Improve subsequent leaching efficiency and extraction rate of germanium in optical fibre cables with pre-treatment

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Abstract. Germanium is an important and rare material which widely used in fibre optic industry, accounting for about 40% of the total germanium product usage. Due to the rarity of germanium, developing an effective recycling process of recovering germanium metal from waste fibre optical cables is significant. Fibre optical cables was arranged to do characteristic analysis, pre-treatment and dissolution in this study. In the characteristic analysis, the content of germanium dioxide in the glass fibre was 0.15%, and the remaining components were all silicon dioxide. In the pre-treatment part, it consists of two steps which are the solvent treatment and roasting. At the solvent treatment step, glass fibre can be separated by acetone with a concentration of more than 50% and ethanol with concentration of more than 75%. At the roasting step, NaOH was used as a roasting additive. Adding 5 molar ratio of NaOH/SiO2 at 500°C for 2 hours can totally convert the optical fibre into the silicate. After roasting, it could be leaching by dilute H2SO4 and its leaching rate is higher than 99.5%. This study can provide a process to recovery germanium from optical fibre effectively. According to the optimal conditions, the recovery of germanium could be up to 99%.

Key word: Germanium, Waste fibre optical, Solvent treatment, Roasting.

1. introduction
Germanium is a rare metal that occurring to the range of 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 [2] and it has none in mineable deposits. With the increased of demand for the semiconductor industry and the optical industry, the European Union has listed germanium as a critical raw material in 2010 [3]. And it is also an indispensable strategic resource in the modern military field. According to statistics, about 30% of the world's use of germanium comes from recycled materials, almost electronic devices. In the global consumer market, the part used for optical fiber accounts for about 40%. Infrared optics accounted for 30% [4]. With the development of 5G networks and advances in optical fiber technology, as the main added material of optical fiber, the demand for it will inevitably continue to rise, and lots of discarded optical fiber cables will also be generated. Germanium as the scarce metals, the future resources will face a shortage of supply. Therefore, the disposal of these discarded optical fiber cables is necessary, and because of the limited resources of germanium, it is necessary to study the recovery process of germanium in waste fibers.

At present, there is only a recycling process for germanium in optical fiber process wastewater [5], and there is no treatment process for the complete set of waste optical fibers. Waste optical fiber cables require pre-treatment, including stripping, crushing, solvent treatment, roasting, pyrolysis, and more. In this study, the solvent was use and the waste fiber was treated by roasting. There are two main methods for recovering germanium from treated optical fiber cables, and pyrometallurgy and hydrometallurgy. The pyrometallurgical process is most commonly used to recover germanium from coal [5-9], but it has high impurity content and energy consumption. Larger, hydrometallurgy on treated fibers is more suitable than pyrometallurgy. Common hydrometallurgical processes for the recovery of germanium include leaching chemical precipitation [10-11], chlorination distillation [12], flotation [13], ion exchange [14-15], solvent extraction [16]. In order to effectively improve the
efficiency of subsequent germanium separation, this study chose the impregnation method to recover the germanium in the waste optical fiber cable.

Optical fiber cables are stripped by stripping machine, and then, the optical fiber cables were processed through two pre-treatments, solvent treatment and roasting. In order to improve the subsequent leaching rate, in the solvent treatment part, the separation effect of different solvents, concentrations and time on the plastic was studied. In the roasting part, different fluxes, temperatures, and dosing amounts were investigated. The results show that two different types of glass fibers and sodium silicate type, which are in the form of silicon dioxide, are formed. In this study, the sodium silicate was selected as the subsequent acid leaching analysis. According to the research, better leaching rate can be obtained under the optimal parameters.

2. Experimental

2.1. Materials, reagents and instruments

In this study, the optical fiber samples were collected from waste cables. According to the previous study, the compounds analysis of optical fiber cable was shown in table 1, the elements analysis was shown in Table 2, which could be found the concentration of germanium in the fibre was 0.1% and other is silica. Figure 1. Show that the XRD and SEM/EDS analysis of optical fibre powder. The acetone (ECHO C3H6O 99.5%) and ethanol (ECHO C2H5OH 99.5%) were used to separate the plastic on the optical fibre cable. The sodium hydroxide (Applichem Panreac NaOH 98%) and sulfuric acid (Sigma-Aldrich H2SO4 98%) used as roasting and leaching agents and dissolved in deionized water. Analysing the metal content for separation and leach efficiency is used by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian, Vista-MPX). Using Scanning Electron Microscope (SEM, Hitachi, S-3000N), X-ray Fluorescence (XRF, SPECTRO XEPOS), X-ray diffraction (XRD, Dandong, DX-2700) and Energy Dispersive X-ray Spectroscopy (EDS) to get information about the sample's surface topography and composition.

