Ion flotation of germanium from fly ash aqueous leachates

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Abstract

The germanium – together with other metals and metalloids contained in the fly ash generated in the Integrated Gasification in Combined Cycle (IGCC) of Elcogas plant (Puertollano, Spain) – may be extracted by aqueous leaching. Here we report the study of the selective recovery of germanium from aqueous leachate by means of ion flotation, using a complexating agent and a surfactant as collector. The use of different ligands with dodecylamine as collector and the effect of the pH were evaluated. The optimal conditions found for germanium recovery are: catechol as complexating agent, triple stoichiometric ratio of the reagents and pH 4–7. In these conditions, germanium recovery was 100% and the extraction of impurities was reduced. The recovered froth was burned and characterized by thermogravimetric analysis (TGA), X-ray fluorescence (XRF) and X-ray diffraction (XRD). A high Ge product (53% GeO_2) was obtained.
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1. Introduction

Germanium is a rare element, which has not been found free in nature; its compounds are widely disseminated in the Earth's crust (6.7 ppm worldwide average) [1]. The optical properties of Ge allow a range of industrial applications, especially in equipment used for detecting and measuring infrared radiation, to which it is transparent. Since GeO_2 has a high refractive index, it is used as a component of glass for optical fibre devices such as cameras and microscope objectives. Furthermore, Ge is used in the manufacture of transistors and components for electronic devices [2] such as rectifiers and photocells, which require a high degree of purity.

Germanium is found in ore deposits, mainly as a substitute for Zn in sphalerite, but also in Cu, Ag, Fe, Ge sulphides such as germanite, argyrodite, renierite, briarite and canfeldite. It is also found as an oxide, mainly argutite (tetragonal-GeO_2), usually substituting for SiO_2 in silicates. Ge also occurs in different amounts in coal, being concentrated and enriched in coal ash during coal combustion and gasification [3–6]. Therefore, coal fly ash is a potential source of Ge. However, only the Russian production of Ge is based mainly on recovery from coal ash, and Ge is produced elsewhere largely as a by-product of Zn processing [7].

Germanium is usually extracted with a pyrometallurgical route, this being followed by a separation process, such as distillation of germanium tetrachloride from 6 N HCl solution, solvent extraction, or ion exchange [8,9].

The industrial interest in the recovery of Ge stems from its high market price (as GeO_2 €474/kg [10]) and its suitability for the manufacture of technological devices, primarily infrared optics and semiconductors [7].

The 335 MW Integrated Gasification Combined Cycle (IGCC) plant of Elcogas in Puertollano (Spain) was launched in 1992 as a THERMIE Targeted Project. Since the plant has been operating commercially, it has been shown that coal can be used with high efficiency (45% net, ISO conditions) with reduced emissions. With a gasifier capacity of 2600 tonnes fuel/day and 200 and 135 MW for gas and steam turbines, respectively, the Puertollano IGCC plant burns a 50:50 blend of a local metal-rich bituminous coal [11] and petroleum coke. The annual production of Puertollano IGCC power plant solid by-products is 12,000

tonnes of fly ash and 90,000 tonnes of slag. The IGCC technology produces fly ash with an uncommon speciation for most elements, such as Ge [6,12]. In the Puertollano IGCC fly ash, Ge occurs largely as water-soluble species, i.e. GeS_2, GeS and hexagonal-GeO_2 [12].

This speciation, together with the relatively high Ge contents in the fly ash of the Puertollano IGCC facility (200–420 mg/kg) [12] allowed the development of a water extraction process for this element [13]. This study demonstrated that high Ge extraction yields (up to 84%) can be achieved using pure water. However, water extraction is not selective and other elements are extracted together with Ge. The content of impurities and the low Ge content in the leachates may be the main limitations for a feasible Ge recovery process from Puertollano IGCC fly ash. For this reason, our research focused on the development of feasible Ge recovery process from leachates arising from water Ge extraction from Puertollano IGCC plant. Since H_2S is produced as a by-product in this plant, a recovery process based on a selective sulphide precipitation was initially designed. However, limitations of this process may arise from the significant technological and hazardous problems associated with the use of H_2S. For this reason other recovery processes, such as ion flotation, were proposed.

