Germanium recovery from gasification fly ash: Evaluation of end-products obtained by precipitation methods

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ABSTRACT

In this study the purity of the germanium end-products obtained by two different precipitation methods carried out on germanium-bearing solutions was evaluated as a last step of a hydrometallurgy process for the recovery of this valuable element from the Puertollano Integrated Gasification Combined Cycle (IGCC) fly ash. Since H_2S is produced as a by-product in the gas cleaning system of the Puertollano IGCC plant, precipitation of germanium as GeS_2 was tested by sulfiding the Ge-bearing solutions. The technological and hazardous issues that surround H_2S handling conducted to investigate a novel precipitation procedure: precipitation as an organic complex by adding 1,2-dihydroxy benzene pyrocatechol (CAT) and cetyltrimethylammonium bromide (CTAB) to the Ge-bearing solutions. Relatively high purity Ge end-products (90 and 93% hexagonal-GeO_2 purity, respectively) were obtained by precipitating Ge from enriched solutions, as GeS_2 sulfiding the solutions with H_2S, or as organic complex with CAT/CTAB mixtures and subsequent roasting of the precipitates. Both methods showed high efficiency (>99%) to precipitate selectively Ge using a single precipitation stage from germanium-bearing solutions.

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1. Introduction

Germanium is a valuable element used in the production of novel and high technological industrial applications. For instance in the manufacture of advanced electronic and optical devices, fibre optics, as a polymerisation catalyst in polyethylene terephthalate plastics, in the field of photovoltaic cells and in the manufacture of thermal solar cells [1,2]. Germanium occurs widely disseminated in the earth crust (1.5 ppm, worldwide average [3]). Important contents of this element (5–10% and 6.3–7.7%) are found exclusively in the germanite–renierite ore bodies of Tsumeb and Kipushi deposits, Namibia [4]. In ore deposits it is commonly found substituting for zinc in sphalerite framework structure [5], and other sulfide species [3]. Germanium is also found as argutite (tetragonal-GeO_2, insoluble in water), usually substituting for SiO_2 in silicates but rarely as water soluble hexagonal-GeO_2 [3]. The zinc ores have large and recoverable quantities of Ge, so nowadays zinc ore processing is

the main Ge source. Besides, around 30% of the germanium used in the world is obtained from recycled materials, basically electronical devices [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 basins [6–11] and, usually, it is concentrated in coal combustion/gasification fly ashes that can reach Ge contents 10 times higher than in coal [12–15]. Commercial Ge end-products are mainly Ge metal and GeO_2, with different purity upon producers.

The industrial recovery of Ge is usually based on hydrometallurgical processes with high economic and environmental cost. 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 proposed recovery processes of Ge from fly ash are similar to those proposed from the recovery from Zn ores. Zouboulis et al. [16] prompted a hydrometallurgical procedure for extracting Ge from fly ash based on H_2SO_4 and NaOH leaching and subsequent Ge recovery from extracted solutions by ion flotation. Other studies reported a recovery of Ge by acid leaching directly from brown coal and subsequent distillation of $GeCl_4$ without filtration of extracts [17], by tannin precipitation [18], by ion exchange [19] or by solvent extraction [20,21].
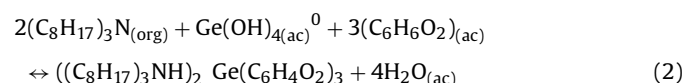
As an alternative to the extraction methods mentioned above, the occurrence of Ge as water soluble species (GeS$_2$, GeS and hexagonal-GeO$_2$) in the fly ash from the 335 MW Puertollano IGCC power plant (Spain), fed with a 50:50 blend of a local metal-rich bituminous coal [22] and pet-coke [23,24], may help to find a low cost and environmentally acceptable germanium recovery process from fly ashes, ending with a commercial Ge end-product. The annual production of Puertollano IGCC plant fly ash is over 12,000 tonnes. The research on the extraction of germanium with water from the Puertollano IGCC fly ash [25] 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 [16,26], adsorption on activated carbon (AAC) [27,28] or solvent extraction (SX) [29,30]. 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 respectively 256 and 1623 mg/L. These 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) [31–33]:

$$Ge(OH)_4{}^0 + 3C_6H_4(OH)_2 \leftrightarrow Ge(C_6H_4O_2)_3{}^{2-} + 2H^+ + 4H_2O \qquad (1)$$
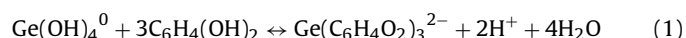
The solvent extraction method is based in the study of Andrianov and Avlasovich that described the extraction of Ge and catechol complex with trioctylamine (TOA) diluted in kerosene at room temperature [34,35]. The equilibrium extraction of Ge–CAT complex by TOA in kerosene is given by the following the overall reaction:

$$2(C_8H_{17})_3N_{(org)} + Ge(OH)_{4(ac)}{}^0 + 3(C_6H_6O_2)_{(ac)}$$
$$\leftrightarrow ((C_8H_{17})_3NH)_2\, Ge(C_6H_4O_2)_3 + 4H_2O_{(ac)} \qquad (2)$$

Once the Ge is in the organic phase, two stripping possibilities are apparently possible, because the ternary complex is not stable in strong acidic or alkaline solutions [29,34].

