (left) and CTAB/Ge = 4 (right).
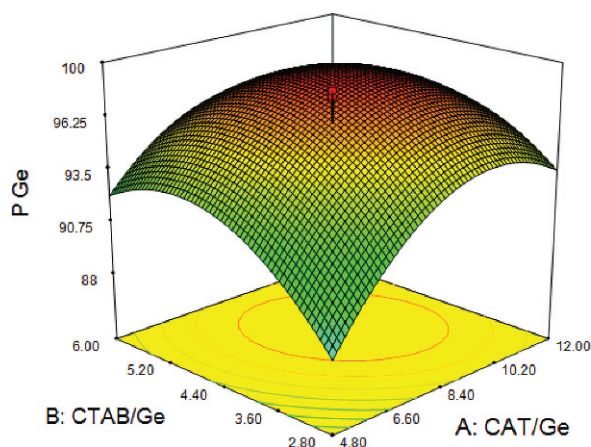
Fig. 5. Response surface of the Ge precipitation for pH = 10.

in raffinate was 58.6 mg/L, a total of 520.4 mg/L of C precipitated. Half of the TOC amount (around 261 mg/L) precipitated as the Ge-CAT-CTAB complex form, but 259.4 mg/L of TOC precipitated in other forms, probably as Ni and Sb complexes.

3.5. Thermo-gravimetric tests

Before submitting the Ge precipitate to a roasting process that renders an end product in the form of GeO_2, a thermogravimetric study was carried out to find the best roasting conditions. Figure 6 shows the mass loss as a function of temperature. From room temperature to 100°C the loss of water occurred, but it was not very significant. In the first step, a 24.5% of mass was reduced (in the range 180–290°C). The reaction was endothermic and took place in a nitrogen atmosphere, so it was not combustion. The second step (reaction) started at 290°C, when air is introduced. The reduced mass in this interval was 19.04%. The third step began at 340°C and the mass loss was 24.42%. The last step began at around 500°C. At constant weight, the roasted precipitate had 16.26% of the initial precipitate mass.

As a result of this study, a mechanism for the decomposition of the germanium-complex could be proposed and the optimum conditions for roasting were determined:
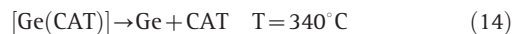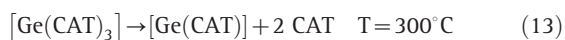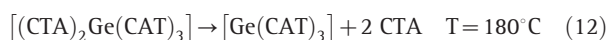
$$[(CTA)_2Ge(CAT)_3] \rightarrow [Ge(CAT)_3] + 2\ CTA \quad T = 180°C \quad (12)$$

$$[Ge(CAT)_3] \rightarrow [Ge(CAT)] + 2\ CAT \quad T = 300°C \quad (13)$$

$$[Ge(CAT)] \rightarrow Ge + CAT \quad T = 340°C \quad (14)$$

Table 4
Metal concentrations in the fly ash catechol leachate and precipitation yields (η) for the elements analyzed in selected trials

	Catechol Leachate	CAT 0	CAT 6	CAT 12
	mg/L	η (%)	η (%)	η (%)
Ge	33.2	87	90	92
As	38.7	–	–	–
Mg	11.3	25.8	23.2	28.4
Ni	35.8	85.2	40.8	39.7
Sb	29.7	24.5	3.3	9.3
V	1.6	60.2	35.2	26.5
Zn	7.4	94.2	40.0	24.5

$$Ge + O_2 \rightarrow GeO_2 \quad T = 500°C \quad (15)$$

$$GeO_2 \ (residue) \quad T > 600°C \quad (16)$$

First, there was a reaction due to the loss of the chemically combined water and after that four reactions occurred: the reaction 12 at a temperature around 200°C, which, according to Barreto et al. (2006), corresponds to the decomposition of the mixed complex into the Ge-CAT complex and CTA. Then, the separation of germanium and CAT would be produced in two steps (equations 13 and 14). The last exothermic reaction (15) is the reaction of formation of germanium dioxide.

