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Application of vacuum reduction and chlorinated distillation to enrich and prepare pure germanium from coal fly ash

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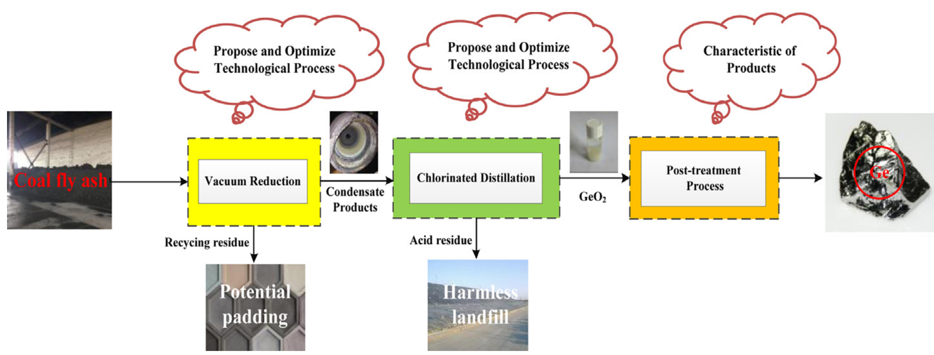
HIGHLIGHTS

- An integrated process of vacuum reduction-chlorinated distillation is proposed.
- Separation principles and reaction mechanism of process are clarified.
- A purity of 98.12 ± 0.54% germanium is obtained by this technological process.
- Environmental performance of this process is superior to traditional process.

GRAPHICAL ABSTRACT



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ABSTRACT

Germanium, as strategic reserve metal, plays critical role in high-tech industry. However, a contradiction of increasing consumption and scarcity of germanium resource is becoming more and more prominent. This paper proposed an integrated process to recycle germanium from coal fly ash. This technological process mainly consisted of two procedures: vacuum reduction with the purposes of enriching germanium and chlorinated distillation with the purposes of purifying germanium. Several highlights are summarized as follows: (i) Separation principle and reaction mechanism were discussed to understand this integrated process. (ii) Optimum designs and product analysis were developed to guide industrial recycling. The appropriate parameters for vacuum reduction process on the basis of response surface methodology (RSM) were 920.53 °C and 259.63 Pa, with 16.64 wt.% reductant, and for the chlorinated distillation process, adding 8 mol/l HCl and L/S 7, 8 wt.% MnO_2. The global recovery rate of germanium was 83.48 ± 0.36% for the integrated process. (iii) This process overcomes the shortages of traditional process and shows its efficiency and environmental performance. It is significant in accordance with the "Reduce, Reuse and Recycle Principle" for solid waste and further provides a new opportunity for germanium recovery from waste by environment-friendly way.

1. Introduction

Germanium (Ge) is a metallic element in group IVA of the periodic table. As a rare metal, germanium resource is extremely scarce in nature. The average abundance of germanium is only about 1.5 ppm in the earth crust and there is no independent germanium ore deposit [1]. Most of the germanium in the lithosphere is

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Table 1
Main Chemical Composition of Germanium-Rich Coal Fly Ash.

element	C	O	Si	Cl	S	Ca	Fe	Al	As	Zn	Pb	Cr
content(wt%)	46.3	24.66	5.96	6.24	1.96	6.53	3.57	2.57	0.44	0.28	0.09	0.01

associated with some other minerals, such as sphalerite, and Cu, Ag, Fe sulphides deposits [2–4]. It is also found as an oxide, mainly argutite (tetragonal-GeO_2, insoluble in water), usually substituting for Si in SiO_2 and rarely as water soluble hexagonal-GeO_2 [5,6].

Germanium has been as strategic reserve in some developed countries, due to strategic value for both civilian and military purposes, and it is a critical component of the high-tech industry. Specifically, germanium is used in integrated circuits, optoelectronic devices, semiconductors, and optics fiber etc. Germanium is consumed about 100 tons/year in global, but the reserve of germanium is only 8600 tons worldwide [7,8]. In 2015, the price of metallic Ge and GeO_2 have reached to 2000 and 1600 $/kg, respectively. A contradiction of increasing consumption and scarcity of germanium resource is becoming more and more prominent.

Lignite is often used as fuel for many small and middle scale coal-fired power plants [9]. In Yunnan and Inner Mongolia of China, there is a certain type of lignite, which contains rich germanium resource [10,11]. The content of germanium in lignite can reach 200 mg/kg, much higher than that of the other types of coal [12,13]. When germanium in lignite is burned into coal fly ash, the concentration of germanium could still reach ten or even dozens of times higher than that of feed coal [4,14,15]. Hence, this part of the coal fly ash containing germanium can be totally taken advantage of as resources. On the other hand, coal fly ash contains some toxic elements, such as arsenic. In case of being sent directly to landfill without taken advantage of, coal fly ash will cause both environmental damage and waste of resources.

