

Using Ion-Exchange to Recovery of Germanium from Waste Optical Fibers by Adding Citric Acid

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Abstract. Germanium is the raw metal of the optical fibers which become more important with the rapid development of optical communication in recent years. Owing to the importance of germanium and the problematic of waste optical fibers, we using the hydrometallurgical process to recovery germanium in this study. The process can be divided into two parts, the first part is pretreatment and leaching, the second is separation and metal recovery. In the first part, we collected the optical fibers and dissolved them by roasting and leaching. Then, the separation process which we used is ion-exchange. At the ion-exchange process, IRA900 is chosen as the resin and citric acid as the new addition agent, and other parameters were also considered. Finally, the metal oxides, GeO_2 , was obtained from the separation process through concentration and calcination. With the optimal conditions, the recovery rate of germanium is about 99%. The purity of obtained products is over 99%.

1. Introduction

Germanium is the rare metal in the earth which concentration only has 1-7 ppm [1] and it also is a useful element in optics and electronics. According to the U.S. Geological Survey research, the world reserve of germanium only has 8600 tons and it has none in mineable deposits [2]. With the semiconductor and optical industries increased demand for germanium, the European Union has listed germanium as a critical raw material in 2010 [3]. And germanium is also an indispensable strategic resource in the field of modern military applications [4]. In the global germanium consumer market, the largest amount of germanium used is fiber optics which account for 40% [4]. With the optical fiber technological advances and the demands of the Internet, the global optical fiber market would reach 3.72 billion U.S. dollars in the future [5]. However, germanium which added in the fiber would increase in demand. As the rare and important strategic metal resource, germanium would have the problem of underproducing, so recovering germanium in the future is necessary. And then, 30% of the germanium is obtained from recycled materials which like electronic devices or fly ash [4]. Because the lots of waste optical fibers would be produced and the value of germanium would increase, the process of recycling germanium from the waste optical fibers must be studied.

There are two major recycling ways for germanium recovery which are pyrometallurgy and hydrometallurgy. Pyrometallurgical process is the most used to recover germanium from coal [6]-[9], but it has the disadvantage of the high energy consumption and low purity products. On the other hand, the hydrometallurgical process is more suitable than the pyrometallurgical processes for treating optical fibers. The general hydrometallurgical processes for recycling germanium included chemical precipitation [10], [11], chlorination distillation [12], [13], solvent extraction [14]-[20] and ion-exchange [21]-[26]. Because of the separation efficiency, treating capacity, continuous operation and reusable of agents, the ion-exchange is the better way which was chosen in this study. According



to the literature, the germanium adsorption efficiency of cation resin is lower than anion resin and several anion resins have experimented, such as IRA900[21,22], IRA958[21], PA312[26] and D-403[23]. As mentioned above, it is required which makes germanium ion turn into the anion and it would be formed the anion complexes usually by adding agents, such like catechol[21], [22], [25], [26], 3-methylcatechol[25], [26] or oxalic acid [27]. However, the new agent we used in this study is the citric acid which also can complex with germanium and cheaper than other agents.

In this study, the optical fibers after pre-processing were dissolved in solution by alkali roasting and leaching. The amount of NaOH, pH value and solid-liquid ratio were experimented in this step. To optimize the adsorption efficiency of germanium, we choose IRA900 as the resin and citric acid as the new addition agent. The parameters such as the pH value, citric acid mole ratio and the concentration of eluting agent which is HCl were studied. Finally, we can recover germanium effectively and get high purity GeO_2 to reuse.

2. Experimental

2.1. Materials, reagents and instruments

The optical fibers samples were our targets in this study which collected from the waste cable. According to the previous study, the elements analysis was shown in Table 1 which could be found the concentration of germanium in the fiber was 0.1% and other is silica [28]. The sodium hydroxide (Applichem Panreac NaOH 98%) and sulfuric acid (Sigma-Aldrich H_2SO_4 98%) used as roasting and leaching agents and dissolved in deionized water. In the ion-exchange process, IRA900 (Alfa-Aesar) was used as resin, citric acid as the new addition agent (J.T.Baker 99.5%) and hydrochloric acid (Sigma-Aldrich HCl 37%) was used as eluting agent. Analyzing the germanium content for roasting, leaching and ion-change efficiency is used by Inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX). X-ray diffraction (XRD, Dandong, DX-2700) was used to determine crystalline phase of sample and the final product.