4. Conclusions

- Recovery of germanium from coal fly ash aqueous leachates by precipitation adding CAT and CTAB occurred with very high yields (> 83%) achieving a maximum yield close to 99%.
- The highest yield (98.8%) was obtained in the following conditions: CAT/Ge molar ratio = 12, CTAB/Ge molar ratio = 4 and pH of 10.
- The most important interference found in the precipitation method proposed is nickel, because its content in the water fly ash leachate is similar to the germanium content and the precipitation yields are in the range: 57–99%. The order of interference of other metals is as follows: Ni> Sb> Zn> Mo> V> As.
- Germanium precipitation from catechol leachates is also possible by adding only CTAB (87%). The main interfering element in this case is Nickel.
- To recover Ge, a roasting process of the mixed Ge-CAT-CTAB complex was studied using thermogravimetric techniques. This study shows that a temperature of 600°C was

Table 3
Metal concentrations in the fly ash leachate and precipitation yields (η) for the elements analyzed in selected trials

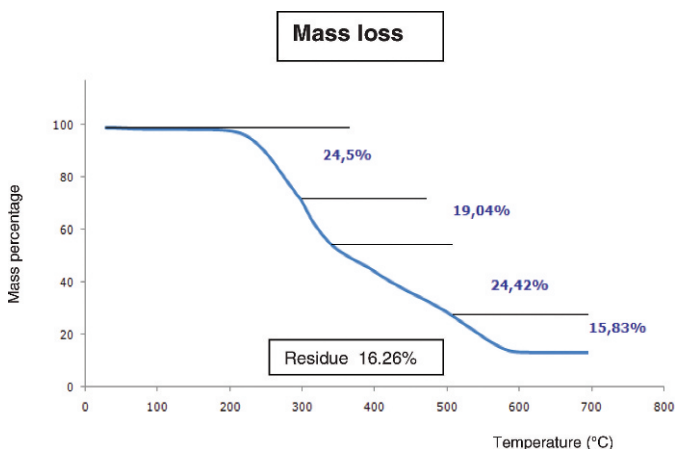|	Leachate	Test No. 1		Test No. 8		Test No. 9		Test No. 10		Test No. 11		Test No. 17	
	mg/L	mg/L	η	mg/L	η	mg/L	η	mg/L	η	mg/L	η	mg/L	η
As	15.2	16.8	–	13.3	12.5	16.1	–	13.8	9.2	14.3	5.9	15.8	–
Mo	0.43	<0.01	100	<0.01	100	<0.01	100	<0.01	100	<0.01	100	<0.01	100
Ni	37.7	0.3	99	16.0	58	8.0	79	11.5	69	<0.01	100	9.5	75
Sb	19.1	14.1	26	13.0	32	13.1	31	11.2	41	11.0	42	14.1	26
V	0.33	0.12	64	0.04	88	<0.02	100	0.07	79	0.14	58	0.07	79
Zn	2.04	0.04	98	0.28	86	0.24	88	0.48	76	0.85	58	0.15	93

Fig. 6. Mass loss of the precipitate as a function of temperature in the thermogravimetric test.

needed to achieve a constant weight. In addition, a mechanism of decomposition of the complex in four stages was proposed.

References

Adams, J.H., 1992. Germanium and germanium compounds, in: Ullman's Encyclopedia of Industrial Chemistry, Handbook of Metals: Specific Metals and Alloys, Wiley-VCH Verlag GmbH & Co., pp. 733–738.

Aineto, M., Acosta, A., Rincón, J.M., Romero, M., 2006. Thermal expansion of slag and fly ash from coal gasification in IGCC power plant. Fuel 85, 2352–8.

Alastuey, A., Jiménez, A., Plana, F., Querol, X., Suárez-Ruiz, I., 2001. Geochemistry, mineralogy, and technological properties of the main stephanian (carboniferous) coal seams from the Puertollano basin, Spain. International Journal of Coal Geology 45, 247–265.