In industry, recovery of germanium from wastes/tailings is based on pyrometallurgy and hydrometallurgical processes with high economic and environmental cost. Residue enriched in germanium is gained through pyrometallurgy. Then germanium could be extracted though hydrometallurgical process. At present, hydrometallurgical process to extract germanium mainly includes: tannin precipitation [16,17], distillation of strong acid [18,19], ion exchange/flotation [20–22], or solvent extraction [21,23]. F. Arroyo Torralvo et al. [24] studied germanium recovery from real fly ash leachates by using germanium complexation with catechol in an aqueous solution and followed by the retention of the Ge-catechol complex onto a anionic resin (IRA-900). Hydrometallurgical process for extracting Ge is feasible. But, there are still several defects: (1) some methods of solvent extraction have good separation of Ge from Zn, Cd, Ni, Co and As, but phase separation in the extracted liquid for Ge stripping is difficult [22]; (2) consumption of reagent is vast. Taking extraction through tannin for example, when the content of germanium is 26–45 mg/l in the solution, consumption of tannin is 23–33 times of the content of germanium [17]; (3) waste water and residues are produced and their cost of post-treatment and disposal would be increased.

Vacuum separating technology is mainly applied in the separation of alloy and ore deposits [25,26]. It has the advantages of high efficiency and better environmental properties. This technology does not need secondary off-gas or wastewater treatment. It can be considered as a complementary approach to hydrometallurgy [27]. In our previous study, this method has successfully separated indium from waste liquid crystal display panel and recycled copper, lead and zinc from waste printed circuit boards [28–30]. A vacuum dynamic flash reduction was used to remove arsenic and antimony from anode slime by Lin [31]. 98.92% arsenic and 93.67% antimony can be removed under 1083 K, 60 min, and air flow rate of 400 ml/min corresponding to the residual gas pressure of 250 Pa. Hence, vacuum technology can effectively separate some metals from wastes. In this study, we mainly focus on the preparation of pure germanium by a novel and comprehensive technology. Herein, an integrated technological process of vacuum reduction-chlorinated distillation was proposed to prepare pure germanium from coal fly ash. This process has three significant advantages: (1) an integrated vacuum reduction and chlorinated distillation process with a high recovery of germanium is proposed; (2) residues produced by vacuum reduction process are not hazardous wastes to avoid environmental pollution; (3) usage amount of acid were greatly reduced, due to only for the purification of enriched products. For vacuum reduction process, the principle and parameters were studied to get an optimal result which can meet industrial requirements. For chlorinated distillation process, the reaction mechanism and critical influence factors were investigated. Through the two-step processes, pure GeO_2 was prepared. Finally, pure germanium product was obtained through a reduction process.

2. Materials and methods

2.1. Materials and chemicals

A germanium-rich coal fly ash from Inner Mongolia province of China was chosen as sample. The reductant used in this study was coke powder (0.3-0.5 mm). An exploratory vacuum induction melting furnace was designed and fabricated by ourselves at laboratory scale (as shown SI Fig. S1). The vacuum melting apparatus consisted of three sections: furnace body, control cabinet, and vacuum pump team. Induction coil is used to heat the graphite crucible. The recovery unit was set on the condensed cover, which can recover the crude products enriched germanium through the way of condensation. For chlorinated distillation process, the distillation apparatus were set up. HCl, 30% H_2O_2 and MnO_2 were used in this study. The main components of germanium-rich coal fly ash by XRF analysis were shown in Table 1. The content of germanium in coal fly ash by measurement of benzfluorenone spectrophotometric method was 4986 mg/kg.

2.2. Design of technological process

Fig. 1 presented schematic diagram of an integrated recovery process of germanium. This process mainly consisted of two procedures: first procedure was vacuum reduction with the purposes of enriching germanium from coal fly ash. Crude products enriched germanium can be obtained by the procedure of vacuum reduction. In order to further purify the crude products, a chlorinated distillation process was proposed as the second procedure. The equipment of distillation was designed and set up. HCl was used as chlorinating agent in this experiment. The collection bottles containing a certain amount of water were used to absorb the germanium products. After the chlorinated distillation process, pure solid GeO_2 was gained. Finally, pure germanium can be prepared by a reduction reaction.

In vacuum reduction process, coal fly ash mixed with a certain dosage of reductant was placed in the graphite crucible of vacuum furnace. Opened vacuum pump and kept vacuum state of furnace body, and then sample was heated to certain temperature under vacuum. After the vacuum reduction process, the remaining residues were taken out from the graphite crucible, weighed, and