Table 1. Elements analysis of optical fiber powder

Elements	Ge	Silica	Fe	Mg	Ca
XRF analysis	0.11%	99.48%	0.23%	0.04%	0.13%
ICP analysis	0.1%	99.9	Not-detected	Not-detected	Not-detected

2.2. Roasting and Leaching

First of all, the optical fibers were collected from cables. Because the fibers contained silica[28], it should dissolve silica and take germanium out of them by alkali roasting. Adding NaOH at 500°C makes silica turn to sodium silicate and leach easily for its water solubility property. The parameters like NaOH/ SiO_2 mole ratio, pH value and solid-liquid ratio were investigated. The pH value was set from 1 to 7 and the effect of liquid-solid ratio from 10 to 100 ml/g which were tested to get better leaching efficiency.

2.3. Ion exchange and calcination

IRA900 was strongly basic resin which was used to exchange anion ions efficiently. In this study, we make germanium be the anion complexion by adding the new agent which is citric acid and the formation pH value of complexion is lower than 7[29]. We also compare the germanium adsorption efficiency without citric acid because germanium in high pH value would turn to anion that the pK_1 and pK_2 of germanic acid is 9.01 and 12.3[30]. At eluting step, we use HCl to strip germanium from resin. The parameters of the ion-exchange experiments were set, the pH value (1-14), addition agents mole ratio of germanium (1-6 mol/mol), bed volume number and eluting molarity(0.1-2M).

The eluting solution which contained lots of germanium was obtained after ion-exchange. The metal oxides can be received through calcination which the products were GeO_2 . The purity, composition and crystal phase of the product would be investigated in this study.

3. Results and Discussion

3.1. Roasting and Leaching

The optical fibers were roasting by adding NaOH at 500 °C and considered the NaOH/SiO₂ mole ratio effect. The result was shown in figure 1, that amount of NaOH is enough when mole ratio higher than 6. The figure 2 showed that fiber was actually turned to sodium silicate from silicon dioxide by XRD. After roasting, the fibers were leached by dilute H₂SO₄ and showed the pH value and liquid-solid ratio effect in the figure 3 and 4. It was found that germanium and silicon leaching rate decreased significantly at neutral environment in figure 3. The reason of that was that silicon would precipitate and germanium would be precipitated together when pH value at neutral. In figure 4, both of germanium and silicon leaching rate were decreased with the liquid-solid ratio decreasing because of the excessive silicon concentration and insufficient for volume of acid aqueous. The excessive silicon concentration would also make them precipitate that the leaching efficiency decreased. To sum up, adding 6 mole ratio of NaOH at 500 °C to roast and pH value lower than 5, 40ml/g at leaching step was chosen as optimal condition. Under this condition, the leaching efficiency were higher than 99.5%.

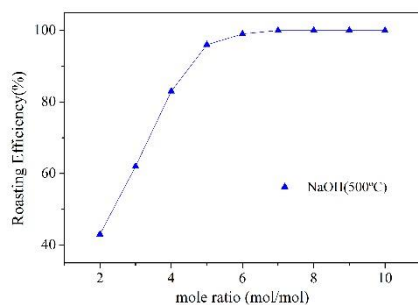


Figure 1. Effect of the roasting efficiency on NaOH/SiO₂ mole ratio.

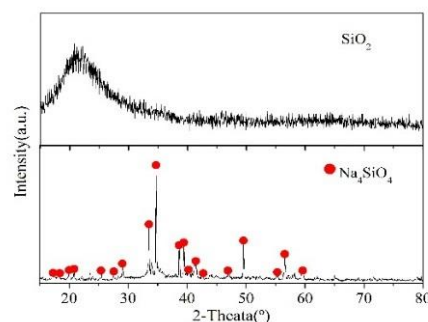


Figure 2. The XRD pattern of optical fibers after roasting.

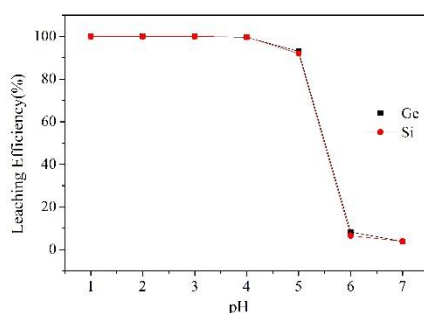


Figure 3. Effect of the leaching efficiency on pH value (L/S=40ml/g, 25 °C).

