

Recovery of Germanium from Coal Fly Ash Leachate by Precipitation

Fátima Arroyo^a, Natividad Pérez Camacho^a, Pilar Coca^b and Constantino Fernández-Pereira^a

^aEscuela Superior de Ingenieros de Sevilla, Dpto. ingeniería Química y Ambiental, Camino de los Descubrimientos s/n, 41092 Seville (Spain)

^bELCOGAS S.A., 13500 Puertollano, Ciudad Real, Spain

KEYWORDS: germanium, fly ash, leachate, catechol, cetyl trimethyl ammonium bromide, response surface methodology, optimization

ABSTRACT

The valorization of coal gasification fly ash is studied by leaching the fly ash with water and a subsequent precipitation of trace amounts of germanium from the leachates. Experimental investigations were focused on the optimization of the precipitation of a germanium–catechol (CAT) complex with cetyl trimethyl ammonium bromide (CTAB).

The influences of pH and the amounts of CTAB and CAT on the precipitation yield were investigated. For a appropriate set of experiments, a statistical technique such as the response surface methodology (RSM) has been used. A central composite rotatable design was employed for experimental design and analysis of the results. 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%. The analysis of variance was performed to validate the regression model. Also, the response surface plots were drawn for spatial representation of the regression equations.

The precipitation of germanium as a complex compound with catechol and CTAB can be selective towards germanium and this element can be effectively separated from As, Mo, Sb, V or Zn.

Thermo-gravimetric analysis has been applied to the germanium-complex solids and 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 is concentrated in very few minerals such as argirodite, canfieldite, germanite or ranierite. Some silver, tin, copper or iron 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 by-product of the zinc metal extraction^{1,2}.

Germanium is mainly used in fiber optics, optical infrared devices, polymerization catalysts for the manufacture of polyethylene terephthalate (PET), solar panels and different electronics. As a consequence of its important uses, demand for germanium (and its price) has been growing every year. Secondary sources of germanium are very important because 60% of the consumed germanium is used in the manufacture of electronic devices and it can be obtained by recycling^{1,2}.

Coal and coal combustion/gasification by-products may be an attractive source of Ge. For instance, the element occurs in relatively high concentrations in a number of coal basins³⁻⁸ and it is usually concentrated in coal combustion/gasification fly ashes that can reach Ge contents 10 times higher than in coal⁹⁻¹². Commercial Ge end-products are mainly Ge metal and GeO₂, with different purity depending on 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 (GeS₂, GeS and hexagonal-GeO₂) in the fly ash from the 335 MW Puertollano Integration Gasification with Combined Cycle (IGCC) power plant (Spain), fed with a 50:50 blend of a local metal-rich bituminous coal¹³ and pet-coke^{14,15}, may help to find a low cost and environmentally acceptable germanium recovery process from fly ashes, culminating in a commercial Ge end-product. The research on the extraction of germanium with water from the Puertollano IGCC fly ash¹⁶ revealed that relatively high extraction yields (up to 86%) were obtained using pure water.

These promising results conducted research towards the study of enrichment and precipitation methods for Ge recovery, such as ion flotation^{17,18}, adsorption on activated carbon (AAC)^{19,20} or solvent extraction (SX)^{21,22}. Using AAC and SX enrichment methods, germanium concentration was raised up to 8 and 40 times the initial leachate concentration respectively, achieving Ge-bearing solutions with 256 and 1623 mg/L respectively. Those enrichment methods are mainly based in the formation of a germanium complex with catechol (CAT) (Fig. 1). The formation of the complex is shown in Eq. (1)²³⁻²⁵:



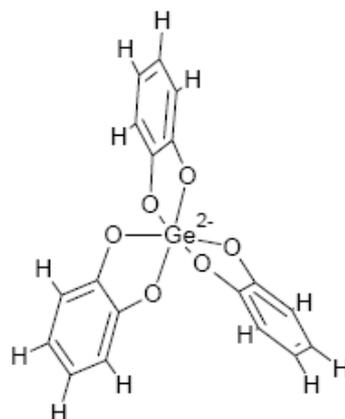


Figure 1. Complex structure of germanium-catechol

This article focuses on evaluating the feasibility of a novel method for the precipitation of germanium from the Puertollano IGCC fly ash leachates, based on precipitating Ge with cetyltrimethylammonium (hexadecyltrimethylammonium) bromide (CTAB) and catechol (CAT).

