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4 **Selective separation of Ge(IV) from simulated industrial leachates containing**
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7 **heavy metals by non-dispersive ionic extraction**
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Abstract

Germanium can be found in industrial leachates of coal gasification fly ashes or zinc plant residues, containing various heavy metals. In this research, the selective separation of germanium from simulated water coal gasification fly ash leach liquors containing Zn(II), Ni(II), Cd(II), and Co(II) through the flat sheet and hollow fiber supported ionic liquid membrane (FSSLM & HFSLM) systems was developed using an ionic liquid Aliquat 336 as a carrier. As a result, Aliquat-336 was a very fast and effective carrier for the selective transport from these types of solutions. The selective transport of germanium through the mentioned FSSLM system was carried out from a simulated zinc acidic leach liquor containing the aforementioned metals and 0.5 mol/L of H₂SO₄ under the condition found for the neutral solutions. As a result, an insignificant difference was observed between the germanium transports from both solutions. The germanium transport from both types of solutions was selective and its efficiency reached >98%. Finally, a facilitated transport of germanium was conducted in an HFSLM under the same condition obtained for the FSSLM system. It was observed that this system could transport major amounts of germanium species in the first 30 min showing faster transport than the FSSLM system.

Keywords: Supported liquid membrane; Ge(IV); Aliquat 336; Selective separation; heavy metals

1. Introduction

Germanium compounds such as GeO₂ are widely used in many industries such as optics, telecommunication, alloys etc. (Liu et al., 2015; Rieke, 2007). Germanium is a critical element found in restricted resources. Therefore, it is important to recover this rare metalloid from these restricted resources. Coal fly ashes and zinc plant residues are waste materials, the management of which can eliminate their potential risks and make economical values. The industrial effluents

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4 obtained from zinc and fly ash purification processes are potential resources of germanium.
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6 Germanium can be found in coal gasification fly ash water leachate and acidic solutions of zinc
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8 ore/residue leaching processes. Germanium in these effluents is found along with some heavy
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10 metals such as zinc, nickel, cobalt etc. (Arroyo et al., 2009b; Liu et al., 2016; Sethurajan et al.,
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12 2017). One of the appropriate processes for germanium extraction from coal gasification fly
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14 ashes is water leaching (Arroyo and Fernández-Pereira, 2008; Arroyo et al., 2009b). The
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16 presence of heavy metals in coal fly ashes (Chaudhary and Banerjee, 2007; Sijakova-Ivanova et
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18 al., 2011) can be unwanted metals affecting the separation of germanium. Furthermore, zinc ores
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20 or related residues obtained from zinc industries are commonly leached in the sulfuric acid
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22 medium (Liu et al., 2016; Nusen et al., 2015). The presence of heavy metals such as cadmium,
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24 nickel, cobalt, and iron is common in zinc resources (Kamran Haghighi et al., 2015; Nusen et al.,
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26 2015). Therefore, the separation of germanium from these unwanted heavy metals can be
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28 valuable. Various types of hydrometallurgical processes such as solvent extraction (Nusen et al.,
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30 2015), adsorption (Marco-Lozar et al., 2007), membrane process (Takemura et al., 2013), ion
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32 exchange (Arroyo and Fernández-Pereira, 2009), and precipitation (Liang et al., 2008) were used
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34 in the recovery of germanium from aqueous solutions. Some advantages such as high selectivity,
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36 high capacity, rapid extraction, and production of a pure product have caused the dispersive
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38 solvent extraction process to be significant in the purification industries (Wei et al., 2016). The
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40 SLM systems such as hollow fiber (HFSLM) and flat sheet (FSSLM) can be considered as non-
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42 dispersive solvent extraction having some similarities to solvent extraction. The extraction and
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44 stripping mechanisms of both methods are the same, but these stages in SLM systems are
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46 simultaneously carried out in a process. Higher selectivity, low capital and operational costs,
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48 operative easiness, and low extractant consumption are the other advantages of SLM systems
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4 (Chaturabul et al., 2015; Kandwal et al., 2011; Yang et al., 2002). These advantages will be
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6 effective when a solution containing valuable trace metals such as germanium or rare earth
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8 elements is treated (Campderrós and Marchese, 2001). However, flat sheet SLM systems have
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10 been faced with challenges in industrial usages such as maintenance issues (Swain et al., 2015).
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12 On the other hand, a hollow fiber SLM system based on non-dispersive solvent extraction,
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14 merging solvent extraction and flat sheet SLM advantages. In this study, the effective area of
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16 HFSLM is 127000 times more than that of FSSLM. Therefore, it can be expected that the
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18 transport rate in HFSLM is comparable to solvent extraction. These advantages have spread the
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20 use of HFSLM in industrial works (Wannachod et al., 2014).
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26 In SLM systems, the detection of a proper extractant as a carrier of the species is vital to design a
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28 proper germanium separation process. There are many extractants used to separate and recover
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30 germanium from aqueous solutions such as KELEX 100 (Bauer et al., 1983), LIX 63 (Boateng et
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32 al., 1990; de Schepper, 1976), Ionquest 801 (Boateng et al., 1990), Cyanex 301 (Harbuck et al.,
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34 1991; Kamran Haghghi et al., 2018b), and TOA (Arroyo and Fernández-Pereira, 2008; Kamran
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36 Haghghi et al., 2018c). Ionic liquids (ILs) are the other organic materials that can be used
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38 instead of classical extractants for the recovery of species. Insignificant vapor pressures, high
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40 thermal stabilities, and good affinity towards metals are some advantages of ionic liquids (Jha et
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42 al., 2014; Wei et al., 2016; Won et al., 2014). Only two ionic liquid systems have been used to
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44 transport germanium from aqueous solutions in the literature; however, in a research tri-
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46 capryloyl methyl ammonium chloride (Aliquat 336S) as a hydrophobic quaternary ammonium
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48 salt with the formula of $[R_3NCH_3]^+Cl^-$ was used to separate germanium from citric acid solutions
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50 in a liquid-liquid extraction system (Vibhute and Khopkar, 1986). According to this study, 0.1 M
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52 of Aliquat 336 diluted in xylene could selectively extract germanium among various metals from
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4 0.001 M of the citric acid solution at a pH of 3.5. With respect to this discussion, IL Aliquat 336
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6 has been first used as a carrier of the supported liquid membrane in the current study. In addition,
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8 Kamran Haghghi et al. (2018a) used methyl-N, N-dioctyl chloride (Aliquat 336) to extract and
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10 separate germanium from heavy metals from a solution containing nickel, cadmium, cobalt, and
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12 zinc. The high extraction efficiency of germanium has been reported for this system.
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16 In this research, Aliquat 336 was selected as a carrier of HF-SLM and FS-SLM systems for the
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18 selective transport of germanium from simulated solutions with similar composition to zinc
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20 resources/fly ashes leach liquors. The effects of various parameters such as Aliquat 336
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22 concentration, complexant concentration, and strip solution concentration were examined in
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24 details. SLM processes proposed in the present research can be considered as a novel opportunity
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26 to recover germanium from various industrial leach liquor as potential resources of germanium.
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33 **2. Theory**

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35 Aliquat 336 is an ionic liquid stated as $R_4N^+Cl^-$ that can extract anionic species. It is a quaternary
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37 ammonium salt formed of a large organic cation along with a chloride ion. The positive
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39 ammonium part of Aliquat 336 can react with various anions in a broad pH range (Nayl, 2010).
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41 Since germanium species in water/sulfuric acid media is not in anionic form, thus, in order to
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43 form germanium anionic complexes, a complexant namely tartaric acid was used to form
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45 germanium-tartrate anionic species. In the presence of $C_4H_6O_6$ in the feed solution, neutral
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47 germanium species (H_2GeO_3) transform to $Ge(C_4H_4O_6)_i^{2-}$. Considering the values of the tartaric
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49 acid dissociation constants i.e. $pK_1 = 3.04$ and $pK_2 = 4.37$, the stability of a germanium-tartrate
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51 complex is highly dependent on the pH. According to the literature, Ge-tartrates are not stable
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53 complexes at $pHs > 7$ due to the reason introduced in a study carried out by Vartapetian (1957)
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and confirmed by Pokrovski and Schott (1998). Furthermore, Ge-tartrates are decomposed at pHs < 1.24 to germanium species and free tartrate (Everest and Harrison, 1960).