The adsorption onto activated carbon process [27,28] is based on the use of the activated carbon such as sorbent of the Ge–CAT complex and its subsequent desorption in acid media.

These results led towards the investigation of precipitation processes for germanium from the Ge-bearing solutions as a last step of a hydrometallurgy process for the recovery of this valuable element from the Puertollano IGCC fly ash. This article focuses on evaluating the feasibility of two different methods for the precipitation of germanium from Ge-bearing solutions arising from the Puertollano IGCC fly ash leachates was reported.

Due to the low solubility of GeS$_2$ acid in media [3], and the production of H$_2$S in IGCC plants, the precipitation of germanium by sulfiding the leachates may be considered as a potential method to precipitate germanium. The precipitation of Ge as GeS$_2$ occurs

according to reaction (3) where Ge in strong acid HCl medium is expressed as simple cationic species (Ge^{4+}) although it is known that germanium chloride hydrolyses readily to form a complex (GeCl$_6{}^{2-}$) [36]:

$$(GeCl_6)^{2-} + 2H_3O^+ + 2H_2S + 4H_2O \leftrightarrow\downarrow GeS_2 + 6H_3O^+ + 6Cl^- \qquad (3)$$
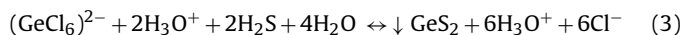
This precipitation method was employed in the recovery of germanium in certain metal mines, such the Apex mine [3] and in "Musto Exploration" process [37]. Furthermore, this precipitation method may give a high isolation potential for germanium from the impurities (other metals) in leachates. This was based on the different sulfide solubilities of these metals at a certain pH [38]. It gives high potential isolation efficiency for Ge, and consequently a high purity GeO$_2$ end-product would be made by roasting the precipitated Ge sulfide.

Furthermore, the use of this gas stream for the precipitation of Ge may reduce the economic costs of the recovery process. However the handling of H$_2$S may suppose significant technological and hazardous problems, so a novel recovery process based on precipitating Ge with cetyltrimethylammonium bromide (CTAB) and catechol (CAT) was also investigated.

The CTAB is a quaternary ammonium salt used as surfactant on detergent industry. Quaternary ammonium surfactants widely provide crystalline molecular complexes with various aromatic compounds as catechol. Barreto et al. [39] claimed that highly stable Mn(II) and Fe(II) complexes with catecholate and semiquinonate ligands could be precipitated with CTAB.

The Ge–CAT complex has a high solubility in water probably due to its polarity, but when CTAB is added to an aqueous solution that contains the Ge–CAT complex, the CTA$^+$ cation and the Ge–CAT complex form a heavy ion pair (PM = 641.8) that precipitates according to the following mechanism:

$$2CTA^+ + GeCAT_3{}^{2-} \leftrightarrow CTA_2GeCAT_3 \qquad (4)$$

Reaction (4) agrees with the mechanism proposed by Scott et al. [40] for the complex CTA$_2$SnCAT$_3$.

2. Experimental

Germanium precipitation as GeS$_2$ was tested by sulfiding the Ge-bearing solutions with H$_2$S. It gives high potential isolation efficiency for Ge, and consequently a high purity GeO$_2$ end-product would be made by roasting the precipitated Ge sulfide. However, limitations of this process may suppose significant technological and hazardous issues that surround H$_2$S handling as previously noted. The Ge precipitation as organic complex was tested by adding CTAB to aqueous solutions that contains the Ge–CAT complex.