CTAB is a quaternary ammonium salt, with a long alkyl group, whose chemical formula is $C_{19}H_{42}NBr$ (Figure 2).

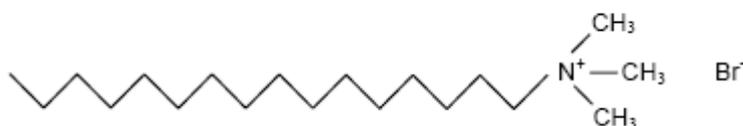


Figure 2. CTAB structure

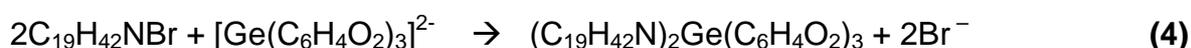
CTAB is a surfactant with a hydrophobic group (the long chain hydrocarbon) and a hydrophilic group (quaternary ammonium). CTAB is dissolved in water as follows:



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 formed a large ion pair (molar mass = 964.6) which precipitates. The ion-pair could be formed as follows:



The global reaction involved would be:



This mechanism agrees with that proposed by Scott et al²⁶ for the complex Sn-CAT-CTA and by Barreto²⁷ for the complex CAT-CTA-Fe.

In a recent article²⁸ we have studied 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. One of these methods, the precipitation with CAT and CTAB, now applied 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 Puertollano IGCC fly ash in water was performed. The leachate was obtained using an L/S ratio of 5 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. The precipitation tests with CTAB were focused on evaluating the selective precipitation efficiency of germanium, and the optimization of the experimental parameters.

The batch experiments were carried out by controlling pH and CAT/Ge and CTAB/Ge molar ratios. The CAT and CTAB were added to the Ge-bearing solutions as complexant and precipitation agent, respectively.

2.2. Design of experiments (DOE)

The design of experiments (DOE) is a practical tool that reduces the number of experiments to conduct a study for a high 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. In this work, a multilevel analysis with three variables has been chosen using a design of central points²⁹ to optimize the Ge precipitation method. In this design the possible experiments which are defined by the values of three independent variables (x, y, z) (x_1, x_2, x_3), are situated in a cube centered in the origin of the coordinate axis. Figure 3 shows the chosen design. For three variables the total number of points is 20: 8 Hadamard points in the cube vertices, 6 central points and 6 star points in the cube faces. The value of Ψ for three variables is 1.682, where Ψ gives the situation of the star points.

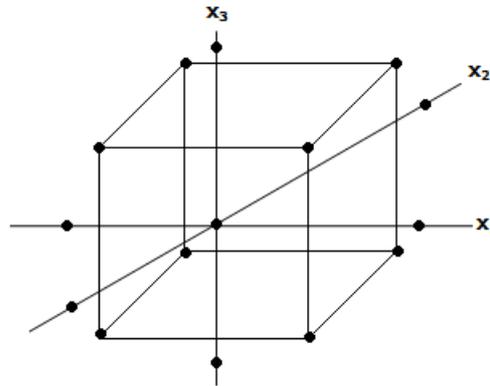


Figure 3. Coded points for a three variable multilevel design

Three variables affecting the precipitation of the germanium contained in leachates were included in the optimization study: the molar ratios of CAT/Ge and CTAB/Ge and the final pH of the solution: two of these variables refer to the reagents needed for the germanium precipitation through the complexation mechanism described in the previous section, while the third variable refers to the medium in which the precipitation occurs.

To design the experiments, it is firstly 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 3 and Table 1).
3. Scale tests to obtain the actual values with the following expressions:

$$A = 0.5 \cdot (x_2 - x_1) / \Psi \quad (5)$$

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

$$A_{\text{actual}} = A_{\text{coded}} + 0.5 \cdot (x_2 + x_1) \quad (6)$$

With the results obtained, the surface response can be calculated. The ranges of variability of each variable were obtained from literature³⁰ and actual and coded values of variables are shown in Table 1.

Table 1. Coded variables used in the precipitation tests

Variable	CAT/Ge (molar)		CTAB/Ge (molar)		pH		Ge in filtrate (mg/L)	η (%)
Range	3-12		2-6		7-13			
Test No.	C_{coded}	C_{actual}	T_{coded}	T_{actual}	P_{coded}	P_{actual}		
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

2.3. Precipitation tests

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.