The recovery of valuable metals coming from fly ash and other germanium-containing minerals has been studied elsewhere. Zouboulis et al. [9,14] describe the Ge recovery by means of leaching in water or preparation of artificial solutions as well as industrial processes used in order to achieve maximum efficiency in recovering metals combine hydrometallurgical route and physical separation methods (such as ion flotation).

This work showed that the ion flotation is a good method for the recovery of Ge when its concentrations is of the order of parts per million. In this study, several ion flotation tests were carried out on the leachates arising from water Ge extraction from Puertollano IGCC fly ash. These tests were performed using different reagents, and ligands under different pH values and reagents concentrations. The main objective of this research is to evaluate the selectivity of this process for the recovery Ge and the purity of the Ge product.

2. Methods and materials

Previous to the ion flotation tests, water Ge extraction experiments were carried out to obtain the Ge leachates. These tests were performed on Puertollano IGCC fly ash (#129) produced under current feed conditions (50:50 coal/petcoke blend, 2.5% limestone addition) of this facility. An exhaustive characterization of IGCC fly ash has been published elsewhere [12] and the main chemical characteristics of this fly ash are summarized in Table 1. The optimal Ge extraction conditions (90 °C, water/fly ash ratio (W/FA) = 5 L/kg), 6 h, mechanical stirring, 500 rpm) from Puertollano IGCC fly ash prompted by Font et al. [13] were selected. Applying these extraction conditions on the IGCC fly ash used in this study, relatively high Ge extraction yields (68%) can be achieved.

Leaching experimental trials were performed in a 1000 mL closed glass vessel with water flow cooling at atmospheric pres-

Table 1
Chemical analysis of IGCC fly ash sample #129

Major elements as oxides	Concentration (%)	Minor elements	Concentration (mg/kg)
SiO_2	52.29	Ni	2268.0
Al_2O_3	21.92	Pb	4330.0
CaO	3.35	Rb	309.8
Fe_2O_3	4.27	Sb	338.1
K_2O	3.90	Sc	47.2
MgO	0.61	Se	18.6
MnO	0.03	Sn	30.9
Na_2O	0.61	Sr	112.0
TiO_2	0.62	Th	22.8
P_2O_5	0.49	Tl	14.4
SO_3	3.35	U	11.8

Minor elements	Concentration (mg/kg)	Minor elements	Concentration (mg/kg)
Ag	<9.8	V	6047.0
As	898.3	W	19.8
Ba	445.9	Zn	6963.0
Be	14.8	Zr	159.8
Bi	7.5	Ce	121.4
Cd	26.9	La	59.1
Co	62.4	Pr	14.9
Cr	109.5	Nd	62.3
Cu	356.9	Sm	13.4
Ga	324.4	Eu	2.5
Ge	432.1	Gd	13.6
Hf	4.8	Tb	1.9
Li	270.7	Dy	10.7
Mo	139.5	Ho	1.9
Nb	16.1	Er	5.7
Nd	62.3	Yb	5.0

sure. The content of major and trace elements on the resulting leachates were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and mass spectrometry (ICP-MS). The mean contents for major and trace elements in the leachates are listed in Table 2, the Ge contained in the leachate was 52 mg/L.

The ion flotation experiments were performed at 25 °C, using a laboratory flotation machine KHD Humboldt Wedag AG with a flotation cell of 1500 mL of capacity. Each batch used 1000 mL of fly ash extraction solution that was vigorously stirred after the addition of the reactants. Dodecylamine was used as collector, and it was pre-dissolved in ethanol to facilitate its addition [15]. Pyrogallol, catechol, hydroquinone and resorcin were evaluated as ligands. Thus, the parameters studied were the complexating agent used, the molar ratios, the pH and the flotation time. All the reagents used were of analytical grade, and for those experiments changing the pH values, it was adjusted with NaOH 2 M or HCl 3 M.