Table 1. Compounds analysis of optical fibre cable

| Aluminium strip | Plastic Jacket | Optical Fiber | Steel wire | Filling compound | Fiber bundle |
|----------------|----------------|---------------|------------|-----------------|-------------|
| 5~8%           | 20~25%         | 5~10%         | 15~20%     | 10~15%          | 2~5%        |

Table 2. Elements analysis of optical fibre 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 |

Figure 1. XRD and SEM/EDS analysis of optical fiber powder
2.2. Plastic softening

The purpose of this part is to process the fiber bundle tube containing germanium. At first, optical fiber cables are stripped by stripping machine. After the discarded fiber optic cable is stripped, the external plastic is removed, and the remaining product is a fiber bundle tube that cannot be physically separated. This is the goal of this study. The fiber bundle tube is composed of glass fiber and acrylic resin coating. Therefore, the use of plastics can be softened by organic solvents, solvent treatment is beneficial to the subsequent hydrometallurgical process. The organic solvent part is selected from 10%, 25%, 50%, 75%, 90% acetone and ethanol as a separating agent to investigate the separation effect of the concentration and time on the plastic.

2.3. alkali roasting

First, the optical fibre was collected from cables. Because the fibre contained silicon dioxide [17], it should dissolve silica and take germanium out of them by alkali roasting. In the alkali roasting part, alkaline fluxes such as sodium carbonate, potassium hydroxide and sodium hydroxide are selected, and the optimum calcination temperature, the selection and addition amount of the agent are discussed. According to the literature, the roasting temperature is selected as 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C as parameters. The dosage is the ratio of the agent to the silicon dioxide molar, and 2, 3, 4, 5, 6, 7, 8 mol / mol is used. The roasting time was two hours and the roasting efficiency was impregnated with deionized water and compared with the aqua regia and HF total dissolution samples, and the crystal phase change was analysed by XRD to provide a set of optimum roasting conditions.

2.4. Leaching

The leaching efficiency of two types of silicon dioxide is discussed. For the solvent-treated fibre, HNO₃, HCl and H₂SO₄ were used as the main leaching liquid, and the leaching efficiency under the addition of HF was investigated. Then discuss the effect of liquid-solid ratio and time on the leaching efficiency. For the alkali roasted fibre, and deionized water is used as a leaching liquid, and H₂SO₄ is used as an acid-base adjusting agent. The influence of pH and liquid-solid ratio on the leaching effect is sequentially discussed. 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 [17].

3. Results and discussion

3.1. Plastic softening

The organic solvent can be used to soften the plastic, and 10%, 25%, 50, 75%, 90% acetone and ethanol are used as the separation agent, and the respective separation time is recorded in Table 2. According to the results, the acetone separation effect is much larger than that of ethanol, and the acetone has no peeling effect at a concentration of 50% or less, and the ethanol has a effect of less than 75%. After the separation is completed, the quality of the plastic and glass fibre in the bundle of fibre bundles is analysed. The results are listed in Table 3. According to the results, the plastic part accounts for about 57% of the bundle weight and the glass fibre accounts for about 43%.

| Table 3. Separation effect of organic solvent on fiber bundle cluster coated plastic |
|-----------------------------------------------|
| **acetone** | 10% | 25% | 50% | 75% | 90% |
| **time**    | x   | x   | 5 hours | 2 hours | 20 minutes |
| **ethanol** | 10% | 25% | 50% | 75% | 90% |
| **time**    | x   | x   | x   | 6 hours | 2 hours |
Table 4. Weight analysis of fiber bundles

| Weight % | Coated plastic | Glass fiber |
|----------|----------------|-------------|
| 57.14%   | 42.86%         |             |

3.2. alkali roasting

According to the composition analysis of the glass fibre, silicon dioxide is the main component of the glass fibre. In this step, the roasting of the silicon dioxide at different temperatures of the alkaline flux of Na₂CO₃, KOH and NaOH is investigated. As a result, the roasting time was 2 hours, and the results are shown in Table 4. The results show that at 900 °C, the addition of Na₂CO₃ can completely react and completely dissolve, KOH is 400 °C and NaOH is 500 °C, which is consistent with the literature reaction temperature [18-19]. According to the above conclusions, the dosage of the flux at the optimum operating temperature is compared with the roasting efficiency. The dosing amount is the ratio of the agent to the silicon dioxide molar. The roasting efficiency is impregnated with deionized water and compared with the aqua regia. The results are shown in Figure 2. According to the results, it can be found that KOH and NaOH can reach complete reaction when the molar ratio is 5, and Na₂CO₃ can be completely reacted when the molar ratio is 8. The temperature and the required amount of the drug can be compared to find that the Na₂CO₃ efficiency is lower than KOH. With NaOH, and because of the amount of flux (the molecular weight of KOH is higher than NaOH) and the price of the flux (effective for NaOH), NaOH is selected as the best alkali roasting additive here. The optimal operating conditions are temperature 500 °C, dosing amount. For 5 molar ratio, the roasting time was 2 hours. Finally, the product obtained under the optimum conditions was analysed by XRD, and the results are shown in Figure 3. According to the map analysis, it can be confirmed that under this roasting condition, the silicon dioxide has been converted into water-soluble sodium silicate, and subsequent leaching can be performed.