Hence, Aliquat 336 can form a complex $((R_4N^+)_2 Ge(C_4H_4O_6)_i^{2-})$ with anionic species of germanium at the feed phase-membrane diffusion layer. This complex diffuses across the membrane phase and is stripped with a stripping reagent (HCl) in the receiving phase-membrane diffusion layer. Fig. 1 illustrates the schematic germanium transport through the ionic liquid membrane of this study.

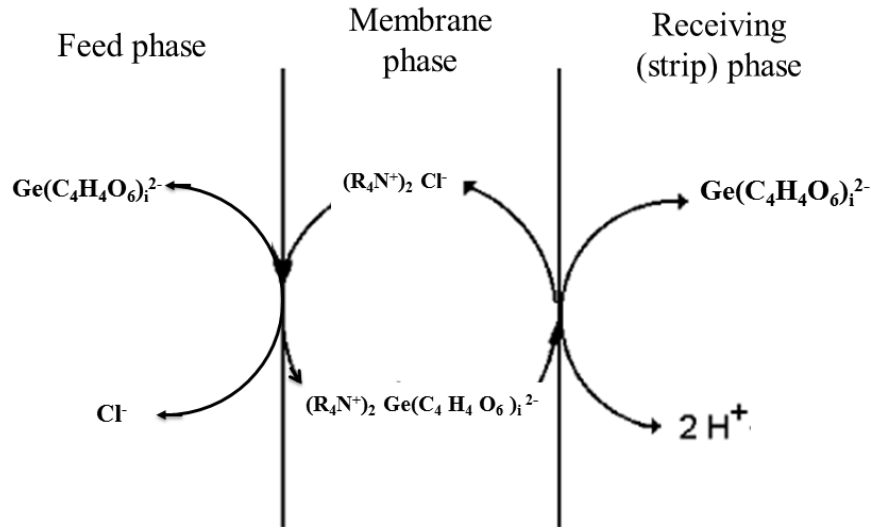


Fig. 1. The schematic transport of germanium through the ionic liquid membrane

The usual parameter to control the system is permeability coefficient P (cm/s). It can be calculated using the slope of the plot of $-\frac{V}{A} \ln(C_f / C_{f,t})$ vs. time with respect to Eq. (1):

$$\ln(C_f / C_{f,t}) = -\frac{APt}{V} \quad (1)$$

Where V represents the volume of feed phase and A shows the effective area of the membrane.

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11 **3. Materials and methods**
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14 *3.1. Materials*
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17 Coal gasification fly ashes contained many heavy metals and trace elements. However, their
18 water leachates may contain germanium, arsenic, iron, arsenic, nickel, antimony, vanadium, and
19 the other heavy metals. On the other hand, nickel, iron, cadmium, cobalt, zinc as well as
20 germanium are the main elements in acidic leachates of Iranian zinc residues. According to the
21 literature, divalent metal ions such as manganese, magnesium, calcium, strontium are not reacted
22 with citric and tartaric acids, meaning that they can not be extracted by amine extractants such as
23 Aliquat 336 (Vibhute and Khopkar, 1986). Furthermore, other elements such as arsenic,
24 antimony, vanadium etc. which may exist in the coal gasification fly ash leachates can not be
25 stripped by an acid (Arroyo et al., 2009a). Hence, since this study deals with two types of
26 leachates (from zinc residues and gasification fly ashes) containing germanium and according to
27 the aforementioned discussion, to ease the comparison and the interpretation of systems, only
28 zinc, cadmium, cobalt, and nickel as well as germanium were selected for the investigation. It is
29 noteworthy that all solutions had the initial pHs around 4, in which ferric iron was precipitated.
30 Therefore, it is supposed that all solutions are iron-removed leachates. In order to simulate the
31 water leach liquor of coal gasification fly ash, synthetic solutions containing 1000 mg/L of Zn,
32 100 mg/L of Ge, Cd, Co, and Ni were prepared by dissolving the desired amounts of
33 ZnSO₄.7H₂O, GeO₂, CdSO₄, CoSO₄.H₂O, and NiSO₄.6H₂O (Aldrich A.C.S. Reagent) in pure
34 distilled water. Aliquat 336 (R₄N-Cl) from Alfa Aesar, Germany diluted in desired volumes of
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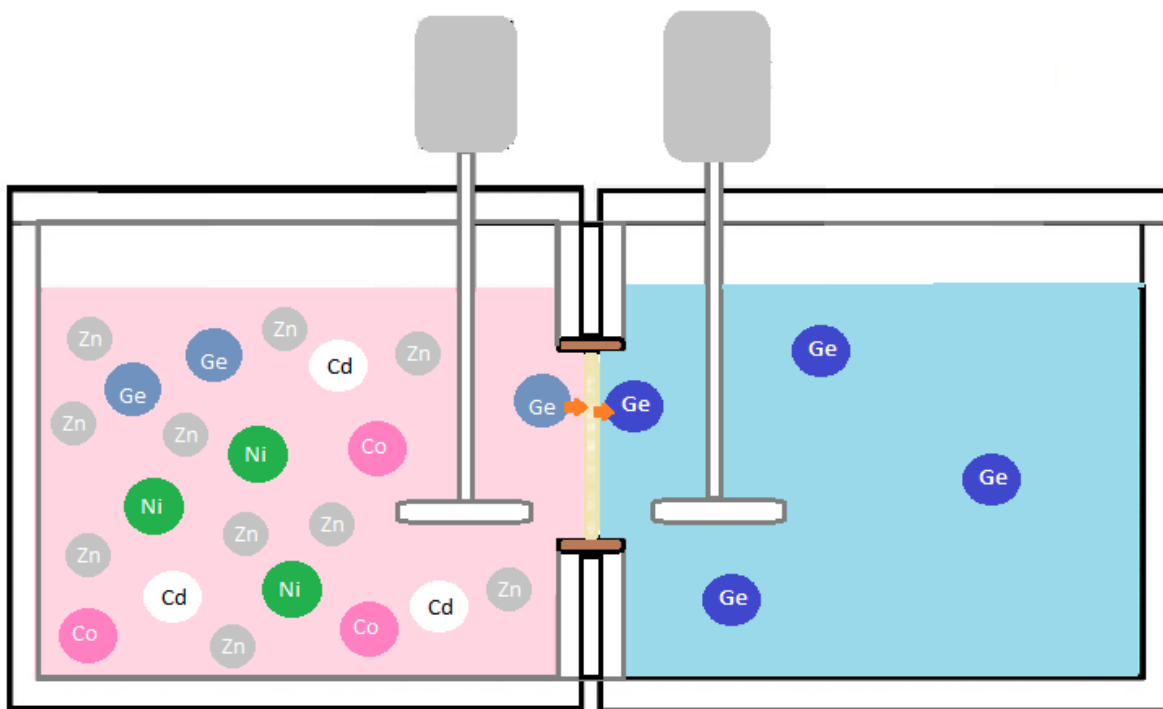
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4 kerosene (Aldrich A.C.S. Reagent) and 1-Decanol (Merck Millipore, Germany) formed the
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6 carrier of the SLM systems. Purified water used in this study was supplied using water purifiers
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8 (Siemens, Germany) during the experiments. The other materials used in this research were
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10 purchased from Merck, Germany. After finding the effect of various parameters, an FSSLM
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12 experiment was carried out to evaluate the effect of sulfuric acid on the transport of germanium.
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14 The aim of this experiment was to obtain a process for the separation of germanium from
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16 solutions obtained from sulfuric acid leaching of zinc ores. In this regard, a solution with a
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18 sulfuric acid concentration of 0.5 mol/L was prepared. The desired amounts of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$,
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20 GeO_2 , CdSO_4 , $\text{CoSO}_4 \cdot \text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were added to this solution to obtain a solution
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22 with the concentrations of 15000, 100, 100, 100, and 100 for Zn(II), Ge(IV), Cd(II), Co(II), and
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24 Ni(II), respectively. Similar to the zinc leaching industries, an amount of neutralizer such as
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26 NaOH was added to neutralize the solution until a pH of 3.5 was achieved.
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34 *3.2. Flat sheet supported liquid membrane*