Thermogravimetric analysis (TGA) of the froth recovered at the optimum conditions was performed using a Setaram TG DTA92 thermobalance, heating rate of 10 °C/min under oxygen atmosphere. Semi-quantitative analysis of the solid obtained was performed by X-ray fluorescence (XRF) and the crystalline phases were examined by X-ray diffraction (XRD).

Table 2
Relative percentage to total trace contained in the leachate

Element	Concentration (%)
Al	1.14
As	12.27
Ba	0.02
Be	0.05
Ca	2.63
Cd	0.35
Co	0.04
Cr	0.01
Cu	0.04
Fe	0.03
Ge	9.40
Mg	1.79
Mn	0.04
Mo	0.07
Ni	6.05
P	0.88
S	9.22
Sb	8.65
Se	0.09
Ti	0.02
V	0.31
Zn	0.21
Total	100

Table 3
Metal concentration using stoichiometric ratios of pyrogallol and dodecylamine

Element	Recovery (%)
Al	51.7
As	50.2
Ca	7.9
Cd	3.8
Ge	55.3
Mg	26.2
Ni	50.0
P	71.4
S	0.5
Sb	31.5
V	54.2

Fig. 1. Metals recovery employing double stoichiometric ratio of pyrogallol and dodecylamine.

The course of the flotation experiments was followed by sampling 2 mL aliquots at different time intervals, immediately filtered through 0.45 μm membrane filters and the liquid filtrate analysed by ICP-OES.

The recovered metal is calculated as:

$$R = \left[1 - \left(\frac{C_t}{C_0}\right)\right] \times 100 \qquad (1)$$

where R is the metal recovery, C_t the metal concentration at a given time and C_0 is the initial concentration.

3. Results and discussion

3.1. Concentration of reagents

The stoichiometric molar ratio of Ge, the complexing agent and the surfactant is 1:3:2 [16]. The recovery results in a preliminary flotation experiment using the theoretical molar ratio of pyrogallol and dodecylamine, at room temperature for 80 min, are shown in Table 3. Other metals were also recovered in high percentages by ion flotation, thus reducing the yield of recovered Ge. This result agrees with previous studies [14,17] also describing the recovery of As and Pb by ion flotation. Thus, an excess of reagents was found necessary to completely recover the Ge. As shown in Table 2, only the analysis of those elements that present a high concentration in the leachate was considered necessary for this study.

The molar ratio was then duplicated and triplicated to evaluate the effect of the excess of reagents on the Ge recovery as a function of time. The results obtained showed a relatively high Ge recovery (up to 57%) when using the double stoichiometric ratio (Fig. 1) whereas 95% Ge can be recovered if the triple stoi-

chiometric ratio is used for reaction times above 120 min (Fig. 2). The recovery of the main impurities (Ni, As, Sb) attained below 15% using double and triple stoichiometric ratio (Figs. 1 and 2).

3.2. Ligand

Pyrogallol (1,2,3-benzenetriol) forms a very stable complex with Ge [8] because of the presence of two OH groups in Ge–pyrogallol complex structure. Ge also forms complexes
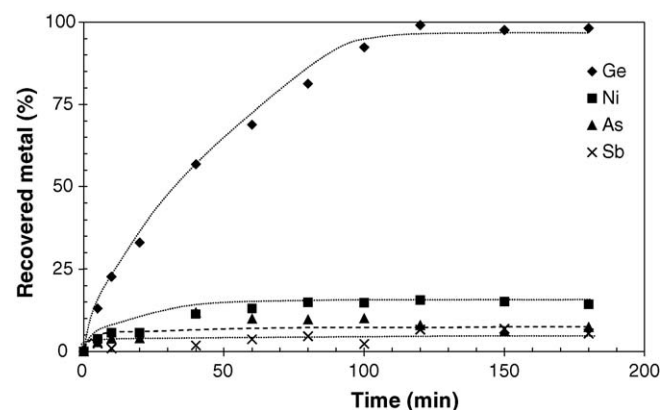