2.1. Precipitation of germanium as sulfide

A number of precipitation tests were carried out using solutions with low (35 mg/L), intermediate (140–256 mg/L) and high (787–1623 mg/L) germanium concentration. Low content solutions were obtained by single water extraction from the IGCC fly ash (90 °C, water/fly ash ratio of 5 L/kg and 6 h) reported by Font et al. [25]. Intermediate and high content solutions were obtained by single water extraction using these optimal conditions and subsequent enrichment by germanium sorption onto activated carbon (AC) [27,28] and solvent extraction (SX) method [29,30], respectively. Low content solutions were characterised by slightly acidic pH (6–6.7), while intermediate and high content solutions by a strong acidic pH given by the use of HCl 1N for desorption of Ge from AC or strong acidic or alkaline pH, being dependent on the striping agent (HCl (1N) or NaOH (1N)) used during the SX enrichment process. Therefore, these Ge-rich solutions may contain high
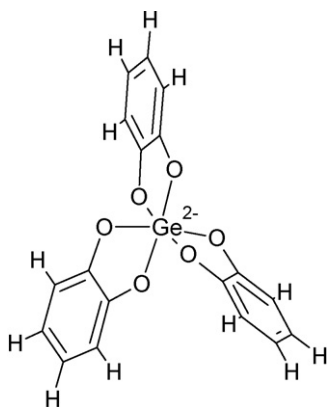

Fig. 1. CAT–Ge complex schematic structure.

Na amounts (20.8 g/L), 12 times higher than germanium content, and may be a major limit to achieve a high purity end-product.

Experimental equipment for Ge precipitation tests with H_2S was based on four connected gas washing vessels coupled to H_2S and (N_2 or CO_2) cylinders (obtaining different H_2S/N_2 and H_2S/CO_2 ratios to reach the H_2S concentrations, selected for the precipitation tests, see below). The reaction occurred in the first vessel, which contains the Ge extracted solution, while the next vessel (empty) prevents a potential contamination of Ge solution in case of a flow return. The third vessel was employed for the sorption of the excess H_2S with a 5N NaOH solution and the last vessel containing a $Cd(NO_3)_2$ solution was used to assure that complete retention of H_2S in the previous vessel (appearance of a yellowish turbidity due to CdS formation is a very sensible reaction).

Precipitation tests sulfiding the solutions were carried out by controlling pH (0–7), HCl concentration (1–6N), H_2S concentration in the gas flow (10–100%) and the H_2S/metal ratio (1:1 the theoretical stoichiometric ratio required for the precipitation reactions considered, 2:1 (two times this ratio) and the H_2S saturation). In order to achieve a H_2S saturation in the solution, the H_2S input flow was adjusted to that necessary to precipitate metals according to stoichiometric H_2S/metals ratio plus the theoretical amount of H_2S needed to saturate the solution. These amounts of H_2S were calculated supposing that reaction times were long enough to achieve the full dissolution of H_2S into the aqueous phase. Variations in H_2S/metals ratio and in H_2S concentration in gas flow meant changes in H_2S input time for each experience. H_2S/N_2 (10:90, 30:70, 50:50 and 100:1, v/v) mixtures were used to test the influence of the H_2S concentration in the gas flow for the precipitation of Ge. H_2S/CO_2 (50:50, v/v) mixtures were then used to adjust experiment to gas composition near to that one of the H_2S stream (claus gas) of the IGCC plant. The H_2S/CO_2 gas flows ranged from 31 to 40 N mL/min for every component during 10–60 min. The addition of flocculants to facilitate filtering of Ge precipitates and, the effect on the purity of the Ge end-product of the use of NaOH or HCl as stripping agents in previous enrichment steps were also evaluated. Organic flocculants were used since those are volatilized during the roasting of the Ge precipitates avoiding reduction of the purity of the Ge end-product.

The Ge precipitates obtained were subsequently roasted at 500–700 °C for 4 h, to obtain GeO_2 as a Ge end-product.

2.2. Precipitation of germanium as organic complex

The precipitation tests with CTAB were focused on evaluating the selective precipitation efficiency of germanium, and the optimisation of the experimental parameters (reagents order of addition, amount of CAT and CTAB and pH). The effect of the SX separation procedure prior precipitation on the purity of the germanium end-product was also evaluated.

The following Ge-bearing solutions were used as starting materials for the germanium precipitation with CTAB: (a) standard germanium solutions (50 and 100 mg/L), (b) leachates from IGCC fly ash water extraction (35 mg/L) and (c) enriched Ge-bearing solutions (700 and 1500 mg/L) by the SX method.