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37 The flat sheet supported liquid membrane experiments were run in two cells with an effective
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39 membrane area of 11 cm^2 to separate germanium from heavy metals similar to a schematic
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41 diagram shown in Fig. 2. The cell of the feed phase (220 mL) was detached from the strip phase
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43 cell (220 ml) by a liquid membrane placed in a flanged chamber. As mentioned before, the
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45 carrier phase of the membrane contained Aliquat 336 diluted in kerosene and 1-decanol.
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47 Polyvinylidene fluoride (PVDF) and polytetrafluorethylene (PTFE) are common commercial
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49 membranes having good physical and chemical resistance (Iorhemen et al., 2016; Le and Nunes,
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51 2016). They have appropriate abilities in the facilitated transport systems, in which various
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53 species can be permeated (Bhatluri et al., 2014; Panja et al., 2008; Swain et al., 2007; Swain et
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55 al., 2006). Thus, polymeric Durapore® disc membranes, FHLP series of PTFE film with a
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4 porosity of 85%, 47 mm diameter, and pore size of 0.45 μm and Millipore HVHP04700
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6 Durapore PVDF membrane with hydrophobic nature, pore size of 0.45 μm , diameter of 47 mm,
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8 and thickness of 125 μm , were used as the polymeric supports. The membranes were
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10 impregnated in various concentrations of diluted Aliquat 336 for few minutes followed by
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12 rinsing distilled water to eliminate additional organic extractants from the surface of the
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14 membrane film and placing it in the plunged chamber between two cells. This membrane plays
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16 the role of hydrophobic separator between feed and strip phases. The extractant in the pores of
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18 the membrane acts as a mobile carrier for extraction purposes. Hydrochloric acid solutions were
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20 used as the stripping phase. Moreover, the feed and strip phases in the two cells were agitated
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22 using a mechanical stirrer at room temperature (22 ± 1 $^{\circ}\text{C}$). At desired times, 0.5 mL volumes of
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24 samples were taken from both sides and the concentrations of ions were analyzed by inductively
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26 coupled plasma atomic emission spectroscopy (ICP-AES Agilent, USA).
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4 Fig. 2. A schematic diagram of the FSSLM system used in this study for the separation of
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7 germanium.
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9 3.3. *Hollow fiber supported liquid membrane (HFSLM)*

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11 A hollow fiber supported liquid membrane (HFSLM) system was used in this experiment as
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13 illustrated in Fig. 3. In this system, a hollow fiber module was placed as a contactor of strip and
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15 feed phases. This module had an operational membrane area of 1.4 m². Hence, it was expected
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17 that the transport rate and efficiency would be faster with this high area in comparison with the
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19 flat sheet membranes. The other characterization of the polypropylene/polyethylene Liqui-Cel,
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21 USA module was as follows: the length of 28 cm, the diameter of 8 cm, and the porosity of 0.40.
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23 Before starting the experiment, the module should be saturated with Aliquat 336 (5 % v/v) diluted
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25 in kerosene and 1-decanol as the carrier. In this regard, the carrier was recycled through a lumen
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27 inside the module. For complete impregnation of the pores, a quantity of pressure was applied to
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29 transport the carrier to the lumen side of the module and the operation continued until the entire
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31 organic carrier was transported to the feed container. As seen in Fig. 3, the system contained the
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33 feed and strip containers. Both of the containers were agitated with impellers. In the feed side, 2
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35 L of the germanium solution with a concentration of 100 mg/L was added to the container. In
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37 addition, in the strip side, 50 mL of the carrier was agitated to disperse in the 500 mL of the HCl
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39 strip solution. This pseudo emulsion was recirculated from the strip phase to the lumen side of
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41 the membrane module, making a constant supply of the carrier into the membrane pores (Rathore
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43 et al., 2009). In order to monitor the system, in appropriate time intervals, 1 mL of a sample from
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45 the feed side and 10 mL from the strip side were taken. Since samples from the strip container
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47 contained organic phase, they were transferred to the separatory funnels to separate aqueous and
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organic phases. The feed solution and strip phase were simultaneously recycled by two gear pumps purchased from Micropump®, GJ Series, the US inside the shell and lumen sides.