Antikainen, P.J., Malkonen, P.J., 1959. Chelation of germanic acid with some o-diphenols in aqueous solution. Suomen Kemistilehti B 32B, 179–82.

Arroyo, F., 2007. Recovery of germanium present in the fly ash produced in an IGCC plant that uses coal from ENCASUR (Puertollano), Ph.D. Dissertation (in Spanish). Chemical and Environmental Engineering Department. School of Engineering. University of Seville.

Arroyo, F., Fernández-Pereira, C., Querol, X., Font, O., Coca, P., Chimenos, J.M., Fernández, A.I., 2008. Method for the recovery of germanium present in coal ash. Patent WO/2008/003808.

Arroyo, F., Fernandez-Pereira C., 2008. Hydrometallurgical Recovery of Germanium From Coal Gasification Fly Ash. Solvent Extraction Method. Industrial and Engineering Chemistry Research 47, 3186–3191.

Arroyo, F., Font, O., Fernández-Pereira, C., Querol, X., Juan, R., Ruiz, C., Coca P., 2009. Germanium recovery from gasification fly ash: Evaluation of end-products obtained by precipitation methods. Journal of Hazardous Materials 167, 582–8.

Banks, C.V., Dale, J.M., Melnick, L.M., Musgrave, J.R., Onishi, H. Shell, H.R., 1962. Treatise on analytical chemistry. Part II. Analytical Chemistry of the Elements, section A, Wiley & Sons, New York.

Barreto, J., Barreto, S., Meriera, I., Kawano, Y., 2006. Iron oxide and pyrocatechol: a spectroscopy study of the reaction products. Química Nova 29, 1255–1258.

Clarke, L., 1991. The behaviour of trace elements during coal combustion and gasification: an overview, Managing Hazardous Air Pollutants: State of the Art. IEA Coal Research 15.

Du, G., Zhuang, X., Querol, X., Izquierdo, M., Alastuey, A., Moreno, T., Font, O., 2009. Ge distribution in the Wulantuga high-germanium coal deposit in the Shengli coalfield, Inner Mongolia, northeastern China. International Journal of Coal Geology 78, 16–26.

Font, O., Querol, X., Plana, F., Burgos, S., García, F. Occurrence and distribution of valuable metals in fly ash from Puertollano IGCC power plant, Spain. International Ash Utilisation Symposium (2001, Lexington, Kentucky, USA).

Font, O., Querol, X., Huggins, F., Chimenos, J. M., Fernández, A. I, Burgos, S., García Peña, F. 2005a. Speciation of major and selected trace elements in IGCC fly ash. Fuel 84, 1364–1371.

Font, O.; Querol, X.; Lopez-Soler, A.; Chimenos, J.M.; Fernandez, A.I.; Burgos, S.; Garcia Pena, F, 2005b. Ge extraction from gasification fly ash. Fuel 84, 1384–1392.

Font, O., Querol, X., Plana,F., Coca, P., Burgos, S., García Peña, F., 2006. Condensing species from flue gas in Puertollano gasification power plant (Spain). Fuel 85, 2229–2242.

Font, O. Trace elements in integrated gasification combined cycle fly ash: extraction of potentially valuable elements. PhD. Technical University of Catalonia, 2007.

Hernández-Expósito, A., Chimenos, J.M., Fernández, A.I., Font, O., Querol, X., Coca, P., García-Peña, F., 2006. Ion flotation of germanium from fly ash aqueous leachates. Chemical Engineering Journal 118, 69–75.

Hower, J.C., Ruppert, L.F., Williams, D.A., 2002. Controls on boron and germanium distribution in the low-sulfur Amos coal bed, Western Kentucky coalfield, USA. International Journal of Coal Geology 53, 27–42.

Hu, R.Z., Qi, H.W., Zhou, M.F., Su, W.C., Bi, X.W., Peng, J.T., Zhong H., 2009. Geological and geochemical constraints on the origin of the giant Lincang coal seam-hosted germanium deposit, Yunnan, SW China: A review. Ore Geology Reviews 36, 221–234.

