Germanium Recovery Using Ion-Exchange Membrane and Solvent Extraction

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Abstract
Germanium is a kind of rare metal. For the recovery of germanium ion, the novel recovery process is proposed using the complexation of germanium ion with catechol in solution; germanium ion is complexed with catechol forming anion, and then the anion-containing solution is flowed through quaternary-ammonium-group-containing membrane. In permeation mode, germanium ion is adsorbed to the membrane with catechol via ionic interaction. In actual wastewater of solar panel, silicate ion existed with germanium ion. At pH 3.0, germanium ion was selectively adsorbed to the membrane in the presence of silicate ion. The remained catechol in the effluent from the membrane was removed by solvent extraction with TOPO.

Keywords: germanium recovery, membrane, catechol, solar panel, recovery, solvent extraction

1. Introduction
Germanium has been used for semiconductors, catalysis, and optical apparatuses. Due to heightened interest in renewable energy sources, the production of solar panels has increased\(^1\). In the production of solar panels, germanium is doped to a silicon compound so as to change the energy gap\(^2\). When recycling of germanium from the wastes, some techniques have been proposed. Hydrometallurgy is one of candidates for the recovery. In this process, germanium-containing waste is firstly dissolved to the solution using acid or alkali. Methods of hydrometallurgy address solvent extraction\(^3\), flotation\(^4\), and adsorption\(^5\). In adsorption process, N-methylglucamine-containing resin is contacted with germanium solution. Also, the polymer brush with N-methylglucamine group introduced to the pore of the membrane causing the germanium ion to be adsorbed in permeation mode through N-methylglucamine-introduced membrane\(^6\).

Germanium ion is known to be complexed with catechol in the solution\(^7\) as following equation,

\[
\text{Ge(OH)}_2 + 3 \text{C}_6\text{H}_4\text{OH} \rightarrow \text{Ge}[(\text{C}_6\text{H}_4\text{O}_2)]_3^{2-} + 2\text{H}^+ + 4 \text{H}_2\text{O}.
\]  

The complex structure of germanium and catechol forms the symmetric structure in three dimensions. In solution, the complex has an anionic charge. Using this characteristic, the following process for the recovery of germanium is possibly proposed (Fig. 1)\(^8,9\): (1) germanium ion is complexed with catechol in solution, and (2) anion complex of germanium ion is captured by the quaternary-ammonium-group-introduced membrane in permeation mode. Germanium complex can be adsorbed to the membrane via strong anion-exchange interaction. Membrane has the potential adsorbent in permeation because the target is transported with convection flow to the vicinity of the moiety of adsorption site, causing the high-speed recovery of germanium ion.

In this study, germanium ion was recovered using the novel process as shown in Fig. 1. The effect of pH in solution for complexation was determined. In flow system using the membrane, breakthrough curve of germanium ion to be adsorbed in permeation mode through N-methylglucamine-introduced membrane was examined. The germanium-doped solar panel mainly is composed of silicon. Actual wastewater of germanium and silicate ions was treated with this process for the hydrometallurgy application.

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2. Experimental

2.1 Materials

Germanium oxide was obtained from Wako Pure Chemical Industries, Ltd. Flat sheet anion-exchange membrane, RX-1, was purchased from Toray Industries, Inc. The functional group, functional group density, diameter, thickness, and pore diameter of the membrane were quaternary ammonium group, 2.1 mol/kg, 47 mm, 240 μm, and 0.74 μm, respectively. Anion-exchange membrane has the counter ion of Cl⁻ and was used without further exchange. The waste of solar panel was a gift from NT Corporation, Japan. The other chemicals were of analytical grade or higher.

2.2 Germanium adsorption in batch mode

Germanium solution was mixed with catechol (10 mg) in 10 mL for 6 hours at 303 K. pH was adjusted with 0.1 M HCl and NaOH solution. After the complexation of germanium ion with catechol, the solution was filtered using RX-1 membrane by gravity. Recovery percentage in a batch mode was determined from the concentration in the filtered solution. The concentration of germanium ion was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICPS-8100, Shimadzu, Kyoto, Japan). The pH value in a solution was measured after the filtration of solution.