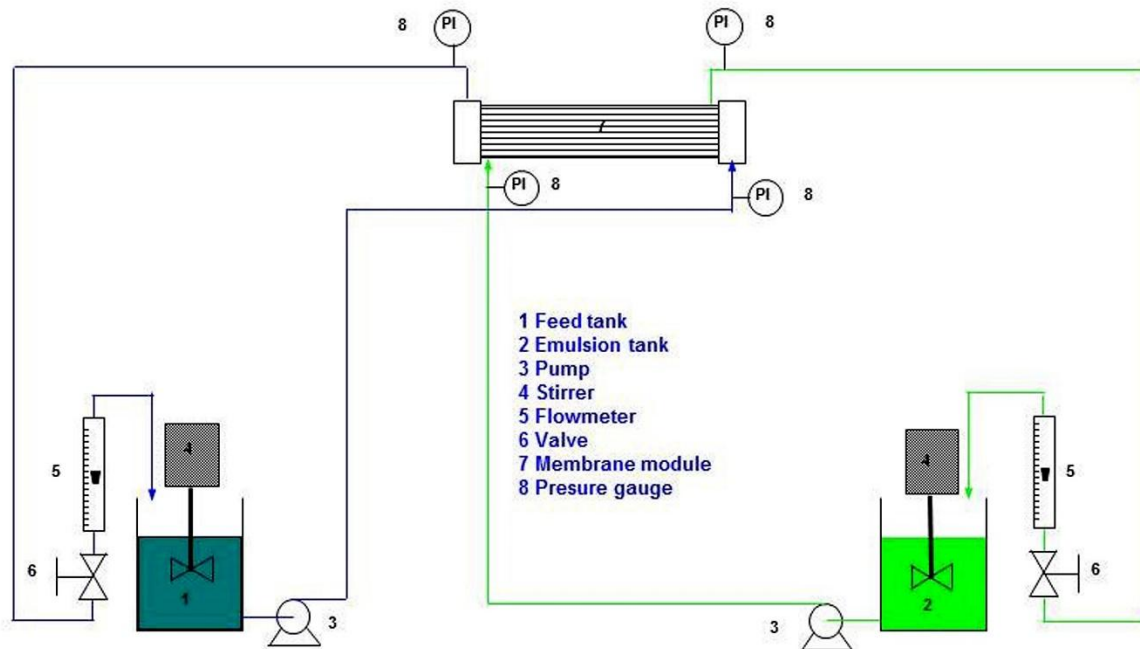


Fig. 3. A hollow fiber supported liquid membrane (HFSLM) system used in this study.

4. Results and discussion

4.1. Determination of proper membrane type

In order to detect the proper membrane for the efficient transport of germanium, two types of membranes, polyvinylidene difluoride (PVDF) hydrophobic membrane and poly tetra fluoro ethylene membrane (PTFE) were used as the supports of Aliquat 336. In this regard, PVDF and PTFE membranes with the pore size of $0.45 \mu\text{m}$ were applied in the module of the FSSLM system. The experiments were run using a solution containing about 100 mg/L of Ge, Ni, Cd, Co and 1000 mg/L of Zn. The other conditions were as follows: the amount of tartaric acid equal to two times the germanium molar concentration in the feed solution (2.76 mmol/L), and the stripping HCl concentration of 1 M . The obtained results were plotted as Fig. 4.

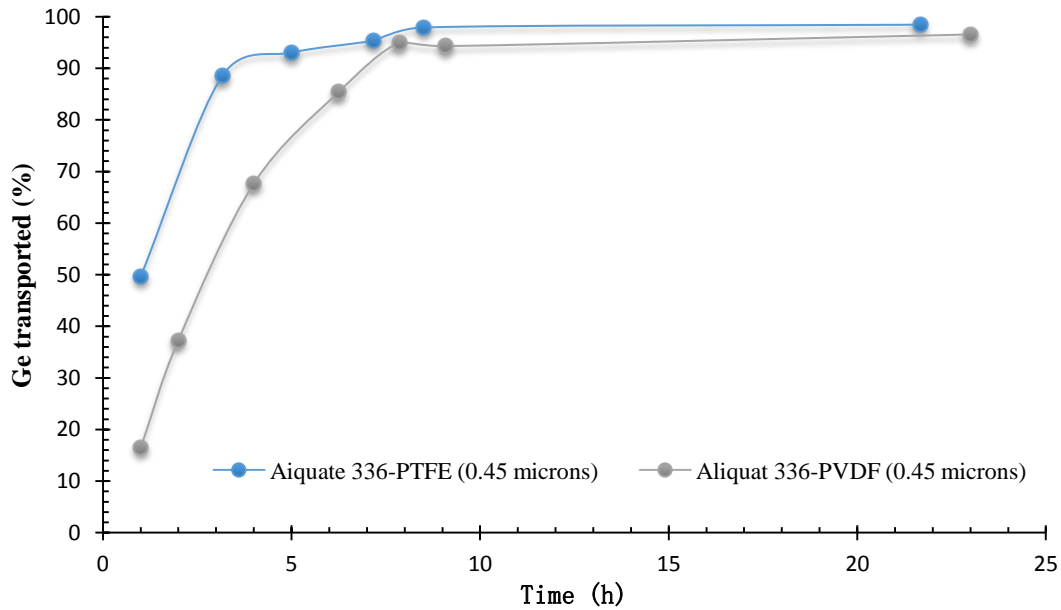


Fig. 4. Transport percentage of germanium vs. time through PTFE and PVDF membranes (100 mg/L of Ge, Ni, Cd, Co and 1000 mg/L of Zn, the tartaric acid to Ge mole mass ratio of 2, and stripping HCl concentration of 1 M).

According to this figure, the transport percentage corresponding to the PTFE disc membrane at systems with a similar condition is higher than that of the PVDF disc membrane. It is noteworthy that the transport percentage of the other ions is close to zero and the corresponding results have not been shown. The permeability coefficients of germanium transport through the PVDF and PTFE membranes were found to be 1.98×10^{-3} and 2.65×10^{-3} cm/s, respectively. Hence, the PTFE membrane type was a proper membrane for the facilitated transport of germanium by Aliquat 336 carrier. Such results were reported in the literature. PTFE membranes have improved efficiency in operations and greater mass transfer coefficient (Adnan et al., 2012; Zhang et al., 2009).

4.2. Effect of carrier concentration

The effect of the carrier concentration on the selective transport of germanium from a solution containing 100 mg/L of Co(II), Cd(II), Ni(II), and 1000 mg/L of Zn(II) was investigated in the concentration range of 0.5-10 %v/v in an FSSLM system with a PTFE disc membrane with the pore size of 0.45 μm . The initial pH of the feed solution (after the addition of tartaric acid to the water medium) was 2.63 ± 0.10 . According to the discussion carried out in the theory section, the Aliquat 336 molecules within the membrane phase form complexes with germanium anionic species in the diffusion layer and carry the germanium through the membrane toward the receiving side. Therefore, this transport is facilitated and accelerated by increasing the carrier concentration. However, the presence of more carrier concentration in the FSSLM system has an inverse effect on the transport. The extra concentration of the carrier enhances the viscosity of the solvent in the liquid membrane and decelerates the transport rate of germanium species across the membrane. (Bhatluri et al., 2014) The dynamic viscosity increases from 1.46 to 2.77 cP by enhancing the Aliquat 336 concentration from 0.5 to 10 %v/v. Therefore, the determination of an optimum concentration of the carrier to concise the mentioned advantages and disadvantages is vital in an FSSLM system.

Fig. 5 shows the germanium transport efficiency across FSSLM using various concentrations of Aliquat 336. As seen in this figure, the transport percentage of germanium for Aliquat 336 concentration of 0.5 and 1 %v/v was less than 10% after prolonging time up to 21 h. This fact showed that these concentrations were not enough for forming complexes of germanium anionic

species and carrier molecules. However, the transport efficiencies were significantly enhanced by increasing the carrier concentration.