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. After complete dissolution of both, CAT and CTAB, the pH was adjusted by adding the appropriate amount of 4N NaOH or 2N H_2SO_4. A number of batch precipitation tests were performed by mechanically shaking the mixtures in 250 mL glass vessels at room temperature for 30 min to assure a complete dissolution of both reagents. The solutions were then maintained stationary for 1 h for the precipitation advance. The precipitates obtained were filtered through ALBET 145

Table 1
Precipitation of Ge, As, Sb and Ni sulfides from low Ge content solutions at pH ranging from 1 to 7 and at HCl 6N and H_2S saturation conditions with 100% H_2S in gas flow.

	pH					HCl (6N)
	7	5	3	2	1	
Ge	<0.1	2.7	0.2	10.6	14.0	95.6
As	99.6	98.7	97.6	98.3	99.3	97.1
Sb	99.9	100	99.4	100	99.9	34.0
Ni	57.1	59.7	4.2	0.9	0.1	<0.1

filters (ash content < 0.007%) with a pore size of 7–11 μm, washed and subsequently dried at 110 °C for 2 h. To reach high purity germanium end-product the precipitates were roasted in an oven in cycles of 7 h at 750 °C. The heating cycle was repeated two times until constant weight was achieved.

2.3. Analysis

The content of major and trace elements were analysed in the solutions before and after the precipitation experiments, and also in the precipitates as well as in the Ge end-products after digestion, by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). A special two-step sample digestion method for the analysis of potentially volatile elements devised by Querol et al. [23] was used to dissolve the solid samples (precipitates and Ge end-products) prior to the analysis. The crystalline and amorphous components of precipitates and Ge end-products were studied by X-ray diffraction (XRD) and scanning electronic microscopy using energy dispersive X-ray analyser (SEM–EDX).

3. Results and discussion

3.1. Precipitation of germanium as GeS2

The results of the precipitation tests by sulfiding Ge-bearing solutions revealed that >99% of germanium can be precipitated from leachates by a single sulfiding step using 100% H_2S and 50:50 H_2S/CO_2 gas mixture, on enriched Ge leachates previously acidified up to HCl (6N) (Table 1 and Figs. 2 and 3).

As, Sb and Ni are the major impurities to take into account in the precipitation process for obtaining high purity of Ge end-products, due to the relatively high contents in IGCC fly ash and their relatively high water extraction yields [23]. At the above Ge precipitation conditions >73% of As, >65% of Sb and 55–61% of Si precipitate, while close to 100% of Ni remains in solution. It has to be noted that Si was precipitated only at the mentioned conditions. Although the relatively high proportions of Si precipitated, due to the low content
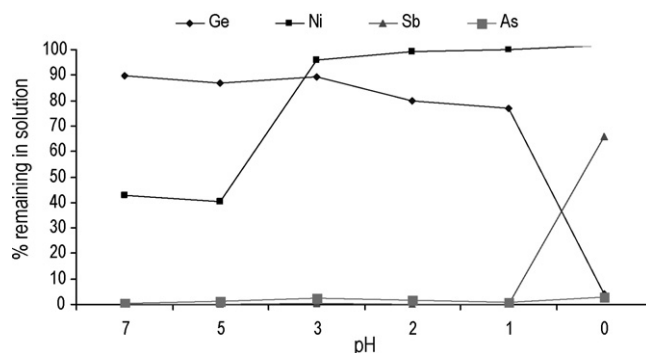

Fig. 2. Percentage of Ge, Ni, Sb and As in the low Ge content solutions after saturating them with H_2S, for pH ranging from 1 to 7 and at HCl (6N) and with 100% H_2S in gas flow.

Table 2
Proportions (%) of Ge and As, Sb and Na precipitated from intermediate and high Ge solutions enriched by AAC and SX methods and stripped with HCl and NaOH in the precipitation test by sulfuring the leachates with H_2S using 50–100% H_2S flows and under H_2S saturation conditions.

	Sulfiding steps						
	1st step (AAC HCl)	2nd step (AAC, HCl)		Single (AAC HCl)	Single (SX, NaOH)	Single with flocculant addition (SX, NaOH)	Single (SX, HCl)
H_2S (vol.%)	100	100	50	100	100	100	50
HCl (M)	1	6	6	6	6	6	6
Element	Precipitation						
Ge	37	52	56	>99.9	99	>99.9	99
As	99	<1	<1	73	>99	>99	80
Sb	>99.9	<0.01	<0.01	<0.01	67	91	75
Na	<0.01	<0.01	<0.01	0.3	22	23	0.1

AAC, HCl: enrichment methods; HCl, NaOH: stripping agents.
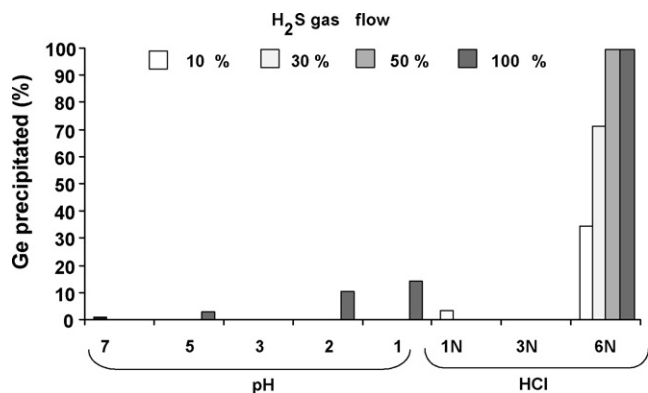
Fig. 3. Precipitation of germanium sulfide from low Ge leachates at different HCl concentrations, H_2S/metal ratio with gas mixtures of H_2S.

of this element in the starting leachates suggest a low significant effect on the purity of the Ge end-product.