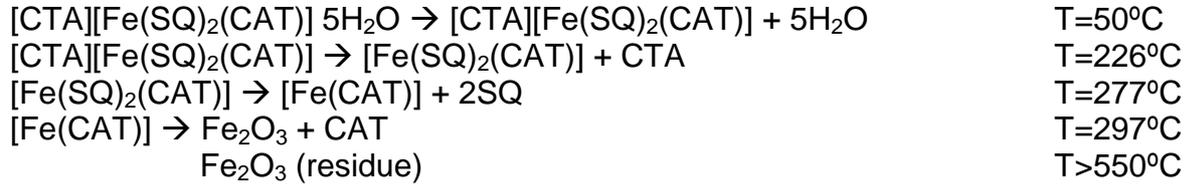
The content of major and trace elements were analyzed in the solutions before and after the precipitation experiments by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).

2.4. 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.

According to Hernández-Expósito et al¹⁸, a similar precipitate formed by Ge, CAT and dodecylamine must be dried up 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 al²⁷ performed a thermogravimetric study of the complex formed by iron (III), catechol 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:



3. RESULTS AND DISCUSSION

3.1. Precipitation optimization

The germanium content in leachate was 35.6 mg/L. The precipitation yield (Table 1) was calculated by a mass balance between the Ge concentrations in leachate ($Ge_{leachate}$) and filtrate ($Ge_{filtrate}$):

$$\eta = \frac{(Ge_{leachate} - Ge_{filtrate})}{Ge_{leachate}} \cdot 100 \quad (7)$$

In general, all the tests achieved high precipitation yields, higher than 83%, indicating that the precipitation method used is very effective. It can be seen that the highest yield was obtained in the test No. 9 with more than 98% of Ge precipitated.

Figure 4 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.

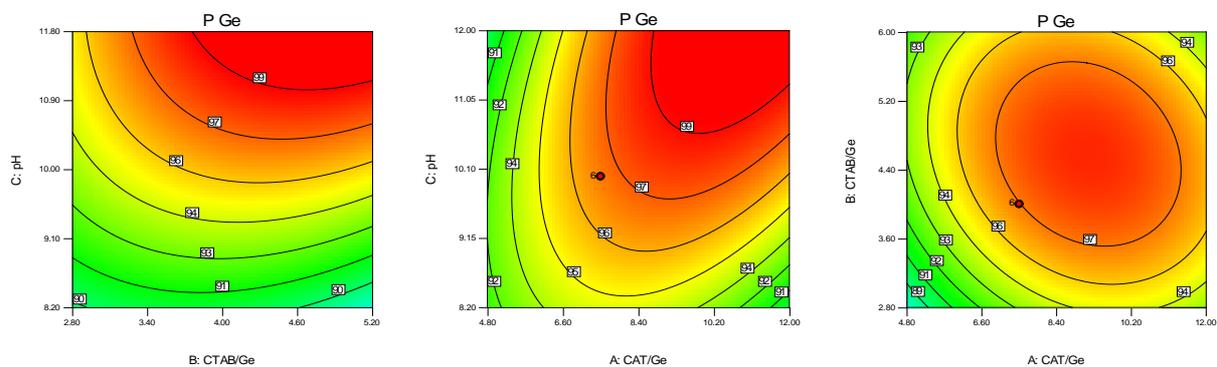


Figure 4. Level curves of germanium precipitation with fixed CAT/Ge = 12 (left), CTAB/Ge = 4 (center) and pH = 10 (right)

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

$$\eta = 59.70 + 1.62 \cdot \text{CAT/Ge} + 4.95 \cdot \text{CTAB/Ge} + 2.18 \cdot \text{pH} - 0.19 \cdot \text{CAT/Ge} \cdot \text{CTAB/Ge} + 0.41 \cdot \text{CAT/Ge} \cdot \text{pH} + 0.73 \cdot \text{CTAB/Ge} \cdot \text{pH} - 0.26 \cdot (\text{CAT/Ge})^2 - 1.14 \cdot (\text{CTAB/Ge})^2 - 0.38 \cdot \text{pH}^2 \quad (8)$$

with $R^2=0.7587$

Figure 5 shows two response surfaces of Ge precipitation yield obtained for CAT/Ge = 12 (left) and CTAB/Ge = 4 (right).