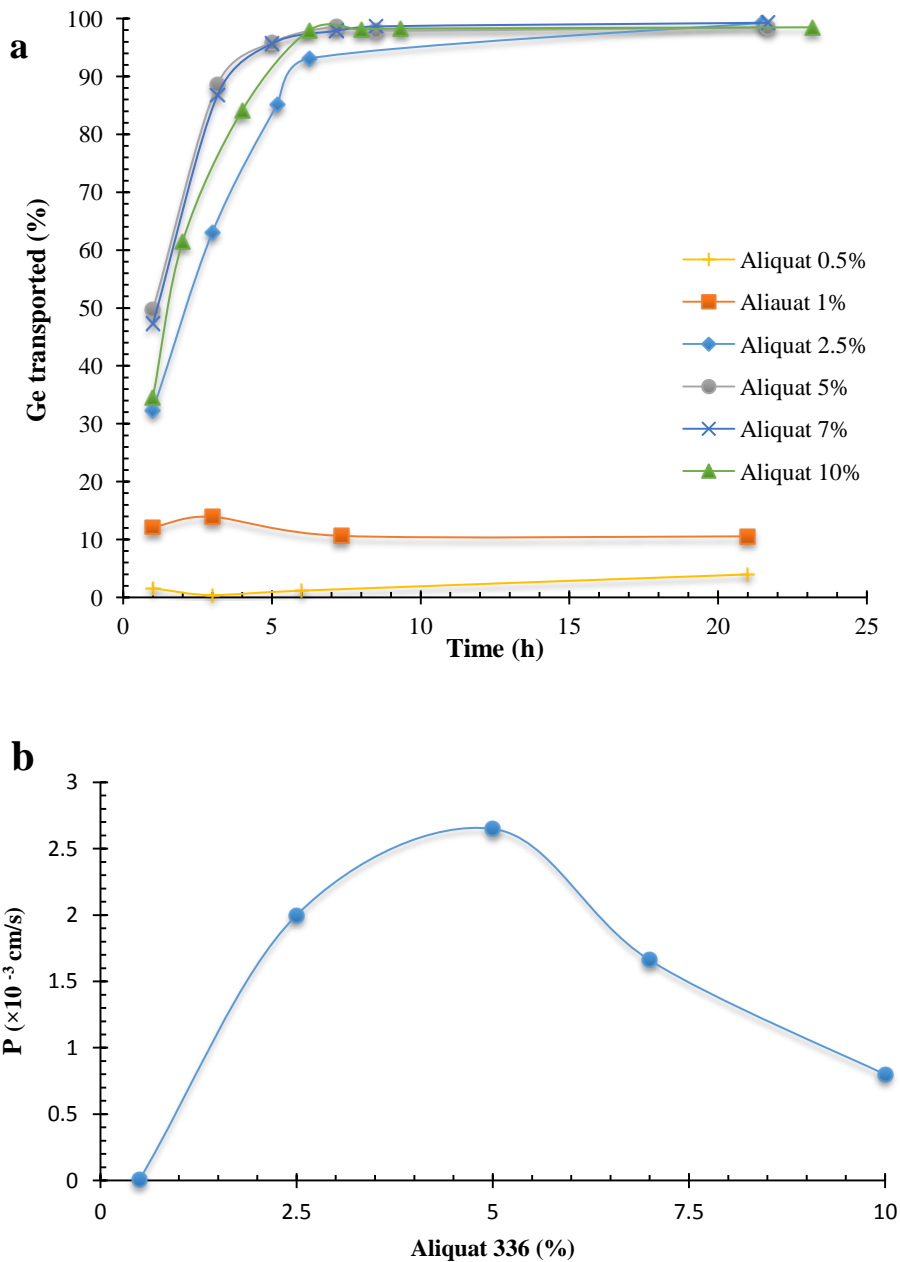


Fig. 5. (a) The transport efficiency of germanium vs. time through PTFE using various concentrations of Aliquat 336 and (b) the effect of carrier concentration on the permeability

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4 coefficient of germanium (100 mg/L of Ge, Ni, Cd, Co and 1000 mg/L of Zn, the tartaric acid to
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6 Ge mole mass ratio of 2, and stripping HCl concentration of 1 M).

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10 As seen in Fig. 5(a), there is not a significant difference among the transport curves for the
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12 carrier concentrations in the range of 5-10%. In this range, after 20 h, all the germanium was
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14 approximately transported to the receiving phase. Furthermore, Fig. 5(b) illustrates the
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16 permeability coefficient variations versus Aliquat 336 concentration. With respect to this figure,
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18 the permeability reached the maximum value of 2.65×10^{-3} cm/s at the carrier concentration of
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20 5%. After this point, the permeability coefficient reduced. This reduction may occur due to an
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22 increase in the viscosity of the carrier at the interface of the liquid membrane resulting in the
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24 reduction of the species diffusion rate.(Bhatluri et al., 2014; Chakrabarty et al., 2009) Taking
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26 into account the inverse relation of the permeability and the viscosity in high viscosity liquids,
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28 this reduction can be justified (Hiss and Cussler, 1973).
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35 In order to find the selectivity of the germanium transport among heavy metals existing in the
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37 solution, the selectivity factor was used for calculation as in Eq. (2):
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$$\alpha_{Ge/Me} = \frac{P_{Ge}}{P_{Me}} \quad (2)$$

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46 Where P denotes the permeability coefficient and Me depicts the metal. The calculated results
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48 were listed in Table 1. As seen in this table, since the transport of germanium in the carrier
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50 concentration below 2.5 %v/v is lower than 10%, the selectivity factors for these concentrations
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52 could not be calculated. The values of separation factors showed that germanium was readily
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54 separated from Cd(II) and Co(II) at any concentration. Furthermore, the complete separation of
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56 germanium from Zn(II) was done at the concentration of 2.5 and 5 %v/v; however, at higher
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58 concentrations of 7 and 10 %v/v, the separation was not completely carried out. In addition, a
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good separation between zinc and nickel was observed. Despite the incomplete separation in some concentrations, the transport efficiencies for heavy metals were less than 0.5% indicating their negligible transport.

Table 1. Selectivity factor in various concentrations of Aliquat 336 (in the same condition mentioned in Fig. 5).

Aliquat (v/v%)	$\alpha_{\text{Ge/Zn}}$	$\alpha_{\text{Ge/Cd}}$	$\alpha_{\text{Ge/Co}}$	$\alpha_{\text{Ge/Ni}}$
0.5	-	-	-	-
1	-	-	-	-
2.5	∞	∞	∞	692.3077
5	∞	∞	∞	607.6433
7	1359.091	∞	∞	600
10	411.4286	∞	∞	480

4.3. Effect of tartaric acid ($C_4H_6O_6$) addition

As mentioned before, the presence of a complexant in a solution containing germanium is important to convert it to anionic species. Catechol as an organic reagent and carboxylates such as citric acid and tartaric acid are some materials that can be used for this conversion. According to the liquid-liquid extraction experiments, the results of which are published elsewhere, tartaric acid is an efficient and environmental-friendly material that could be used in the current study. In this regard, this complexant was selected for use in this study. In order to find the effect of the tartaric acid amount in the feed solution on the formation of anionic germanium species and its transport, a series of experiments were conducted by changing the mol mass ratio of tartaric acid to Ge(IV) of the feed phase in the range of 0-2. Since the germanium concentration in the initial

feed solution is 100 mg/L (1.38 mol/L); thus, the amount of tartaric acid added to the solution is a multiple of 1.38 mmol/L. The results were illustrated in Fig. 6. As seen in this figure, with prolonging time up to the equilibrium condition, the transport efficiencies were enhanced. Moreover, the results showed that by increasing the tartaric acid amount to the feed phase, the transport efficiency increased. However, after an amount of 1.5 (of tartaric acid to Ge molar ratio), the efficiency was not significantly changed. As a result, the complete transport of germanium (100%) from the feed solution to the receiving solution was done at the tartaric acid to Ge ratio of 2. Table 2 shows the permeability coefficient of germanium transport through the FSSLM system. Since the transport in the lower tartaric acid concentrations is not complete, the permeability coefficient could not be calculated. As seen in this table, the permeability coefficient rises with an increase of tartaric acid. However, the increase rate at the concentration equal to 2 times of tartaric acid decreases.