Regarding the major impurities (As, Sb and Ni), A different pH precipitation of Ge from those was found for 100% H_2S gas flow and H_2S saturation conditions (Table 1 and Fig. 2). The precipitation of these major sulfide impurities occurs in the following pH ranges (Table 1 and Fig. 2):

(a) As: close to 100% of the As in the leachates is precipitated for all the pH range selected.
(b) Sb: from pH 7 to 1 around 100% of Sb was precipitated, but only a low proportion of this element (close to 30%) precipitated when HCl 6N (pH 0) was added to the leachates.

(c) Ni: only partial precipitation of this metal occurred at pH from 7 to 5 (~50%), close to 100% remained in solution at pH < 5 and at HCl 6N (pH 0).

This differential precipitation of Ge from major impurities could allow isolating Ge by applying two sulfiding steps at different pH and/or HCl concentrations improving the purity of the precipitated and consequently that of the Ge end-product. Nevertheless, when the Ge content in the solutions was high (100–1625 mg/L), a significant proportion (37%, Table 2) of this element precipitated during the first sulfiding step (HCl (1 M)) and consequently lost for its recovery. This may be due to the high Ge/impurities ratio coupled with the use of saturated H_2S/metal ratio conditions. Therefore, the theoretical differential precipitation of Ge and As and Sb sulfide species reported by Hanusch et al. [38] and demonstrated in this study (Table 1 and Fig. 2) is only effective for solutions with low Ge concentrations (<100 mg/L).

The precipitates obtained show the occurrence of hexagonal-GeO_2 instead the expected GeS_2 or GeS. Since GeS_2 is easily hydrolysable [3], it may be hydrolysed to form hexagonal-GeO_2 if the precipitated is washed enough. These solid products were made up of fine crystals of hexagonal-GeO_2 surrounded by an amorphous matrix of Ge and S (probably amorphous GeS and/or GeO_2 and S^0). The low Ge purity of the precipitates avoids considering those as Ge end-product and a subsequent roasting step is necessary to reach high purity GeO_2. The results on the chemical composition of the precipitates allowed adjusting the amount precipitated and the remaining amount in the leachates, certifying that potential loss of mass not take place during the precipitation process.

Relatively high purity Ge end-products (91–93% GeO_2) were produced by roasting at 700 °C for 4 h the germanium precipitates obtained by sulfiding the leachates enriched by AAC and by SX with
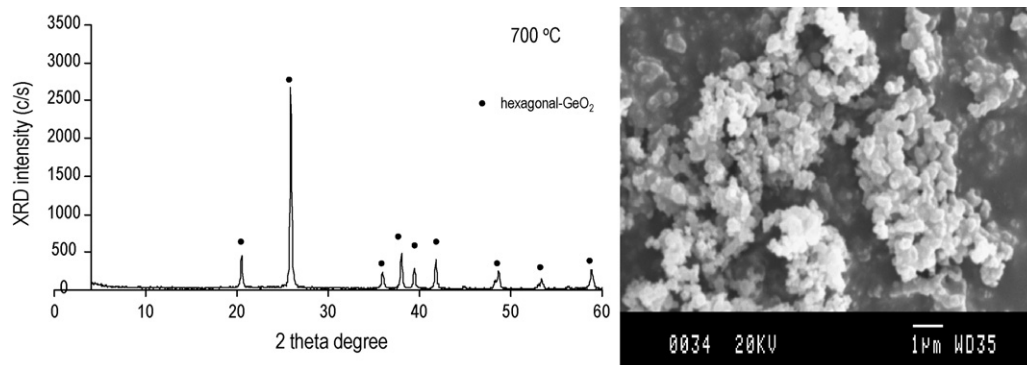
Table 3
Composition of the Ge end-products obtained by roasting the solid products precipitated sulfiding enriched Ge solutions.

