SEPARATION OF GERMANIUM FROM AQUEOUS SOLUTIONS USING LIQUID-LIQUID AND SUPPORTED LIQUID MEMBRANE EXTRACTION

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Abstract: Germanium as a strategic element is found in aqueous solutions of various mining industries. For selective separation of germanium from an aqueous solution containing anionic complexant, tartaric acid, solvent extraction and supported liquid membrane (SLM) were used with Aliquat336. Affecting parameters such as extractant concentration, complexant type and concentration, and the concentration of the stripping phase containing hydrochloric acid, were investigated in the solvent extraction system. According to the results, germanium extraction efficiency rose up to 100% by increasing the concentration of Aliquat336 by 0.2 %v/v. In addition, tartaric acid was found to be the best anionic germanium complexant. With the addition of 0.275 mM tartaric acid, germanium extraction efficiency reached almost 99%. The highest stripping efficiency (99%) was achieved at the HCl concentration of 2 M. In the SLM system, 5 %v/v of Aliquat336 as a carrier was sufficient to transport 99% of germanium in the feed to the strip phase. Comparing two systems, the transfer time of the membrane system (510 min) is higher than that of the solvent extraction system (15 min).

Keywords: Extraction, Transportation, Germanium, Membrane, Amines.

INTRODUCTION

Germanium is an element (Ge) with the atomic number of 32. It is a lustrous, hard-brittle, grayish-white metalloid in the carbon group, chemically similar to its group neighbours, such as tin. The purified germanium is a semiconductor with a very similar appearance to elemental silicon. Recently, germanium is used in fibre-optic, infrared optics, and solar cell applications. Its compounds are also used for the polymerization of catalysts and nano-wires.

Hydrometallurgical methods such as solvent extraction can be used as one of the effective processes for the recovery and refining of solutions containing germanium (Swain et al. 2007). KELEX 100 (epouse Bauer et al. 1983), LIX 63 (De Schepper, Coussement, and Van Peteghem 1984), TOA (Arroyo et al. 2009) and Cyanex301 (Harbuck, Judd, and Behunin 1991) can be used to extract germanium.

Liquid membrane method is one of the solvent-based methods that is applied in water treatment industry. Polymer inclusion membranes (PIM), emulsion liquid membranes (ELM), and supported liquid membranes (SLM) are classified as the liquid membrane techniques. The use of SLM for separating metals and species is relatively simple. This method has advantages such as active transfer, high selectivity, low energy consumption, low investment, and low operating costs. No significant studies have been carried out on germanium transitions using a flat sheet organic membrane, and studies have mostly focused on other types of membranes.

In this research, for the first time, the extraction of germanium from a synthetic solution was carried out using solvent extraction and a flat sheet SLM system. In this system, the polytetrafluoroethylene membrane (PTFE) was used with Aliquat336 as a carrier for the separation of germanium. The effect of different parameters on extraction percentage was investigated, such as pH, and extraction concentration.

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METHODS

In this study, the synthesized solutions with a germanium concentration of 100 mg/L were obtained from the dissolution of GeO2 (Merck, Germany) in an aqueous medium. Zinc sulphate (ZnSO4.7H2O), cadmium sulphate (CdSO4), cobalt sulphate (CoSO4.H2O), and nickel sulphate (NiSO4.6H2O), all were purchased from Merck, and were used to investigate the transportation of heavy metals in the presence of germanium. Tartaric acid, Oleic acid, citric acid, and catechol, all purchased from Merck were used in various experiments as germanium complexants. Aliquat336 ionic solvent was purchased from Alfa Aesar Company. All extractants were diluted by kerosene (Sigma-Aldrich) and 1-Decanol (Merck).

Since the SLM method is based on solvent extraction, the first step is to investigate the germanium solvent extraction using Aliquat336. The effects of important parameters were investigated in solvent extraction experiments. Experiments were carried out with a 1:1 O:A phase ratio, a contact time of 15 minutes, and at the room temperature. A mechanical vibrational device (SBS Spain) was used to thoroughly mix the phases.