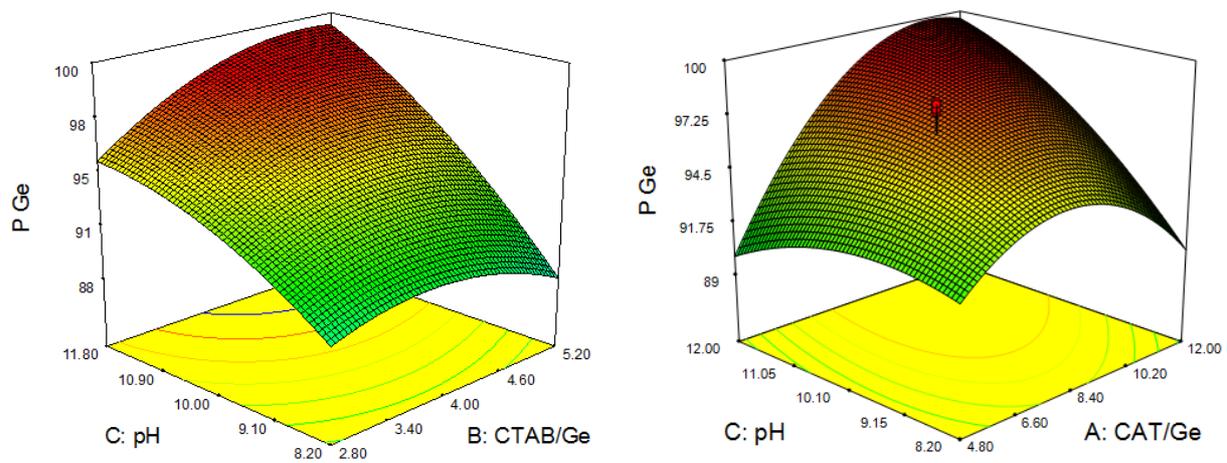


Figure 5. Response surfaces of the precipitation with CAT/Ge = 12 (left) and CTAB/Ge = 4 (right)

Finally, 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 6).

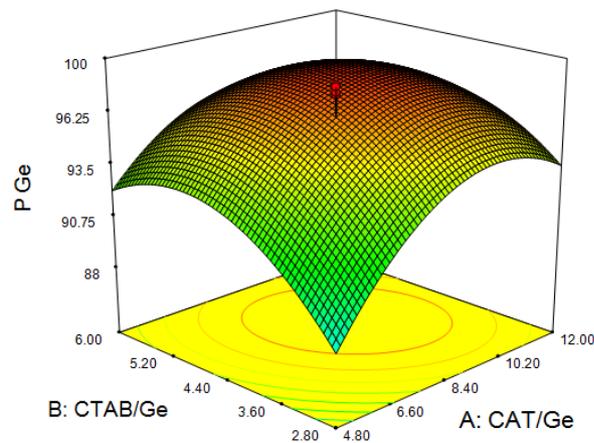


Figure 6. Response surface of the Ge precipitation at pH = 10

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, the most influential values 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 that 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 = 8.71, CTAB/Ge = 4.86 and pH = 11.51.

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. Results obtained minimizing the reagents are summarized in Table 2.

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]	6.6	2.9	9.3	92

As can be seen, 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 interferences

Table 3 shows the concentrations of the metals found in the water leachate of the IGCC fly ash from the Puertollano power plant.

Table 3. Metal concentrations in the fly ash leachate

Element	As	Ba	Cd	Co	Cr	Cu	Hg	Mo
mg/L	15.2	<0.001	<0.003	0.25	<0.002	<0.003	<0.03	0.43
Element	Ni	Pb	Sb	Se	Sn	V	Zn	
mg/L	37.7	<0.03	19.1	<0.04	<0.02	0.33	2.04	

The elements in the fly ash leachate that can interfere in the germanium precipitation process are antimony, arsenic, molybdenum, nickel, vanadium and zinc. 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 4.

Table 4. 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

As can be seen, precipitation of arsenic, an element with similar properties to germanium, was low. The content of nickel in the leachate is virtually the same as Ge (37.7 mg/L for nickel and 35.6 mg/L for germanium) and the precipitation yields were high in all tests, so it could become an important interference in the precipitate. Antimony 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 molybdenum, vanadium and zinc 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. Thermogravimetric 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. 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.

Figure 7 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 following 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.