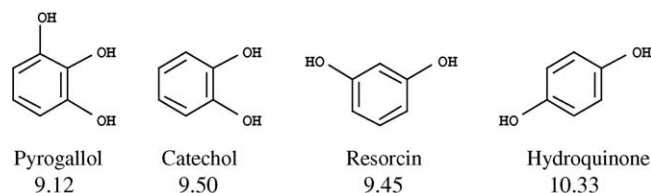Fig. 2. Metals recovery using triple stoichiometric ratio of pyrogallol and dodecylamine.

Pyrogallol 9.12   Catechol 9.50   Resorcin 9.45   Hydroquinone 10.33

Fig. 3. Chemical structures and pK_a of the complexing agents used.

with other chemical substances with similar structure, such as catechol (1,2-benzenediol) [18], resorcin (1,3-benzenediol) and hydroquinone (1,4-benzenediol), all of which were evaluated as possible complexing agents. The chemical structures of these flotation reagents and their first pK_a are represented in Fig. 3.

Experimental series were performed on the Ge leachates arising from IGCC fly ash, described above, triplicating the molar ratio of ligand and using dodecylamine as collector.

After the addition of the ligand, the pH value of the solution decreased to 4–4.5, depending on the ligand, in agreement with Pokrovski and Schott [18]. Table 4 shows the results of the mean recovery of Ge and the main impurities for a flotation time of 90 min. These results reveal that the highest Ge recoveries were obtained for pyrogallol and cathecol, ligands having OH in positions 1 and 2 in the chemical structure. Low Ge recovery rates, 34 and 20%, were obtained using resorcin and hydroquinone, respectively. Simultaneously to high Ge recovery yields, low As (<24%) and Sb (<17%) but high Ni (55 and 45%) recovery yields were achieved when using pyrogallol and cathecol (Table 4).

With pyrogallol as ligand, the tiple stoichiometric ratio was found the best experimental condition. The same ratio was then used with catechol. Ion flotation with catechol as a function of time was evaluated and the obtained results are depicted in Fig. 4. Comparing these results with those obtained with pyrogallol (Fig. 2), it may be observed that Ge may be completely recovered in a short time. However, higher short-term recovery yields were also obtained for the main impurities (Ni, As, and Sb).

A mechanism for the reaction between Ge and catechol is proposed, taking into account that suggested by Zouboulis and Matis [9] and other considerations such as the Ge speciation and the working pH. According to Font et al. [12,13], in Puertollano IGCC fly ash, Ge occurs in high proportions as high water soluble hexagonal-GeO$_2$ and relatively high water soluble Ge sulphides. The hydrolysis of this species by water leaching

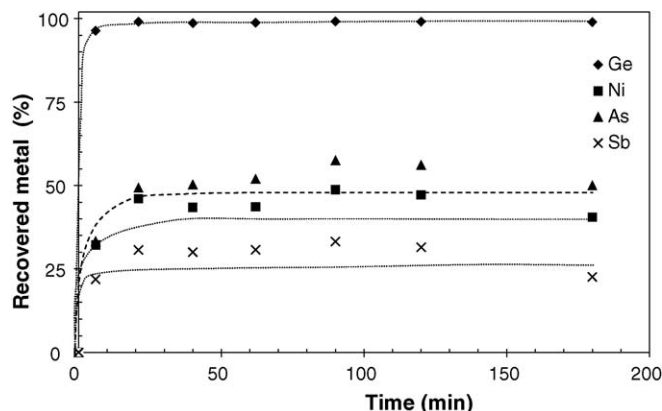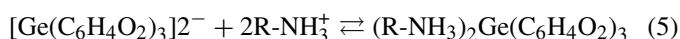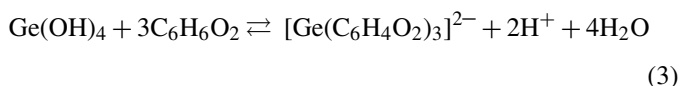Fig. 4. Metals recovery triplicating stoichiometric ratio of catechol and dodecylamine.