In SLM experiments, Aliquat336 was used as a carrier phase in the membrane. The influence of parameters such as carrier concentration was investigated in the range of 0.5 to 10%. The solution composition in SLM tests were similar to the solvent extraction conditions. Experiments were carried out at intervals of 0 to 25 hours.

FINDINGS AND ARGUMENT

In order to investigate the effect of extractant concentrations on germanium extraction with Aliquat336 at the concentration range of 0 to 10 %v/v, a series of experiments were carried out. As shown in Fig. 1, the percentage of germanium extraction rose from about 0% to 100%, while increasing the concentration of Aliquat336 from 0% to 0.2%.

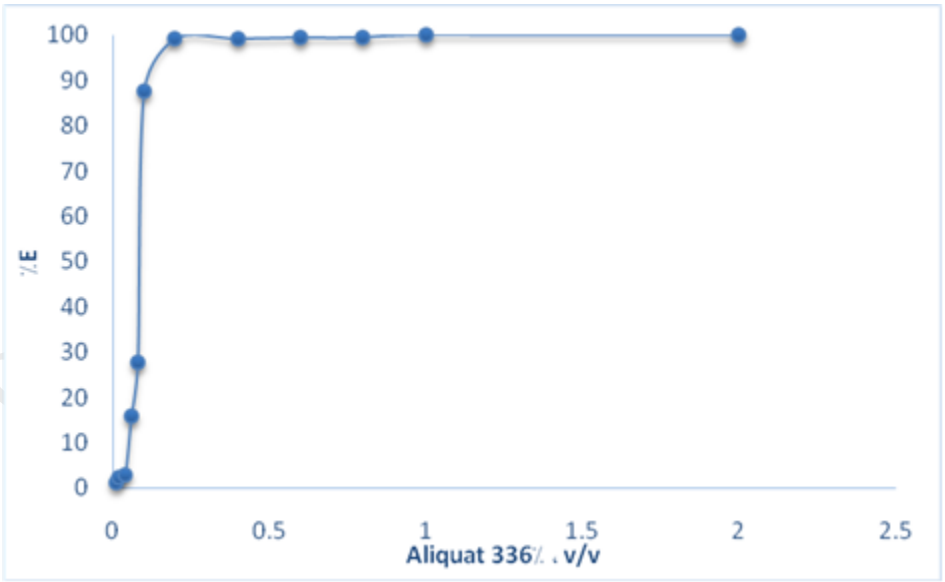

Fig. 1. Effect of Aliquat336 concentration on the extraction efficiency of germanium

The investigation on the effect of complexant types on germanium extraction with Aliquat336 showed that in the presence of tartaric acid and citric acid, all germanium was extracted with 1%v/v of Aliquat336.

According to the result results, tartaric acid was selected as the best complexant among other materials. Also, the concentration of tartaric acid is one of the factors affecting the extraction of germanium by helping the formation of anionic germanium-tartrate complexes, which can be extracted by amines such as Aliquat336. In the absence of tartaric acid, the extraction of germanium species was stopped. In addition, the percentage of germanium extraction increased to 86.88% when the concentration of tartaric acid rose and reached the concentration of germanium in the solution. According to the results, the complete reaction of germanium ions with tartrate is when the concentration of tartaric acid is about twice the molar concentration of germanium.

To study germanium stripping, the loaded organic solution of Aliquat336 was used containing about 100 mg/L germanium. According to research results, mineral acids such as hydrochloric acid can strip germanium from the organic phase. As a result, by increasing the concentration of acid to 1 M, the germanium extraction rose to 98%.

The selective transport of germanium from a solution containing 100 mg/L of germanium, cobalt, cadmium, nickel and 1000 mg/L zinc using FSSLM system with PTFE membrane with the pore size of 0.45 μm, and Aliquat336 as a carrier was also investigated. According to the results, the efficiency of the germanium transport for a carrier concentration of less than 3%v/v is negligible. This conclusion suggests that these concentrations are insufficient for the formation of germanium anionic complexes and carrier molecules. However, the transport efficiency increased significantly by rising carrier concentrations. As shown in Fig. 2, there is no significant difference between the transport graphs for the intervals of 5-10%.

