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Low environmental impact process for germanium recovery from an industrial residue

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ABSTRACT

This paper focused on the germanium recovery from an Integrated Gasification with Combined Cycle fly ash (IGCC FA). The global process comprised the leaching of the IGCC fly ash with an aqueous solution containing tartaric acid, retention of the germanium-tartaric chelate onto a conventional anionic resin (IRA-900) and elution of germanium. The last step consisted of the germanium precipitation which was accomplished with tannic acid. The leaching experiments were performed with tartaric aqueous solutions and with the raffinate from the subsequent ion-exchange (IX) step. Raffinate from the IX step can be reintroduced in the process as leaching solution. When the contact between FA and leaching solution was maintained for 3 h at $pH = 1$, the Ge leaching efficiency achieved 86%. The effect of pH, resin dosage and tartaric acid dosage on the Ge retention onto the IRA-900 resin was investigated employing a centered composite rotatable design (CCRD) for experimental design and analysis of results. The retention of Ge-tartaric acid complex onto IRA-900 was optimized using design-expert software and the optimum predicted efficiency and loading capacity were 90–98% and 3.0–3.5 $mg{\cdot}g^{-1}$. The experimental affinities that IRA-900 showed for the elements extracted (leached) were: Ge > > Sb > V > Ni > As > Sn > B > Zn. Different eluting solutions were tested, and more than 90% of Ge elution was achieved with 2 M HCl. Final solutions contained Ge, Sb and V. Precipitation tests focused on the optimum pH for Ge precipitation adding tannic acid to the elution solutions. A 99.3% of Ge was precipitated from eluting solution, adding 33.3 g of tannic acid per g of Ge. V also precipitated in some extent along with Ge but the rest of elements practically remained in solution.

1. Introduction

The estimated germanium (Ge) in the Earth's crust concentration is within the 1–7 ppm range, but its extraction is not easy, since it is quite dispersed and is concentrated only in some minerals. Since its application is extended to new and high valued fields, the germanium recuperation from residual products is an interesting issue. One of these raw materials containing low contents of germanium (sometimes only a few ppm, except in rare cases) and considerable quantities of other elements is coal fly ash (Font, 2007). After leaching of coal fly ash, generally an acid aqueous solution containing Ge at low concentrations along with other metals such as Zn, Cu or Fe is obtained. Many techniques have been developed to separate germanium from other elements contained in those leachates including distillation of $GeCl_4$ (Jandova et al., 2001), flotation (Matis et al., 1988; Hernandez-Expósito et al., 2006), solvent extraction (Menendez et al., 1989) and sorption onto exchange resins (Harada et al., 1988). One way to increase the selectivity of the previous techniques can be achieved by using a chelating agent. The formation of germanium complexes with carboxylic acids (acetic, salicylic, oxalic, citric, and tartaric acids) and phenolic compounds (phenol and catechol) is well known and has been widely investigated (Pokrovski and Schott, 1998). The published results showed that Ge forms stable chelate complexes with di- and tri-carboxylic acids. For instance, the adsorption of Ge from aqueous solutions on activated carbon impregnated with tartaric, oxalic, and citric acids has been reported in several papers (Evdokimov and Kogan, 1974), as well as the adsorption of the Ge-catechol complex onto activated carbon (Marco et al., 2006). Solvent extraction of catechol-, oxalic acid- or tartaric acid-Ge complexes have been reported (Menendez et al., 1989; Arroyo and Fernandez-Pereira et al., 2008; Liang et al., 2012; Kuroiwa

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et al., 2014; Kamram et al., 2018a). Also, tartaric acid-germanium complexes sorbed onto chelating resins from alkaline solutions have been reported by Chirkst et al. (2008). Recently, the possibility of selective recovery of Ge studying the transport of the Ge-tartaric acid complex from synthetic solutions through supported liquid membranes has been studied by Kamram et al. (2018a, 2018b).

Another process widely used for Ge recovery from aqueous solutions is precipitation. For instance, Hollness published in 1954 the precipitation of germanium by tannin addition form oxalate solutions, McCrory-Joy (1985) reported the GeO_2 precipitation from oxalate solutions by a electrolytic procedure, Menendez et al. (1989) reported the precipitation of polygermanate after a solvent extraction process from tartaric acid solutions and Liang et al. (2008) obtained a germanium precipitate by tannin addition from synthetic solutions similar to those obtained in Zn metallurgy processes. Thus, germanium can be precipitated from oxalate solutions adding tannic acid, which forms large floccules easy to filter. In contrast, this precipitate drags some impurities (Schoeller and Powell, 1932; Holness, 1948). Hilbert (1982) has reported the Ge recovery from Zn bearing solutions by means of tannic acid precipitation in an industrial plant of Bleiberger Bergwerk-Union. According to Liang et al. (2008) in China Ge is produced almost exclusively as by-product of the Zn industry and most of the hydrometallurgical plants are based on the Ge complexation-precipitation with tannic acid. The most recent literature concerning recovery of Ge from secondary sources is addressed to one of the stages of the process here described, such as leaching (Gonzalez et al., 2016; Li et al, 2012 or the following removal or concentration stages (Nusen et al., 2015; Kamram et al., 2018a). Also references exist describing a global Ge recovery process (Chen et al., 2017; Liu et al. 2017a, 2017bLiu et al. 2017a, 2017b).