of IGCC fly ash generates Ge tetrahydroxide (Ge(OH)$_4$) in the leachates. Furthermore, in accordance with Pokrovski and Schott [19], Ge(OH)$_4$ is the dominant species at the working pH as can be seen in Fig. 5.

The proposed reaction mechanism is the following:

$$GeO_2(hex) + 2H_2O \rightarrow Ge(OH)_4 \qquad (2)$$

$$Ge(OH)_4 + 3C_6H_6O_2 \rightleftarrows [Ge(C_6H_4O_2)_3]^{2-} + 2H^+ + 4H_2O \qquad (3)$$

$$R\text{-}NH_2 + H^+ \rightleftarrows R\text{-}NH_3^+ \qquad (4)$$

$$[Ge(C_6H_4O_2)_3]2^- + 2R\text{-}NH_3^+ \rightleftarrows (R\text{-}NH_3)_2Ge(C_6H_4O_2)_3 \qquad (5)$$

3.3. Effect of pH

The effect of the leachate pH value was evaluated for pyrogallol and catechol, since these ligands provide the best results for Ge recovery. A series of experiments were performed using four pH values: very acidic (pH < 2), weakly acidic (pH < 5), slightly alkaline (pH < 9), and alkaline pH (pH > 10). The acidic solution was obtained by adding hydrochloric acid 3 M and the alkaline solution was achieved with sodium hydroxide 2 M. pH was adjusted after the addition of the complexing agent. The

Table 4
Recovery by ion flotation using different complexing agents at triple of the stoichiometric ratio

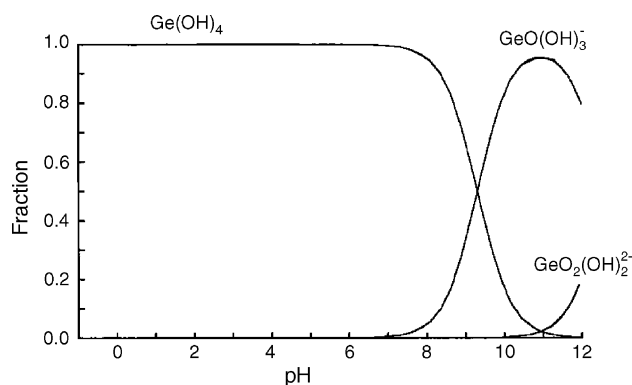| Ligand	Recovery (%)			
	Ge	As	Sb	Ni
Pyrogallol	100	13	13	55
Catechol	100	24	17	49
Resorcin	34	43	32	56
Hydroquinone	20	19	20	23

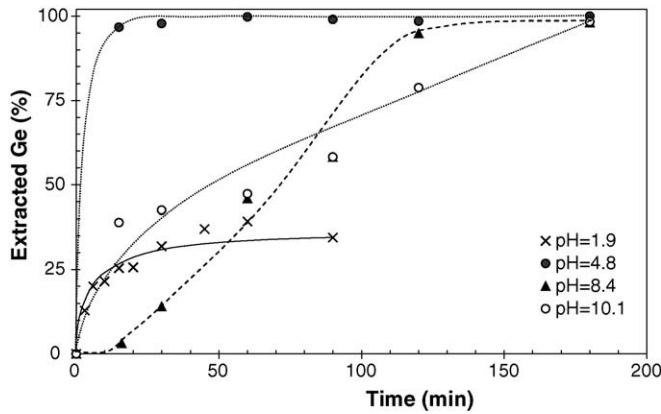Fig. 5. Species distribution diagram as function of pH.