2.3 Continuous recovery of germanium ion by complexation and flow through the membrane

Solution of germanium ion and catechol was added to a beaker with stirring. The solution was flowed through a stack of three sheets of RX-1. The diameter of the membrane was 4.7 mm and the three sheets of the membranes were stacked. The thickness of the membrane was measured by a ruler and the volume of the membrane calculated was 1.5 mL. The effluent was collected continuously using vials. The concentration of germanium ion and catechol was determined using ICP-AES and UV-Vis spectroscopy (Hitachi U-3310, Japan), respectively. The wavelength of UV-Vis was 260 nm.

2.4 Germanium recovery from wasted solar panel using membrane process

Wasted solar panel (1.0 g) was dissolved in 0.1 M NaOH solution (1 L). The quantitative analysis of the wasted solution was performed by ICP-AES. The wasted solar-panel solution was mixed with catechol solution (15 mM) at 150 rpm and 303 K for 6 hours. Then the solution was flowed through RX-1 using peristaltic pump (perista bio-mini pump Atto, AC-2120). The wasted solar panel solution was flowed through the membrane at the flow rate of 60 mL/h. The effluent was collected and the concentration of the germanium and silicate ions was determined using ICP-AES. The concentration of catechol in the effluent was also determined by UV-Vis. The amount of germanium and silicate ions adsorbed was calculated from the concentration in the effluent. After the adsorption of germanium and silicate ions, the metal ions were eluted with permeating 0.1 M HCl solution.

2.5 Solvent extraction of germanium ion by TOPO

The eluted germanium solution in each fraction from treated actual waste water was gathered to one solution. The solution (10 mL) was mixed with 100 mM of TOPO (triocetylphosphine oxide) dissolved to hexane (10 mL). The two-phase solution was stirred for 3 hours at 150 rpm and at 303 K. The concentration of germanium ions, silicate ions, and catechol in water phase was determined by ICP-AES and UV-Vis.

3 Results and Discussion
3.1 Adsorption of germanium ion in a batch mode

Germanium ion forms the complex with catechol as a structure of \( \text{Ge}[(C_6H_4O_2)]_3^{2-} \). The complex is an anion. Using this characteristic, germanium ion can be recovered using 1) catechol complexation and 2) complex adsorption using quaternary-amine-introduced membrane. Here, quaternary-ammonium-containing membrane, RX-1, was used for the interaction with the complex. The illustrated scheme of the process is shown in Fig. 1. Firstly, germanium ion is complexed with catechol in homogeneous solution. Then the solution including germanium-catechol complex is flowed through RX-1, causing the complex is captured to the membrane via ionic interaction. Catechol also was adsorbed to the anion-exchange membrane because phenol group dissociated to form anion, resulting in the adsorption via ionic interaction. In a solution in the presence of germanium ion and catechol ion, the competitive adsorption would occur. In this case, the concentration of catechol was much higher than that of germanium ion, demonstrating that catechol would not only form the complex with germanium ion, but also exist as a free state to adsorb the anion-exchange membrane.

The structure of germanium-catechol complex is dependent on pH of the solution. Generally, quaternary ammonium is a cation form independent on pH. A batch mode of pH dependence is shown in Fig. 2. Here after the complexation, the solution was filtered through RX-1 by gravity. With increasing pH, the germanium recovery percentage increased and then at pH of more than 10 it decreased. At eq. (1), during the complex formation, proton is released, meaning that with increasing pH the amount of germanium complex formation with catechol increased. However, at alkali region catechol is unstable and sometimes forms the polymerization by itself. Thus, at high pH, catechol did not function as a complex ligand to germanium ion.

3.2 Continuous flow through proposed process

The proposed scheme in Fig.1 includes the complexation of germanium ion with catechol in solution, forming an anion, and then the complex solution is flowed through the membrane. In membrane process, because targets transfer to the adsorption site via convection, efficient recovery of germanium would be achieved. The breakthrough curve of germanium through the membrane is shown in Fig. 3. Below bed volume of 80, no elution of germanium was observed after that the concentration of germanium was gradually eluted. The concentration of catechol in the effluent was determined at the same time. The trend of catechol concentration in the effluent was similar to that of germanium ion up to bed volume of 80 and then gradually increased. Here concentration of germanium ion and catechol was 2 and 20 mM, respectively. Ideally, the complexation occurs at the ratio of 1:3 of germanium ion and catechol ion as eq. (1). However, during the processing such as complexation and permeation, the complexation ratio would be changed, and the complex formation and adsorption did not take place in stoichiometry.