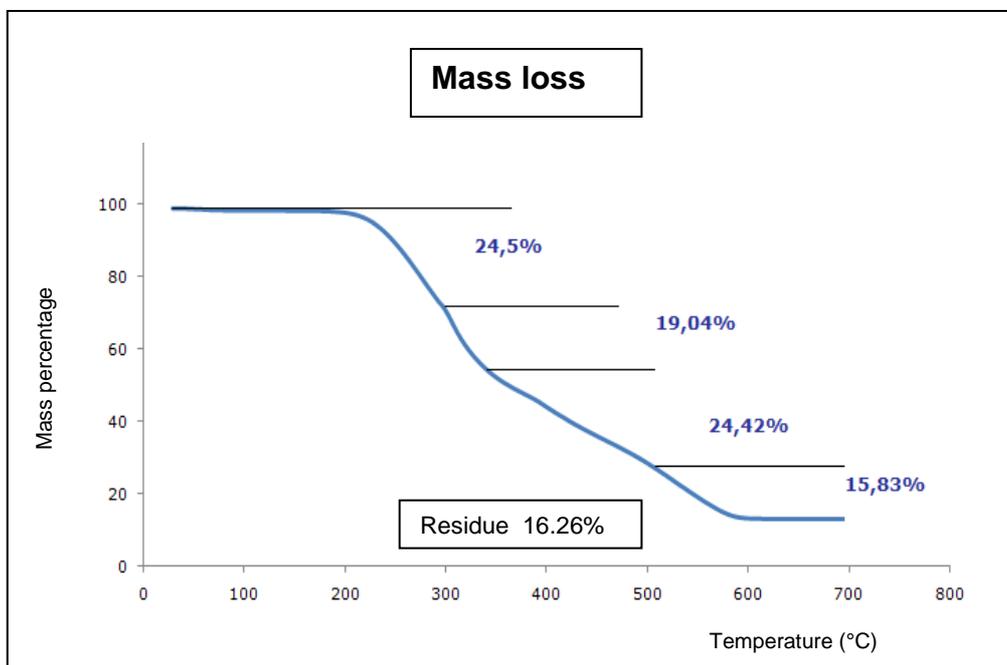


Figure 7. Mass loss of the Ge precipitate as a function of temperature in the thermogravimetric test

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:

- | | | |
|----|--|-----------------------|
| 1) | $[(\text{CTA})_2\text{Ge}(\text{CAT})_3] \rightarrow [\text{Ge}(\text{CAT})_3] + 2 \text{CTA}$ | $T=180^\circ\text{C}$ |
| 2) | $[\text{Ge}(\text{CAT})_3] \rightarrow [\text{Ge}(\text{CAT})] + 2 \text{CAT}$ | $T=300^\circ\text{C}$ |
| 3) | $[\text{Ge}(\text{CAT})] \rightarrow \text{Ge} + \text{CAT}$ | $T=340^\circ\text{C}$ |
| 4) | $\text{Ge} + \text{O}_2 \rightarrow \text{GeO}_2$ | $T=500^\circ\text{C}$ |
| | $\text{GeO}_2 \text{ (residue)}$ | $T>600^\circ\text{C}$ |

First, there was a reaction due to the loss of the chemically combined water and after that four reactions occurred: the first reaction at a temperature around 200 °C, which, according to the literature, 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. The last exothermic reaction 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 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.

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

Acknowledgments

The authors acknowledge the financial support for this research by the European Commission—DG Research, Research Fund for Coal and Steel for supporting this study (ECSC 7220-PR145) and also acknowledge Dr. Ángel Linares, for his suggestions on this work.