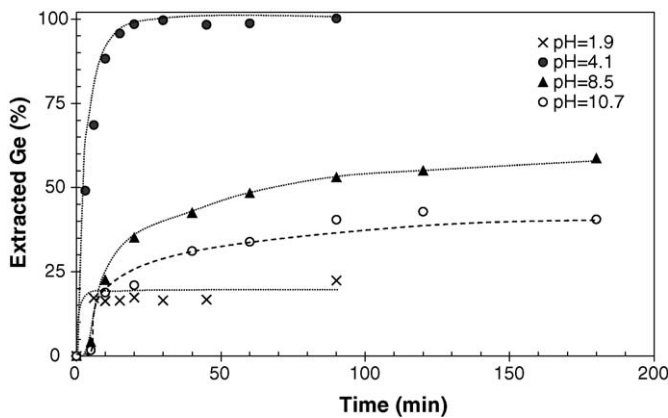Fig. 6. Ge recovery at different pH values using pyrogallol.

Fig. 7. Ge recovery at different pH values employing catechol.

results are depicted in Figs. 6 and 7 for pyrogallol or catechol as ligands, respectively. Each pH result is the mean value of three experimental series.

Tables 5 and 6 illustrate the recovery of the other studied elements (As, Sb, and Ni) at the t_{Ge} time, which is defined as the minimum time to obtain the highest Ge recovery. These results

Table 5
Metals extraction using pyrogallol at t_{Ge} time for maximum Ge recovery

pH	Recovery (%)		
	As	Sb	Ni
1.9	10	57	9
4.8	13	13	55
8.4	17	23	85
10.1	21	17	99

Table 6
Metals recovery employing catechol at t_{Ge} time for maximum Ge recovery

pH	Recovery (%)		
	As	Sb	Ni
1.9	20	48	18
4.1	24	17	49
8.5	16	10	80
10.7	31	31	73

reveal that 100% Ge recovery in a short time (15–20 min) was achieved at a pH between 4 and 5, independently of the complexating agent used.

Under these conditions, the lowest Sb and As recovery yields were achieved (Tables 5 and 6). However, Ni recovery still achieved high proportions (45 and 55%, Tables 5 and 6), the lowest being Ni recovery yields obtained for strongly acidic pH; however, since only low recovery of Ge is achieved, this condition was avoided for the next experiments.

There were no significant differences between the use of pyrogallol or catechol, for Ge recovery (95% Ge in only 15 min and 100% in 30 min). Moreover, the optimal pH value is the one given by the ligand, thus avoiding acidification. Due to the significant lower price of catechol (seven times lower than pyrogallol), it was selected as the optimal complexating agent.

3.4. Recovery of floated Ge complex

The optimal conditions for recovering Ge were fixed: triple stoichiometric ratio of catechol and dodecylamine and 4–7 pH. Ion flotation experiments led to the formation of a froth that was collected and dried at 105 °C for 24 h.

The recovery of floated Ge complex was carried out by means of a roasting process. The roasting temperature was determined by a thermogravimetrical analysis of the floated Ge complex at a heating rate of 10 °C/min and oxygen atmosphere. Fig. 8 illustrates the TGA result showing that the weight loss due to the organic matter oxidation and volatilisation takes place at temperatures lower than 600 °C, this being the fixed roasting temperature used for further experiments.