Enrichment method	AAC[a] (HCl[b], 500 °C)	AAC[a] (HCl[b], 700 °C)	SX[a] (NaOH[b], 700 °C)	SX[a] (HCl[b], 700 °C)
GeO_2 (%)	72.00	91.20	5.90	93.00
NaCl (%)	0.10	0.40	84.20	0.50
S (%)	19.60	0.20	1.20	0.10
As_2O_5 (%)	2.60	0.20	0.10	0.10
Sb_2O_5 (%)	0.05	0.20	2.00	0.10
Al_2O_3 (%)	0.20	0.30	0.20	2.00
CaO (%)	0.10	0.30	0.10	0.30
Fe_2O_3 (%)	0.06	0.20	0.20	0.40
K_2O (%)	0.09	0.30	5.80	0.30
MgO (%)	0.02	0.07	0.05	0.09
MnO (%)	0.003	0.01	0.07	0.009
P_2O_5 (%)	0.06	0.20	0.07	0.20
Mo_2O_5 (%)	0.004	0.02	0.30	0.04
NiO (%)	0.008	0.08	0.03	0.06

[a] Enrichment methods.
[b] Stripping agents.

Fig. 4. XRD spectrum and SEM image of the #4 Ge end-product (93% purity) obtained by roasting Ge precipitate at 700 °C and 4 h. The SEM images revealed the very fine particle size (<1 μm) of the Ge end-products.

HCl stripping (Table 3). The highest GeO$_2$ purity (93%) was obtained for solid product enriched by SX method with HCl stripping (Table 3 and Fig. 4). The GeO$_2$ crystals produced show a very fine particle size (<1 μm, Fig. 4). Even though this Ge end-product was obtained using a single sulfiding step), the content of major impurities (As, S, Al, Ca, Mg and K species) is <0.5% (Table 3) improving the suitability of applying a single sulfiding step for precipitate Ge from solutions with high Ge/impurities ratios.

It can be noticed that the use of NaOH for the stripping of Ge during the SX enrichment results coupled with the acidification with HCl results in a high NaCl content (84%) in the precipitate obtained after sulfiding. Since NaCl is stable up to 800 °C, the occurrence of high proportions of this salt reduced drastically the purity (6%) of the Ge end-product. Furthermore, low roasting temperatures (550 °C) also reduced significantly the purity of the Ge end-product (from 91% to 72% GeO$_2$, Table 3) due to the low S loss.

It can be concluded that relatively high purity GeO$_2$ end-product (91–93%) was obtained by roasting at 700 °C and 4 h the Ge precipitates obtained by leachates (using 100% H$_2$S and 50:50 H$_2$S/CO$_2$ gas mixture), on enriched germanium-bearing solutions previously acidified up to HCl (6N) arising from water extraction from the Puertollano IGCC fly ash with subsequent enrichment in HCl media by using AAC and/or SX extraction).

3.2. Precipitation of germanium as organic complex

The precipitation tests of germanium as CAT–Ge–CTA organic complex revealed that 99% of Ge can be precipitated from enriched Ge-bearing solutions by adding CAT (CAT/Ge molar ratio of 5) and CTAB (CTAB/Ge molar ratio of 3) at pH 11 and room temperature, after 1 h of contact.

The following effects of the experimental parameters on the precipitation of Ge as organic complex were observed:

(a) The pH is a very important factor in the Ge precipitation. The highest Ge precipitation yield was obtained at pH 13 (>99% Ge precipitated) decreasing slightly down to 97% when pH decreases to 8.9 and down to 40% at acid pH (4.1). The pH also affected the size of precipitated particles, enlarging them as pH was increased. On one hand this would allow an easy filtration; but on the other hand, pH increased viscosity of the solutions, most probably due to the oxidation of catechol [41], which makes quick filtration difficult. Thus, an alkaline range of pH (9–11) was selected as the optimal pH for precipitation of germanium with CTAB.
(b) The germanium precipitation is high (>97% of Ge precipitated) when the pH was adjusted after CAT and CTAB addition. When the pH adjustment was previous to the addition of both reagents, the precipitation of germanium decreased most prob-