References

- [1] R.R. Moskalyk. *Min. Eng.* 17 (2004) 393–402.
- [2] J.H. Adams, Germanium and germanium compounds, in: *Ullman's Encyclopaedia of Industrial Chemistry, Handbook of Metals: Specific Metals and Alloys*, Wiley-VCH Verlag GmbH & Co., 1992, pp. 733–738.
- [3] L. Wang. *Inner Mongolia Geol.* 3 (1999) 16–21.
- [4] A. Alastuey, A. Jiménez, F. Plana, X. Querol, I. Suárez-Ruiz. *Int. J. Coal Geol.* 4 (2001) 247–265.
- [5] X. Zhuang, X. Querol, A. Alastuey, R. Juan, F. Plana, A. Lopez-Soler, G. Du. *Int. J. Coal Geol.* 66 (2006) 119–136.
- [6] V.V. Seredin, Y. Danilcheva, L. Magazina, I. Sharova. *Lith. Min. Res.* 41 (3) (2006) 280–301.
- [7] D.J. Swaine, *Trace Elements in Coal*, Butterworth & Co. Publ., London, 1990.
- [8] C.V. Banks, J.M. Dale, L.M. Melnick, J.R. Musgrave, H. Onishi, H.R. Shell, *Treatise on analytical chemistry. Part II. Analytical Chemistry of the Elements*, section A, Wiley & Sons, New York, 1962.
- [9] L. Clarke. *The behaviour of trace elements during coal combustion and gasification: an overview*, *Managing Hazardous Air Pollutants: State of the Art* (1991) 15.
- [10] R. Meij. *Fuel Proc. Tech.* 39 (1994) 199–217.
- [11] X. Querol, J.L. Fernández-Turiel, A. López-Soler. *Fuel* 74 (1995) 331–343.
- [12] O. Font, X. Querol, F.E. Huggins, J.M. Chimenos, A.I. Fernández, S. Burgos, F. García Peña. *Fuel* 84 (2005) 1364–1371.
- [13] N. Moreno, *Valorización de cenizas volantes para la síntesis de zeolitas mediante extracción de sílice y conversión directa. Aplicaciones ambientales*, Ph.D. Dissertation (in Spanish), Departamento de Ingeniería Química y Recursos Naturales de la Universidad Politécnica de Cataluña, 2002.
- [14] X. Querol, J.L. Fernández-Turiel, A. López-Soler. 2nd Report, European Coal and Steel Community Project 7220/ED/014, 1993.
- [15] O. Font, X. Querol, F. Plana, P. Coca, S. Burgos, F. García Peña. *Fuel* 85 (2006) 2229–2242.
- [16] O. Font, X. Querol, A. López-Soler, J.M. Chimenos, A.I. Fernández, S. Burgos, F. García Peña. *Fuel* 84 (2005) 1384–1392.
- [17] A.I. Zouboulis, I.N. Papadoyannis, K.A. Matis. *Chim. Chro. New Series* 18 (1989) 87–97.

- [18] A. Hernández-Expósito, J.M. Chimenos, A.I. Fernández, O. Font, X. Querol, P. Coca, F. García Peña. *Chem. Eng. J.* 118 (2006) 69–75.
- [19] J.P. Marco, D. Cazorla, A. Linares, Procedimiento para la recuperación de germanio en disolución mediante carbón activo. ES Patent 2,257,181 A1 (2006).
- [20] J.P. Marco-Lozar, D. Cazorla-Amorós, A. Linares-Solano *Carbon* 45 (2007) 2519–2528.
- [21] F. Arroyo, C. Fernández-Pereira, X. Querol, O. Font, P. Coca, J.M. Chimenos, A.I. Fernández, Method for the recovery of germanium present in coal ash. Patent WO/2008/003808, 2008.
- [22] F. Arroyo, C. Fernandez-Pereira. *Ind. Eng. Chem. Res.* 47 (2008) 3186–3191.
- [23] P.J. Antikainen, P.J. Malkonen. *Suomen Kemistilehti B* 32 (1959) 179–182.
- [24] A.M. Andrianov, V.A. Nazarenko. *Zhurn. Neorganic. Khim.* 8 (10) (1963) 2281–2284.
- [25] A.M. Andrianov, V.A. Nazarenko. *Zhurn. Neorganic. Khim.* 8 (10) (1963) 2276–2280.
- [26] R.W.J. Scott, N. Coombs, G.A. Ozin. *J. Mater. Chem.* 13 (2003) 969–974.
- [27] W.J. Barreto, S.R. Giancoli Barreto, I.M. Yoshio Kawano. *Quim. Nova* 29 (6) (2006) 1255–1258.
- [28] F. Arroyo, O. Font, C. Fernández-Pereira, X. Querol, R. Juan, C. Ruiz, P. Coca. *J. Hazard. Mater.* (2009), doi: 10.1016/j.jhazmat.2009.01.021.
- [29] D. C. Montgomery. *Design and Analysis of Experiments*. 6th Edition. John Wiley & Sons, Hoboken, NJ, 2005.
- [30] F. Arroyo Torralvo. Recuperación del germanio presente en la ceniza volante producida en una planta GICC que emplea carbones de la cuenca de ENCASUR en Puertollano. Ph.D. Dissertation (in Spanish). Departamento de Ingeniería Química y Ambiental. Escuela Superior de Ingenieros. Universidad de Sevilla. 2007.