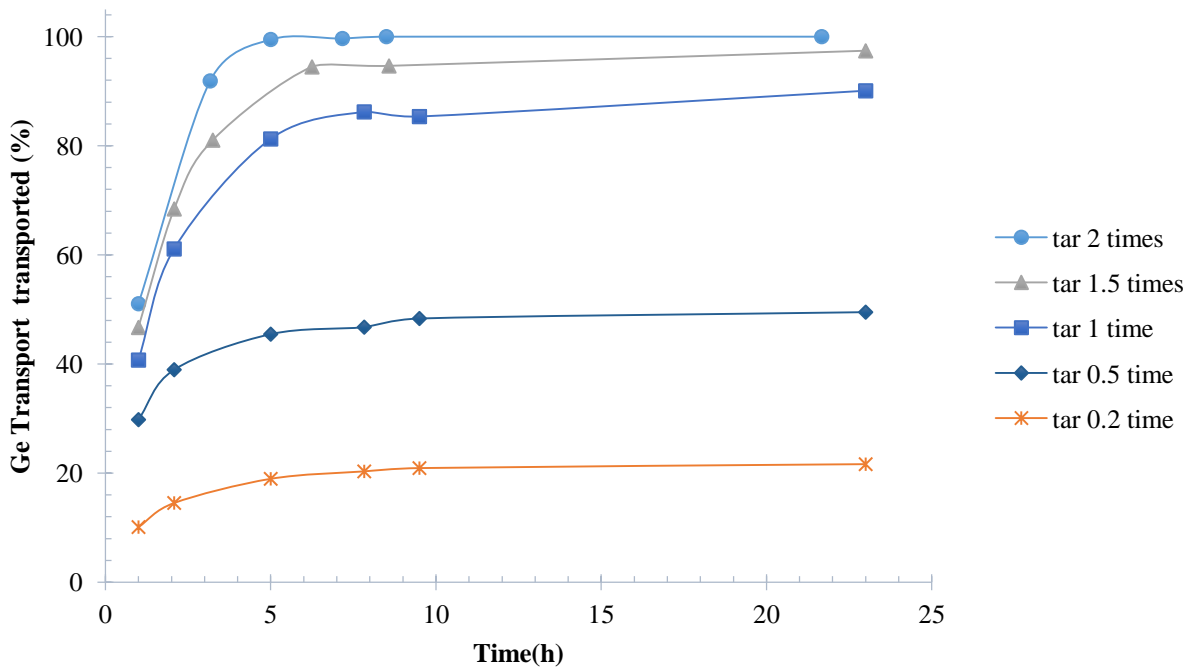


Fig. 6. Effect of tartaric acid on the germanium transport (Ge, Ni, Cd, and Co of 100 mg/L as well as Zn 1000 mg/L, Aliquat 336 concentration of 5 %v/v and HCl concentration of 1 M).

Fig. 7 shows the transport efficiency of heavy metals transported through the membrane. As seen in this figure, the transport efficiency of zinc decreased with an enhancement of the tartaric acid up to 0 % at the 2 molar ratios. Also, the transport of nickel was increased up to a steady level of 1% after the addition of 1 mol mass ratio of tartaric to Ge. Moreover, the values of cadmium transport efficiency did not show a specific trend. Since the transport efficiency of these metals is less in comparison to germanium transport, these unordinary variations are not significant.

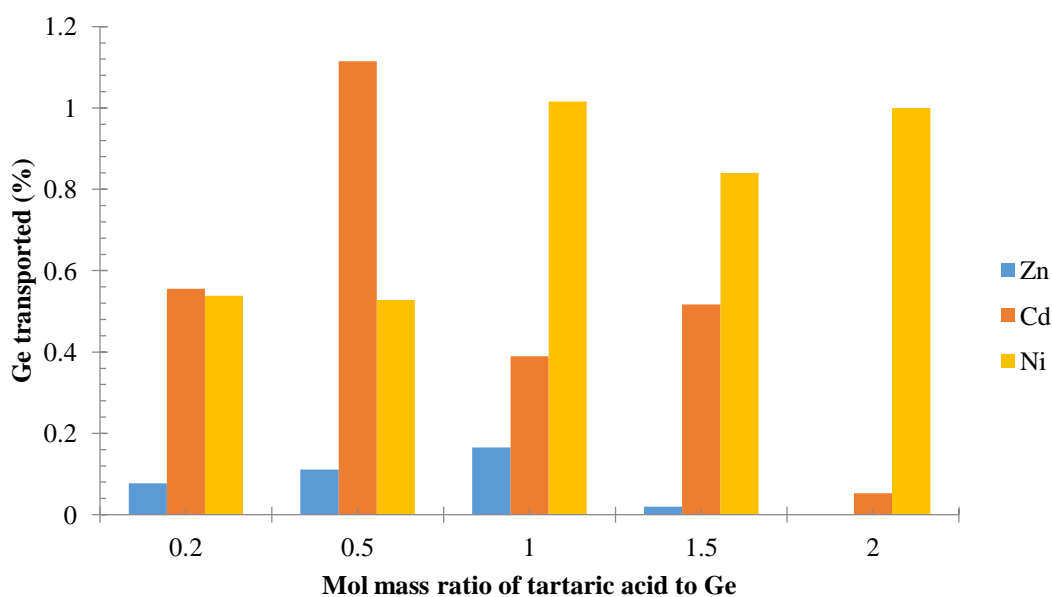


Fig. 7. Effect of tartaric acid on the transport of heavy metals (with the same condition mentioned in Fig. 6).

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7 Table 2. Effect of the tartaric acid amount on the permeation coefficient (the condition is as mentioned in

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9 Fig. 6)

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tartaric acid: Ge	Permeability
ratio	coefficient (cm/h)
0.2	*
0.5	*
1	5.84
1.5	9.29
2	9.54

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28 *4.4. Effect of HCl concentration as the receiving solution on the permeation*

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30 According to the liquid-liquid extraction studies, hydrochloric acid is an efficient acidic reagent
31 for the stripping of extracted germanium. The stripping efficiency of various concentrations of
32 HCl in the receiving solution was investigated in the range 0.25–2.0 M. Fig. 8 illustrates the
33 effect of HCl on the transport efficiency of germanium. The figure obviously shows the
34 enhancement of the transport efficiency with an increase in HCl concentration. The preliminary
35 growth in the germanium transport corresponding to the HCl concentrations less than 1 M is
36 because of the increase in the germanium species decomplexation occurred at the interface. The
37 transport efficiency for the HCl concentrations of 0.5-2 M approximately remained constant;
38 however, for the concentration of 1 M, it tended to be maximum. In the strip solution
39 concentration above 1 M HCl, the extracted germanium species by the carrier are decomposed
40 and this process is induced by the interfacial reactions during the stripping. At the mentioned
41 concentrations, this decomposition takes place rapidly, as the following diffusion of species into
42 the strip solution does not depend on the acid concentration. Consequently, the proton
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4 concentration gradient in the stripping phase does not create an important driving force during
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6 the transport of germanium.(Duan et al., 2017) According to the literature, this behavior occurs
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8 because the driving force saturation for the diffusion across the membrane takes place when
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10 metal compound concentrations enhance at the interfacial level in the membrane-strip solution
11
12 interface.(Venkateswaran and Palanivelu, 2005) Moreover, the effect of HCl on the transport of
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14 heavy metals in the feed solution showed that the transport of these metals is not significant in
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16 comparison to germanium transport because the transport efficiencies of all these metals were
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18 less than 0.5%.