3.5. Characterization of roasted Ge complex

A semi-quantitative analysis of the roasted solid was performed by means of X-ray fluorescence followed by X-ray diffraction to determine crystalline phases in the sample. Table 7 shows the XRF results, thus revealing that the main constituents are Ge oxides and nickel oxides. Fig. 9
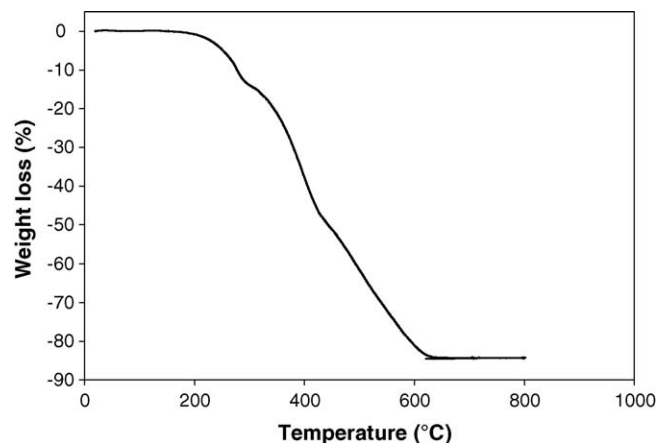

Fig. 8. Thermal decomposition of the froth containing the Ge complex.

Table 7
Results of the semi-quantitative XRF analysis of the roasted Ge complex

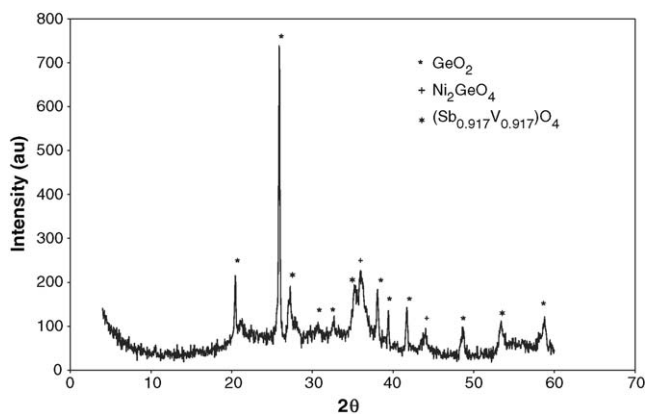| Oxides	(%)
Na_2O	0.6
Al_2O_3	3.9
SiO_2	0.7
P_2O_5	1.4
SO_3	0.1
K_2O	0.7
CaO	0.6
Fe_2O_3	1.3
V_2O_5	1.1
Cr_2O_3	0.1
MnO	0.2
CoO	0.2
NiO	21.9
CuO	0.1
ZnO	0.8
GeO_2	53.0
As_2O_3	9.3
MoO_3	0.3
Ag	0.1
Sb_2O_3	2.9
WO_3	0.3
PbO	0.4

Fig. 9. XRD pattern of the roasted Ge complex.

illustrates the XRD pattern, with the major Ge oxide peaks identified.

4. Conclusions

At laboratory scale, it was demonstrated that ion flotation is an effective method for recovering Ge from IGCC fly ash water leachate when the concentration is about tens of ppm.

The Ge complex formation is strongly influenced by the location of the OH group, and pyrogallol and cathecol are the most interesting ligands for Ge recovery, whereas neither resorcin nor hydroquinone was found to be selective for the complex formation.

The maximum Ge recovery in the lowest flotation time was achieved with weakly acidic pH values. The optimal pH is reached at natural pH without the addition of acid solutions. According to the equilibrium reaction (see Eq. (3))

and the acidity constants of the complexing agents, should be thought that the best flotation conditions are achieved under alkaline pH values, since in these conditions the lost of acidic protons is favoured. On the other hand, the reaction is optimized with the highest $Ge(OH)_4$ contents, which take place in a pH range of 1–7 as shown in Fig. 5. For this reason a compromise between acidic and alkaline pH values should be assumed.

The optimal conditions for pre-concentrating Ge from leached IGCC fly ash are the following: dodecylamine as a surfactant, catechol as a ligand because of its lower cost and pH values of 4–7. Under these conditions, 100% of Ge is recovered in only 30 min, and the recovery of some impurities was reduced.

Roasting the Ge-containing froth at temperatures above 600 °C leads to a high Ge dioxide final product having nickel oxide as major impurity, followed by As, Sb, Al, Si, P, V and Fe. A high purity GeO_2 may be obtained by this recovery procedure, thus reducing the content of some impurities in the leachates.

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