ably due to the oxidation of catechol that avoids the ion pair formation. At pH > 13, germanium precipitation was less than 5%.
(c) As expected from the precipitation equilibrium (Eq. (4)) the increase in the amount of catechol added (up to five times the CAT/Ge molar ratio) improves the precipitation of germanium from 86–89% (achieved with the stoichiometric ratio CAT/Ge = 3/1) to 90–94%.
(d) The occurrence of remaining catechol in the final solutions from the SX enrichment process accounts for a slight increase of the precipitation yields of germanium (98.7% (1N NaOH solution) and 92.2% (1N HCl solution)) as compared with that obtained with standard solutions (94%) at pH 9.
(e) On the other hand, the occurrence of impurities in fly ash water leachates produces a slight reduction of the precipitation yields of germanium (23.5 mg/L that means 90%) when compared with standard and with enriched solutions. From water leachates, only small quantities of As (0.2 mg/L), Mo (0.6 mg/L), Mg (0.2 mg/L), Ni (0.4 mg/L), P (0.2 mg/L) and Sb (8 mg/L) were precipitated.
(f) Apart from Ge, only Sb (36 and 50% when HCl and NaOH enriched solutions from SX were used, respectively) and Na (only when NaOH enriched solutions from SX were used) precipitated, so the precipitation method is highly selective for germanium. Other elements such as As, Mn, Ni, V or Zn remained in solutions.
(g) The SX Ge-enriched solutions (purified extract) contained catechol, so the precipitation without adding fresh CAT to the solutions was also checked. To this aim only CTAB (CTAB/Ge molar: 3) was added to a purified extract (1N NaOH) obtained using the SX enrichment method. The pH was then adjusted to 13. The Ge precipitation yield reached only 5.4%, probably because

Table 4
Composition of the Ge end-products obtained after roasting the organic precipitates.

| Solution	R #6 Basic extract	R #7 Acid extract	R #9 Acid extract	R #8 Leachate
GeO$_2$ (%)	78.10	90.20	91.40	87.10
Al$_2$O$_3$ (%)	<0.50	0.80	1.70	2.55
CaO (%)	1.30	3.10	1.10	0.81
Fe$_2$O$_3$ (%)	0.20	0.40	0.30	1.16
MgO (%)	0.20	0.20	<0.30	0.12
MnO (%)	ND	ND	ND	ND
Na$_2$O (%)	18.10	5.00	3.70	<1.00
As (%)	0.005	0.003	0.002	0.04
B (%)	0.04	0.04	0.01	0.008
Ba (%)	0.01	97.9	0.01	0.005
Cu (%)	0.06	0.02	0.04	0.01
Mo (%)	<0.001	<0.001	<0.03	1.86 (Mo$_2$O$_3$)
Ni (%)	0.005	0.008	0.008	0.23 (NiO)
Sb (%)	0.001	0.006	0.006	3.48 (Sb$_2$O$_5$)

ND: not detected.
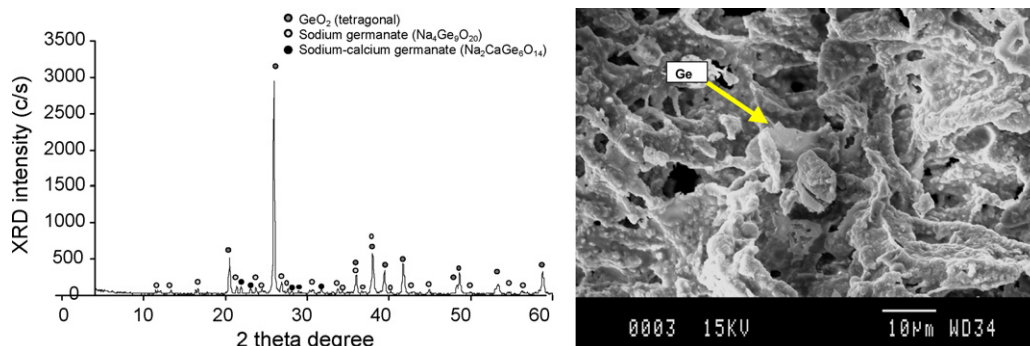
Fig. 5. XRD spectrum and SEM image of the Ge end-product #7 (90.2% purity) in which only small crystals were observed.
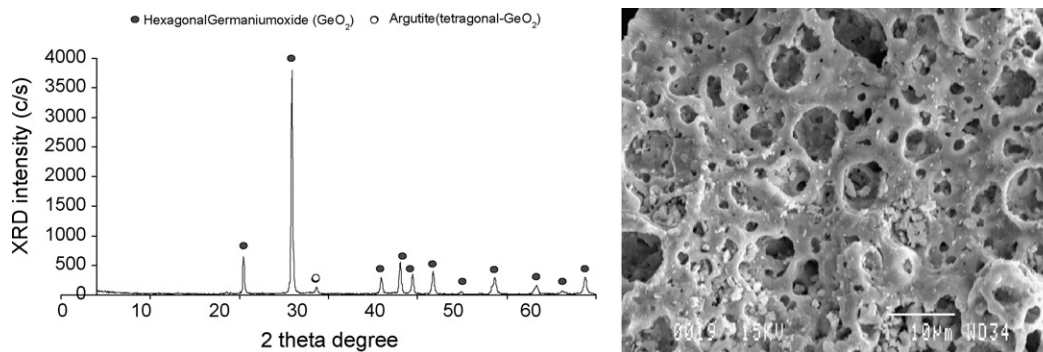

Fig. 6. XRD spectrum and SEM image of the Ge end-product #8 (94.9% purity).

the amount of catechol or the form of the reagent in alkaline solution (or both factors) did not allow the precipitation.

