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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.

Keywords: IGCC fly ash; Coal gasification; Germanium; Leaching; Ion flotation; Recovery

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

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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.

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

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 pressure. 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).