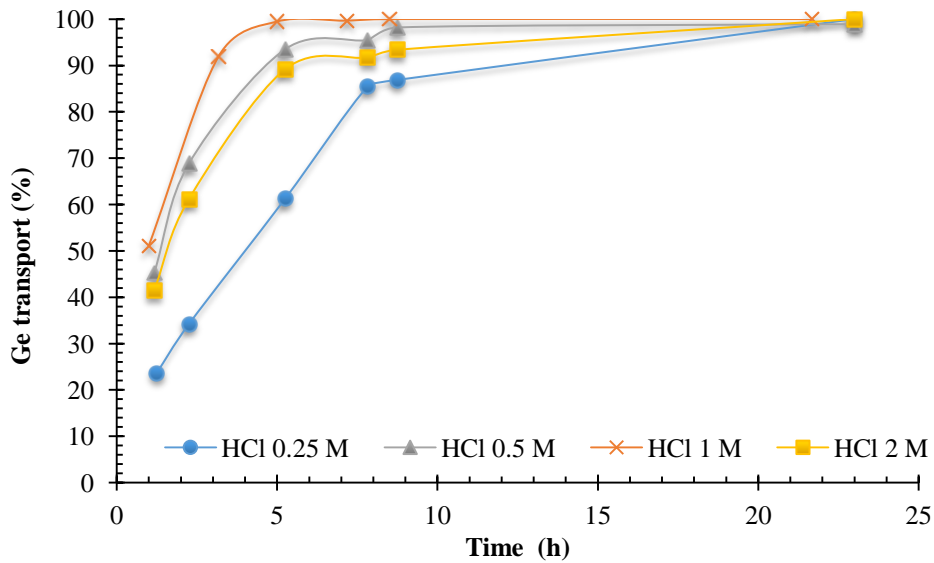


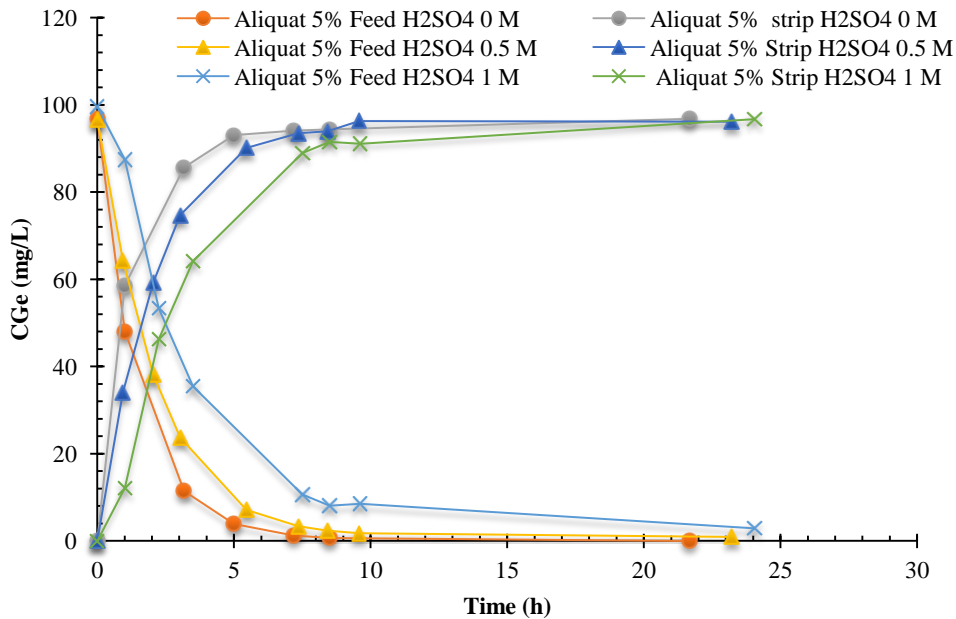
Fig. 8. Effect of hydrochloric acid in the strip phase on the transport of germanium (Ge, Ni, Cd, and Co of 100 mg/L as well as Zn 1000 mg/L, Aliquat 336 concentration of 5 %v/v, the tartaric acid to Ge mole mass ratio of 2, and HCl concentration of 1 M).

4.5. Transport of germanium from simulated zinc leach liquor

All the experiments in the previous sections were carried out in the water medium being the simulated solution obtained from leaching of gasification fly ashes. As discussed in the

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4 introduction section, one of the germanium resources is zinc ore. Therefore, to know the
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6 behavior of germanium transport through the FSSLM system of this study, an experiment was
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8 conducted in a solution containing 0.5 mol/L H₂SO₄ neutralized with NaOH solution until the pH
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10 reached a value of 3.5. The appropriate concentrations of H₂SO₄ for leaching of zinc
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12 ores/residues were reported to be in the range of 0.15-2 M.(Fattahi et al., 2016; Kamran
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14 Haghghi et al., 2015; Sadeghi et al., 2017; Sethurajan et al., 2017) In a sulfuric acid medium,
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16 iron commences precipitating at the pH of .(Claassen et al., 2002; Ismael and Carvalho, 2003;
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18 Kamran Haghghi et al., 2013) Thus, the pH range of the simulated solution in this study is
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20 similar to a solution in which iron has been removed by a precipitation process. An amount of
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22 tartaric acid (2.76 mmol/L) was added to this solution to keep converting germanium to anionic
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24 species. The concentrations of germanium, cadmium, nickel, and cobalt added to the
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26 aforementioned solution were about 100 mg/L, whereas the concentration of zinc added was set
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28 at 15 g/L similar to the concentration of a real zinc leach liquor. The other conditions of this
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30 system were similar to the optimum condition obtained before. Fig. 9 shows the concentrations
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32 of germanium in the feed and strip phases vs. time corresponding to the water medium (without
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34 H₂SO₄) and the simulated acid sulfuric zinc leach liquor. As seen in this figure, the curves
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36 corresponding to H₂SO₄ 1 M and 0.5 M show that an enhancement of the sulfuric acid
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38 concentrations in the solution changes the extraction equilibrium constant of the reaction
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40 between germanium-tartrate species with extractant molecules resulting in a reduction of
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42 transport rate at earlier times. The permeability coefficients corresponding to 1 M H₂SO₄, 0.5 M
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44 H₂SO₄, and water were calculated to be 1.58, 2, and 2.65 ($\times 10^{-3}$ cm/s), respectively. Hence, the
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46 transport rate and the permeability decreased with increasing sulfuric acid concentration. imilar
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48 results have been observed in the other studies.(Bhowal and Datta, 2001; Strzelbicki et al., 1984;
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Venkateswaran and Palanivelu, 2005) The conversion of germanium-tartrate anionic species to other forms such as H_2GeO_3 or Ge^{4+} in higher sulfuric acid concentration can be the probable reason of the mentioned decline. Similarly, it was seen that the conversion of $\text{Cr}_2\text{O}_7^{2-}$ species, i.e. those which could be extracted by Aliquat 336, to $\text{H}_2\text{Cr}_2\text{O}_7$ and HCr_2O_7^- in higher acidic concentration decreased the Cr(VI) permeation through liquid membranes using Aliquat 336.(Strzelbicki et al., 1984) It is noteworthy that since the transport of the other metals was approximately close to zero, the related results were not shown. Therefore, it can be concluded that this system can efficiently separate germanium from a zinc concentrated solution in the presence of some important impurities such as cobalt, nickel, and cadmium. The remaining zinc in the feed solution can be proceeded to a zinc solvent extraction using 30 %v/v D2EHPA for the selective separation of zinc from nickel, cadmium, and cobalt to obtain a concentrated solution containing about 90 g/L of Zn. This solution can be treated in an electrowinning process to obtain zinc cathodes. These results can be used to develop and design processes for the separation of germanium from zinc leach liquors.