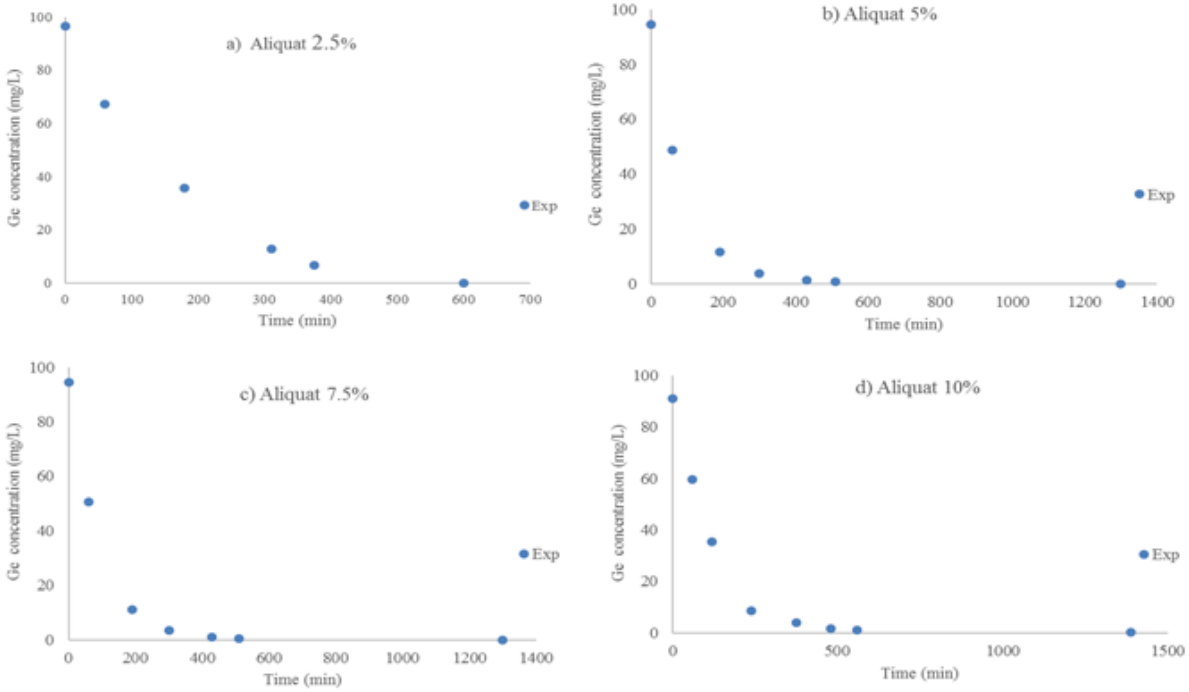

Fig. 2. Effect of Aliquat336 concentration on the concentration of germanium in the feed phase.

Comparing solvent extraction and SLM systems showed that the complete transportation time of species using two different methods were 15, and 510 minutes, respectively, showing a slow rate of the transportation in the membrane process.

Conclusion

- In the solvent extraction system, the effect of various complexant types, extractant, and HCl concentration in the strip phase was investigated.
- In the extractant concentration of 2 %v/v, the germanium extraction reached a constant level of 100%.
- Tartaric acid and citric acid, as well as catechol, showed the highest extraction results. Results showed that about 100% of germanium was extracted using 2% v/v of Aliquat336 when the concentration of tartaric acid equals twice the molar concentration of germanium in the solution.
- By rising the concentration of HCl to 2 M, the extraction percentage of germanium was increased. According to the results of SLM experiments, the increase of carrier phase concentration and subsequent increase in the viscosity declined the permeability coefficient.
- With a rise in the concentration of Aliquat336 to 5% v/v, the transportation rate increased.
- Comparing solvent extraction and SLM systems showed that the complete transportation time of species using two different methods were 15, and 510 minutes, respectively, showing a slow rate of the transportation in the membrane process.

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