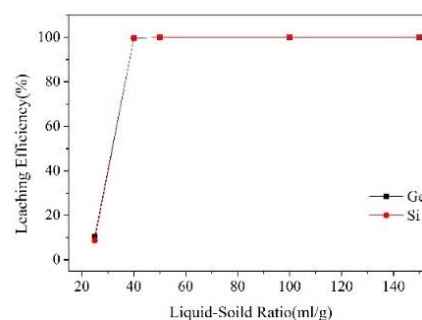


Figure 4. Effect of the leaching efficiency on liquid-solid ratio(pH=3, 25 °C).

3.2. Ion exchange

After leaching process, the elements were almost dissolved in the solution which the major elements were sodium, silicon and germanium. It was used ion-exchange to separate germanium from them in this study. The concentration ratio of germanium, silicon and sodium were set 25 、10000 、40000 mg/L which was based on the leaching result.

The figure 5a and 5b was shown that the relationship between pH value and adsorption efficiency of germanium. In figure 5a, the adsorption efficiency of germanium without adding citric acid(Cit) was obviously lower than adding Cit. For reasons outlined above, adding Cit is necessary for adsorbing germanium in this study. And then, it was also found that the silicon and sodium were hardly adsorbed and germanium had the highest adsorption efficiency at pH value equaled to 3 in the Figure 5b. By

comparing Cit with catechol[21], adsorption capacity of germanium by using Cit is higher than using catechol and the cost is lower than using catechol. It means using Cit as the new addition agent is usable for germanium adsorption. The result of figure 5c showed that Cit mole ratio effect for adsorption efficiency. At the molar ratio equal to 4, it has the highest adsorption efficiency of germanium. After adsorption, it was used HCl to elute germanium and the concentration effect was shown in Figure 5d. To get the best efficiency and benefit, the concentration of HCl to elute germanium is 1 mol/L. Based on the result, we did column experiments at the optimal condition which was chosen the pH value equal to 3, Cit/Ge molar ratio equal to 4, IRA900 as the resin and 1mol/L HCl as the eluting agent at 25 °C and its result were shown in figure 6a and 6b. At the optimal condition, the adsorption efficiency of germanium was 92% and silicon, sodium were both lower than 0.001%. After eluting, the recovery of germanium could be recycled to 99% by column in series.

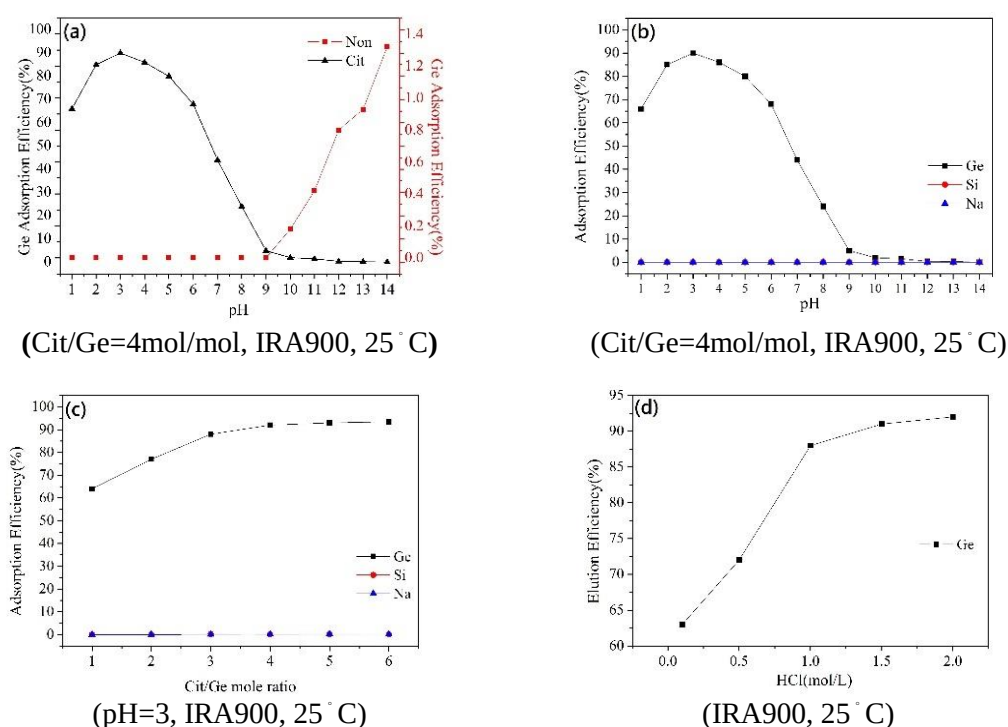


Figure 5. Effect of germanium adsorption or eluting efficiency on (a) addition Cit (b) pH, (c) Cit mole ratio, (d) concentration of HCl.