Total removal of organic matter was not achieved in tests and analyses of roasted solids showed organic matter (after several experiments the organic content was around 20%). In Table 4 the composition of the precipitates referred to the inorganic fraction is shown. A 90% GeO_2 purity may be produced (Table 4) by roasting of the organic complex precipitates coming from the HCl stripped (enriched) Ge-bearing solutions with tetragonal-GeO_2 as the major component with traces of sodium–calcium germanates ($Na_4Ge_9O_{20}$ and $Na_2CaGe_6O_{14}$) (Fig. 5). The roasted precipitates from leachates showed an 87.1% of GeO_2 (Table 4 and Fig. 6), with some minor impurities such as: Al_2O_3, CaO, Fe_2O_3, Mo_2O_3 and Sb_2O_5. The SEM microphotographs (micrographs) showed small crystals (2–3 μm) sometimes included into an organic porous matrix, probably CTAB not volatilized during roasting. Less purity germanium end-products (78% GeO_2) were obtained by this precipitation–roasting method when NaOH enriched germanium solutions were used as starting material for precipitation. In this case, the high amounts of Na promoted the formation of Na germanate species instead of GeO_2.

It can be concluded that relatively high purity GeO_2 end-product (90%) was obtained by roasting at 750 °C and 7 h the germanium precipitates obtained by adding stoichiometric CAT and CTAB amounts at pH 11, room temperature and 1 h of contact, to leachates extracted with water from the Puertollano IGCC fly ash and subsequently enriched by SX and stripped with HCl (1N).

4. Conclusions

High purity Ge end-products can be obtained by two different precipitation procedures (as GeS_2, sulfiding the solutions with H_2S, and as organic complex with CAT and CTAB) from Ge-bearing solutions arising from the water extraction of the Puertollano IGCC fly ash. Both precipitation methods showed high efficiency (>99%) to precipitate selectively germanium in a single stage precipitation. The best conditions found in the two precipitation methods studied are summarised as follows:

For the precipitation of germanium as sulfide, 93% hexagonal-GeO_2 purity was reached by roasting at 700 °C and 4 h the Ge precipitates obtained by sulfiding leachates (using 100% H_2S or 50:50 H_2S/CO_2 gas mixture, on solutions previously acidified up to HCl 6N) arising from the Puertollano IGCC fly ash water extraction with subsequent enrichment in HCl media by using AAC and/or SX extraction. The main limitations for the germanium recovery process proposed in this study may be the difficult handling of H_2S (g), so that the use of this gas is restricted to a potential germanium recovery plant set at the own IGCC facility, in which the ash is produced.

(a) A 90% tetragonal-GeO_2 purity can be achieved by roasting at 750 °C and 7 h the precipitates obtained at room temperature and pH 11 by adding CAT and CTAB at CAT/Ge and CTAB/Ge molar ratios of 5 and 3 respectively, to the Puertollano IGCC fly ash water leachates, subsequently enriched by SX and stripped with HCl (1N), after 1 h of contact. The main limitation of this precipitation method is the occurrence of germanium species (germanates) other than the hexagonal-GeO_2 and the difficulty of removing organic matter when roasting. Future work is conducted to achieve complete organic matter elimination.

(b) The complete hydrometallurgical process for the recovery of germanium from IGCC fly ash proposed may be summarised as follows: (a) extraction of germanium from IGCC fly ash at 90 °C with a water/fly ash ratio of 5 L/kg and 6 h extraction time using pure water, (b) optional subsequent enrichment by AAC or SX method (HCl media), and (c) precipitation sulfiding a 6N HCl germanium-enriched solution with H_2S flows (100% H_2S or 50:50 H_2S/CO_2) and subsequent roasting at 700 °C and 4 h or precipitation by the addition of CAT (CAT/Ge = 5) and CTAB

(CTAB/Ge = 3), and pH adjustment (9–11) and subsequent roasting at least at 750 °C during 7 h.

Using the above-mentioned optimal conditions, the total germanium recovery from IGCC fly ash yielded 50–62%, enabling a theoretical production of 3500 kg of GeO_2/year with the current annual production of fly ash in the Puertollano IGCC power plant. Although further purification of the Ge end-product obtained is mandatory for obtaining the high grade purity GeO_2, requested for many of the current industrial uses of germanium [3], the purity of the Ge end-products obtained after the proposed recovery process from IGCC fly ash is much higher than that obtained by other industrial germanium recovery processes.

Acknowledgements

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