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4 Fig. 9. The concentrations of germanium in the feed and strip phases vs. time in a sulfuric acid
5 medium of 0,50 and 1 mol/L as well as water medium (Ge, Ni, Cd, and Co of 100 mg/L as well
6 as Zn 15 g/L, Aliquat 336 concentration of 5 %v/v, the tartaric acid to Ge mole mass ratio of 2
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8 and HCl strip solution concentration of 1 M)
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10 11 12 *4.6. Hollow fiber supported liquid membrane* 13 14

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16 The hollow fiber supported liquid membrane is a developed supported liquid membrane with the
17 same mechanism as FSSLM. However, HFSLM difference in comparison to FSSLM is in the
18 structure of the membrane in which a cylindrical module with so much high interfacial area per
19 unit is used.(Gabelman and Hwang, 1999) Because of this area, the transfer in HFSLM is faster
20 than FSSLM. One of the aims for carrying out FSSLM experiments was to find an appropriate
21 condition by which an experiment was conducted by the HFSLM technique. In this regard, a
22 solution containing Ge, Ni, Cd, and Co of 100 mg/L along with Zn of 1000 mg/L was prepared
23 in the presence of the optimum tartaric acid concentration mentioned in the FSSLM system.
24 Aliquat 336 5 %v/v as a carrier and HCl solution with a concentration of 1 M as a strip solution
25 were used in the experiment. As mentioned in the experimental and method section, the feed
26 volume was selected 4 times that of the strip phase volume to enrich germanium in this solution.
27 This selection was a systematic choice and merely arbitrary for the test. Thus, it was expected
28 that the concentration in the strip phase reached a maximum concentration of 400 mg/L. The
29 result of the experiment is illustrated in Fig. 10. As seen in this figure, the transport percentage of
30 germanium in the feed phase was rapidly increased to reach a steady state. This state was
31 achieved in less than 30 min, which was comparable to liquid-liquid extraction equilibrium
32 times. On the other hand, the germanium concentration enhanced in the strip phase with an
33 expected factor of 4 times to reach a maximum concentration of ≈ 400 mg/L. Due to the existence
34 of mass transfer resistance restrictions corresponding to the strip side, the germanium
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enhancement rate in this side is lower than that of the feed side. Thus, as shown in Fig. 10, an amount of germanium remained in the membrane phase in the time range of 0-120 min. Several researchers reported similar results.(Manna et al., 2014; Staszak et al., 2017; Wannachod et al., 2014) However, after an approximate time of 240 min, all germanium ions were transported to the strip phase. This showed that the transport rate in HFSLM is much faster than that in the FSSLM system. Since no transports were observed for the other metals, their results are not presented here. Consequently, the HFSLM system of this study is an effective technique for the treatment of solutions such as leachates obtained from gasification fly ash leach liquors or wastewaters containing germanium.

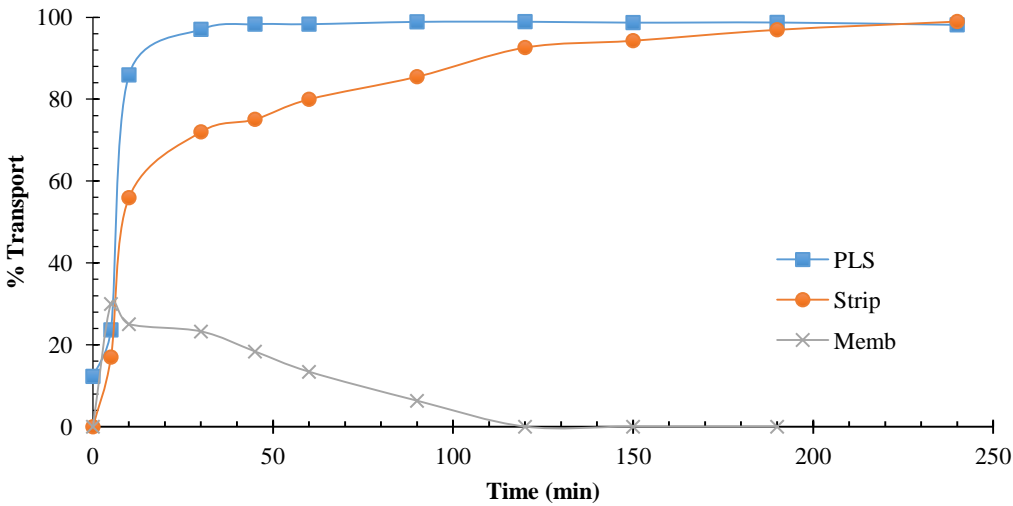


Fig. 10. Hollow fiber SLM results (Ge, Ni, Cd, and Co of 100 mg/L as well as Zn 1000 mg/L, Aliquat 336 concentration of 5 %v/v, the tartaric acid to Ge mole mass ratio of 2 and HCl strip solution concentration of 1 M).

5. Conclusion

FSSLM processes using the carrier of Aliquat 336 were developed to transport germanium from the simulated gasification fly ash-water/zinc sulfuric acid leach liquors containing heavy metals.

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4 Based on the experiments on the simulated gasification fly ash-water leachate, the optimum
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6 condition was found to be Aliquat 336 concentration of 5 %v/v, the molar mass ratio of tartaric
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8 to Ge equal to 2 and HCl strip concentration of 1 M. In this condition, more than 98% of
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10 germanium was selectively transported without transporting the other heavy metals. According
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12 to the results, an enhancement of the carrier concentration up to 5 %v/v increased the germanium
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14 transport. Under this condition, an FSSLM process was conducted in a simulated zinc acidic
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16 leachate neutralized by NaOH up to a pH of 3.5. Similar results were observed in this medium,
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18 showing an insignificant influence of sulfuric acid on the germanium anionic species transport.
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20 Finally, an HFSLM system was developed to transport germanium from a water medium to the
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22 diluted HCl and results showed that germanium was completely transported to the strip phase
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24 after 240 min. Since the volume ratio of the strip to the feed solution was set at 4, the
25
26 concentration of germanium in this solution was enriched up to 400 mg/L.
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