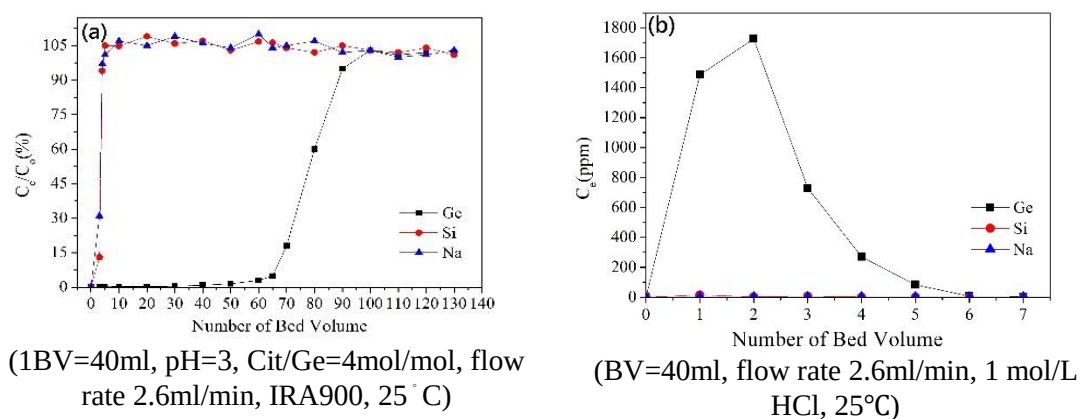


Figure 6. Column experiments for germanium (a) adsorption curve, (b) elution curve.

3.3. Calcination

After ion-exchange, germanium was enriched in eluting solution and separated from silicon and sodium. By concentrating and calcining, the TG and XRD analysis of the metal oxides are shown in figure 7 and 8. From the TG diagram, the temperature was set at 500 °C to turn into germanium dioxide. There is no impurity phase is detected and the ICP analysis also showed that the purity of GeO₂ is higher than 99%.

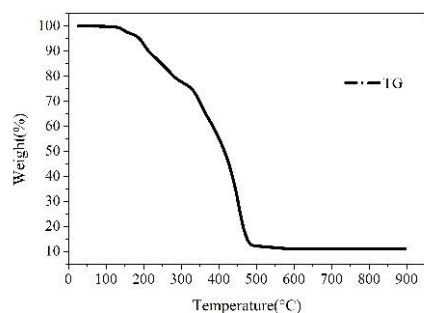


Figure 7. TG analysis of product.

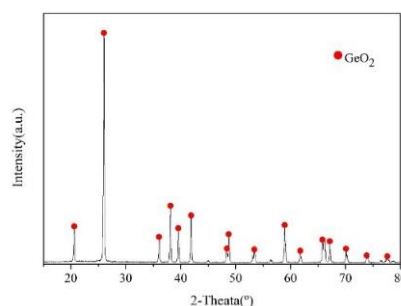


Figure 8. XRD pattern of GeO₂.

4. Conclusions

This study proposed a hydrometallurgical way to recovery germanium effectively from the optical fibers. In roasting step, we add NaOH/SiO₂ mole ratio equal to 6 at 500 °C to make SiO₂ be sodium silicate necessarily. And then in leaching step, the leaching efficiency of germanium was higher than 99.5% under the optimal conditions which were pH 6 and 40ml/g. In ion-exchange step, germanium can be separated from silicon and sodium effectively with pH 3, Cit/Ge mole ratio equal to 4, IRA900 as the resin and 1mol/L HCl as the eluting agent at 25 °C. With this condition, germanium adsorption rate was 92% and silicon and sodium was lower than 0.001%. Finally, the GeO₂ product could be get by calcining at 500 °C and its purity was higher than 99%. This process which was shown in this study can provide an effective method to treat the related wastes containing germanium and silicon.

5. References

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