Table 5. Alkali roasting effect of different agents at different temperatures

| temperatures | 300°C | 400°C | 500°C | 600°C | 700°C | 800°C | 900°C |
|--------------|-------|-------|-------|-------|-------|-------|-------|
| Na₂CO₃       | ×     | ×     | ×     | ×     | ×     | ×     | ○     |
| KOH          | ×     | ○     | ○     | ○     | ○     | ○     | ○     |
| NaOH         | ×     | ×     | ○     | ○     | ○     | ○     | ○     |

(×: silicon dioxide does not fully react; ○: completely reacts and dissolves)

(roasting time: 2 hour)
Figure 2. Effect of the roasting efficiency on mole ratio

Figure 3. The XRD pattern of optical fibre after roasting.

3.3. Leaching

For the type of silicon dioxide, the effect of leaching efficiency on concentration and HF of different acids was investigated. The results are shown in figure 4. The operating conditions is L/S=100, 5%v/v HF, time=3hr. The results show that if HF is not added, the germanium coated in the silicon cannot be leached. For this reason, HF must be added. In terms of acid concentration, the impregnation rate of ruthenium will decrease with concentration at a certain acid concentration, and the results are in accordance with the literature. Therefore, the concentration is selected to be 0.1M H2SO4. According to the above, HF is necessary, so the influence of the concentration on the leaching efficiency is examined, and the results are shown in figure 5. The results show that the leaching efficiency of germanium rises as the HF concentration rises, so 5% v/v HF is selected. Using the optimized leaching liquid and concentration, the effect of leaching efficiency on liquid-solid ratio was investigated. The results are shown in figure 6. The results show that when the liquid-solid ratio is
reduced, in other words, when the leaching liquid is reduced, the driving force of the reaction is lowered, resulting in leaching efficiency of germanium drops. So L/S=100ml/g is selected. Finally, the effect of leaching efficiency on leaching time was investigated by using the above parameters. The results are shown in figure 7. The results show that the reaction reaches equilibrium at 3hr.

**Figure 4.** Effect of the leaching efficiency on concentration and addition of HF.
(L/S=100, 5%v/v HF, time=3hr)

**Figure 5.** Effect of the leaching efficiency on concentration of HF.
(L/S=100, 0.1M H2SO4, time=3hr)
Figure 6. Effect of the leaching efficiency on liquid-solid ratio. 
(5%v/v HF, 0.1M H2SO4, time=3hr)

Figure 7. Effect of the leaching efficiency on leaching time. 
(L/S=100, 0.1M H2SO4, 5%v/v HF)
According to previous research [17], after roasting, the fibre was leached by dilute H$_2$SO$_4$ and showed the pH value and liquid-solid ratio effect in the figure 8 and 9. It was found that germanium and silicon leaching rate decreased significantly at neutral environment in figure 8. The reason of that if the image of the liquid and solid leaching rate were decreased with the liquid-solid ratio. The excessive silicon concentration would also make them precipitate that the leaching efficiency decreased.

![Figure 8](image1.png)

**Figure 8.** Effect of the leaching efficiency on pH value. (pH=3, 25 °C).

![Figure 9](image2.png)

**Figure 9.** Effect of the leaching efficiency on liquid-solid ratio. (L/S=40ml/g, 25 °C).
4. Conclusion
This study proposes a hydrometallurgical method that can effectively improve the subsequent leaching efficiency and extraction success rate of germanium in optical fibre cables with pre-treatment. In the characteristic analysis part, the bundle of optical fibre is composed of an acrylic resin coating and a glass optical fibre. The plastic part accounts for 57.14% of the bundle of optical fibre and the glass fibre accounts for 42.86%. The analysis of the glass fibre can be found to be composed of amorphous silicon dioxide. Germanium is embedded in silicon dioxide, and the content of germanium dioxide is 0.15%, and the remaining components are silicon dioxide. In the part of separated the acrylic resin coating by the organic solvent, the plastic coating can be removed by using acetone having a concentration more than 50% or ethanol more than 75%, and the efficiency is preferably acetone. In the alkali roasting part, NaOH is selected as the optimum roasting additive. The additive can convert the glass fibre into sodium silicate at a temperature of 500 °C. Adding 5 molar ratio of NaOH / SiO₂, and the roasting time of 2 hours. In the optimal leaching parameter part of sodium silicate type, adding 5% v/v HF, under the conditions of liquid-solid ratio 100 ml/g, reaction time 3h and 25°C, the efficiency can reach 99.5%. In the optimal leaching parameter part of sodium silicate type, deionized water is used as the substrate, and H₂SO₄ is used as the acid agent. The leaching is performed under the conditions of pH 1-4, liquid-solid ratio 40 ml/g, reaction time 20 minutes and 25°C. The efficiency is greater than 99.5%. Comparing the two types of leaching, alkali roasting requires the addition of alkali agent and high temperature treatment, but less leaching liquid can be used in the leaching part, faster reaction time and avoiding the addition of HF. Therefore, this study suggests the choice of alkali roasting as the preferred method. This study shows a process of pre-treatment which can effective improve subsequent leaching efficiency and extraction success rate of germanium in optical fibre cables.
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