Linares Solano, A., Cazorla Amoros, D., Marco Lozar, J.P., 2009. Flocculation method for recovery of germanium in dissolution, involves selecting organic compound for allowing formation of complex, and adding quaternary amine to complex germanium for easy removing of germanium. ES Patent ES 2299371.

Marco, J.P., Cazorla, D., Linares, A., 2006. Recuperation of germanium in solution by activated carbon comprises adsorption by activated carbon, for acid desorption of the germanium and concentration. ES Patent 2257181.

Marco-Lozar, J.P., Cazorla-Amorós, D., Linares-Solano, A., 2007. A new strategy for germanium adsorption on activated carbon by complex formation, Carbon 45, 2519–2528.

Meij, R., 1994. Trace element behaviour in coal-fired power plants. Fuel Processing Technology 39, 199–217.

Montgomery, D.C., 2005 Design and Analysis of Experiments, 6th Edition. John Wiley & Sons, Hoboken, NJ.

Moreno, N., 2002. Valorisation of fly ashes for zeolite synthesis from silica extraction and direct conversion. Environmental applications, Ph.D. Dissertation (in Spanish). Departamento de Ingeniería Química y Recursos Naturales de la Universidad Politécnica de Cataluña.

Moskalyk, R.R., 2004. Review of germanium processing worldwide. Minerals Engineering 17, 393–402.

Pokrovski, G.S., Schott, J., 1998. Experimental study for the complexation of silicon and germanium with aqueous organic species: implications for germanium and silicon transport and Ge/Si ratio in natural waters. Geochimica et Cosmochimica Acta 62(21/22), 3413–3428.

Pokrovski, G., Martín, F., Hazemann, J-L., Schott, J., 2000. An x-ray absorption fine structure spectroscopy study of germanium-organic ligand complexes in aqueous solution. Chemical Geology 163, 151–165.

Qi, H., Hu, R., Zhang, Q., 2007. Concentration and distribution of trace elements in lignite from the Shengli Coalfield, Inner Mongolia, China: Implications on origin of the associated Wulantuga Germanium Deposit. International Journal of Coal Geology 71, 129–152.

Querol, X. Fernández-Turiel, J.L. Lŭpez-Soler. A., 1993. 2nd report, European Coal and steel community Project 7220/ED/014.

Querol, X., Fernández-Turiel, J.L., López-Soler, A., 1995. Trace elements in coal and their behaviour during combustion in a large power station. Fuel 74, 331–343

Scott, R.W.J., Coombs, N., Ozin, G.A., 2003. Non-aqueous synthesis of mesostructured tin dioxide. Journal of Materials Chemistry 13, 969–974.

Seredin V.V. Danilcheva, J., 2001. Coal-hosted Ge deposits of the Russian Far East. In: A. Piestrzynski, Editor, *Mineral Deposits at the Beginning of the 21st Century*, Swets & Zeitlinger Publishers, Lisse, The Netherlands, 89–92.

Seredin, V.V., Danilcheva, Y., Magazina, L., Sharova, I., 2006. Ge-bearing coals of the Luzanovka Graben, Pavlovka brown coal deposit, southern Primorye. Lithology and Mineral Resources 41, 280–301.

Swaine, D. 1990. Trace elements in coal. Butterworth & Co Publications, London.

Wang, L., 1999. Introduction of the geological feature and exploration of germanium deposit in Xilinguole League, Inner Mongolia. Inner Mongolia Geology 3, 16–21.

Yudovich, Y.E., 2003. Notes on the marginal enrichment of Germanium in coal beds. International Journal of Coal Geology 56, 223–232.

Zhuang, X., Querol, X., Alastuey, A., Juan, R., Plana, F., Lopez-Soler, A., Du, G., 2006. Geochemistry and mineralogy of the Cretaceous Wulantuga high-germanium coal deposit in Shengli coal field, Inner Mongolia, North-eastern China. International Journal of Coal Geology 66, 119–136.