3.3 Germanium recovery from actual solar-panel waste

There are many opinions regarding energy crisis. To
overcome the crisis, some strategies for the energy production have been founded. Among them, solar panel production has been one of important candidate. The production speed of solar panel is exponentially increased, thus, the waste of solar panel also is increased. Germanium is sometimes doped to silicon substrate to control the energy gap. Because germanium is a kind of rare metal, it should be recovered against the silicate ion using hydrometallurgy.

In this study, at first, wasted solar panel was dissolved to alkaline solution for hydrometallurgy. Mainly, the panel was composed of SiO$_2$ and GeO by X-ray fluorescence analysis. Therefore, the metal ions in alkaline were germanium and silicate ions at the concentrations of 0.32 and 14 mM, respectively. The ratio of germanium ion per silicate ion was calculated to be 0.022.

The obtained germanium-containing solution was treated by recovery process. The pH value is the crucial parameter to control the recovery efficiency of germanium. In this case, germanium ion co-existed with silicate ion. Therefore, the selectivity of germanium ion against silicate ion should be considered. The pH value was changed from 3.0 to 12.0, demonstrating that the breakthrough curve at pH 3.0 was the most preferential result because the selectivity of germanium ion was higher. Increasing pH enhanced the adsorption of germanium ion, silicate ion, and catechol ion to the membrane because the amount of germanium–catechol complex as well as free catechol ion were increased. In this study, pH of the solution was set at 3.0. The concentration of germanium ion, silicate ion, and catechol from the membrane was determined and the breakthrough curves of them were obtained, as shown in Fig. 4. Catechol added to the wasted solution was at 1.5 mM, which is much higher than that of germanium ion. Germanium ion was selectively adsorbed compared with silicate ion. At a lower pH, germanium ion stably forms the complex with catechol in homogeneous solution. Also, silicate ion has the ability of the complex with catechol. However, germanium ion forms the more stable complex with catechol. The concentration of silicate ion in wasted solar-panel solution was high compared with germanium ion. Germanium ion and catechol in the solution at low concentration was gradually adsorbed to the membrane, while, silicate ion was quickly saturated at the steady state in permeation mode as shown in Fig. 4. Catechol was gradually eluted with germanium ion and silicate ion from the membrane, in which catechol either formed the complex with metal ions or existed as a free state.

To elute the adsorbed germanium ion to the membrane, high concentration of HCl is a powerful reagent. The HCl solution (0.1 M) was flowed through the germanium-ion-adsorbed membrane and the concentration of germanium ion was determined, demonstrating that germanium ions, silicate ion, and catechol were 0.064 mM, 0.073 mM, and 0.60 mM, respectively. The ratio of germanium ion per silicate ion in the eluate was calculated to be 0.087, meaning that the ratio was increased up to four times compared with initial wasted solution.

TOPO in solvent extraction was known to form a complex with catechol in a lower pH region. The –P=O group in TOPO is predicted to form the stable complex with hydroxyl group in catechol. Catechol has some hydroxyl groups of phenol like catechol. Therefore, catechol would be extracted with TOPO using solvent extraction. The obtained eluted solution including germanium ions, silicate ions, and catechol was conducted with TOPO dissolved in hexane. After the extraction, the concentrations of germanium ion, silicate ion, and catechol ion in water phase were 0.064, 0.072, and 0.11, respectively, demonstrating that the extraction percentage of catechol was 81%, whereas there was no extraction for two metal ions. This solvent extraction is very powerful to remove catechol.

### 4. Conclusions

The novel process of germanium recovery including complexation in solution and permeation through the membrane was proposed. Germanium ion forms the complex of an anion with catechol. For the recovery of germanium, firstly germanium ion was complex with catechol and then the complex-containing solution was flowed through quaternary-ammonium-containing membrane. The anion was captured via ionic interaction in the membrane. In continuous process, germanium ion was selectively adsorbed to the membrane in the presence of silicate ion. Using a real wastewater, the solar panel including germanium ion was dissolved to alkaline solution and then the solution was treated by the proposed process, demonstrating that the concentration of germanium ion against silicate ion increased after processing. The remained catechol was removed using solvent extraction with TOPO. This technique has the potential for the smart germanium recovery in hydrometallurgy.

### Acknowledgements

Wasted solar panel was donated from NT Corporation, Saga, Japan.

### References

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