In previous research works (Arroyo and Fernandez-Pereira, 2010; Arroyo and Fernandez Pereira, 2011), the germanium retention onto conventional anionic resins was tested from standard solutions and real leachate solutions after previous complexation with catechol. The papers demonstrated the possibility of achieving a selective retention of germanium using conventional anionic resins from aqueous fly ash leachates by adding catechol. However, the proposed procedure has two drawbacks: (1) the catechol amount consumed is high and due to its price, the process could not be commercially competitive, and (2) the amount of process water used (especially in the leaching stage) is also very high, and it could be a handicap for the implementation of the process at an industrial scale. The present study addresses these two problems, replacing catechol by a more accessible and cheaper reagent, such as tartaric acid and studying the possibility of the reintroduction of the raffinate in the process as leaching solution instead of fresh water.

Regarding the leaching stage, it must be borne in mind that Ge in fly ash is in the form of germanium oxides and sulphides (Font, 2007) and that, on the other hand, these forms increase their solubility significantly in the presence of citric, oxalic, or tartaric acids (Pokrovski and Schott, 1998). Therefore, the addition of citric, oxalic or tartaric acid to the leaching solution is supposed to increase the Ge leaching efficiency. In the ion exchange (IX) stage, it was considered that Ge in solution and tartaric acid form an anionic complex at pH < 3 according to Eq. (1) (Pokrovski and Schott, 1998) and the complex may be retained by anionic resins (Eq. (2).

$$Ge(OH)_4^0 + H_3Tart^- \leftrightarrow Ge(OH)_2(HTart)^- + 2\ H_2O \quad (1)$$

$$R\text{-}NR_3Cl + Ge(OH)_2HTart^- \leftrightarrow R\text{-}NR_3Ge(OH)_2HTart + Cl^- \quad (2)$$

Based on this background the present study focused on the evaluation of a global process of Ge recovery from IGCC FA. For this purpose, each of the stages that comprise the hydrometallurgical process has been studied within the global process. Firstly, the leaching procedure was evaluated comparing the Ge extraction yield using tartaric acid solutions and the IX raffinates as leaching agents. In a second stage, the possibility of recovery the Germanium-tartaric complex from the leachates employing commercial anionic resin was evaluated, and finally, the precipitation of a germanium bearing solid was tested using tannic acid as precipitation agent.

2. Experimental

2.1. Materials

All reagents were analytically pure and used without further purification. IRA-900 in chloride form (from Rohm-Haas) was chosen according to a previous published work (Arroyo Torralvo et al., 2010). IRA-900 is a macroreticular strongly basic quaternary ammonium resin, with a total exchange capacity of 1 eq L^{-1}. Particle size is in the range 16–50 mesh (US std screens) and pore sizes are sufficiently large to absorb the germanium-tartaric acid complex.

Fly ash was produced in Puertollano IGCC power plant in 2009. An exhaustive characterization of IGCC fly ash has been carried out and the results have been published elsewhere (Font et al.., 2001, 2005; Aineto et al., 2016) in which the main chemical characteristics, granulometry and mineral composition by XRF-diffraction and scanning electronic microscopy using energy dispersive X-ray analyser (SEM-EDX) of the fly ash used in this study are shown. Main chemical components of the fly ash used in the present study (wt %) are: SiO_2 (59.3), Al_2O_3 (20.6), Fe_2O_3 (4.2), K_2O (3.5), CaO (3.2), SO_3 (2.4), and MnO (0.04). Ge content in this fly ash is 420 mg kg^{-1}. The content of fly ash in other minor components contents are shown in Table 1.

2.2. Process

The process proposed consists of four stages: leaching, sorption, elution and precipitation (Fig. 1). Because the two first stages (leaching and sorption-IX) are interdependent, firstly, the possibility of retaining the germanium tartaric acid complex by conventional anionic ion exchange resins was confirmed from standard solutions. A parametric study was performed to optimize the Ge retention onto the resins. Once optimal conditions were determined, the possibility of eluting Ge from resin was investigated. In a second phase the possibility of leaching fly ash using the raffinate from the IX step was checked. After checking each phase separately, the global process was performed.

2.3. Leaching procedure

Leachates were obtained by contacting coal fly ash with different leaching solutions at room temperature. The leaching procedure was performed in 500 mL agitated flasks at 20 °C. The liquid/solid ratio was chosen to be 5 and contact time was varied throughout the study. The leaching agent was aqueous solutions containing tartaric acid and raffinate from the ion exchange step. Tartaric acid content and pH were varied through the study. pH adjustment were performed adding 1 M H_2SO_4 to solutions. After the required contact time, fly ash and leachates were separated by filtration through a membrane filter (0.45 µm), and the filtrates were analysed for element contents by inductively coupled plasma-mass spectrometry (ICP-MS), model VG PLASMAQUAD PQ2.

2.4. Ion–Exchange procedure

All experimental tests were performed using a batch technique. In each experiment, 50 mL of pregnant solutions (containing

Table 1
Minor components of FA (mg kg^{-1}).

As	955	Co	53	Ga	320	Pb	4796	Sn	67
Ba	433	Cr	155	Mo	135	Sb	381	V	6256
Cd	24	Cu	392	Ni	2296	Se	19	Zn	7230

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