



## Recovery of germanium from waste solar panels using ion-exchange membrane and solvent extraction



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### ARTICLE INFO

#### Article history:

Received 17 April 2013

Accepted 3 October 2013

Available online 6 November 2013

#### Keywords:

Germanium

Solar panel

Catechol

Membrane

Solvent extraction

Recovery

### ABSTRACT

Germanium was recovered from the waste solar panels using the processes of selective catechol complexation, membrane adsorption and elution, and solvent extraction. Because the solar panels included a high concentration of germanium, the key technique used was high selectivity against silicate ion using hydrometallurgy. Due to the selective complexation of germanium ions with catechol, the operation at low pH enhanced the selectivity. 0.1 M hydrochloric acid was used to elute the germanium ions. To remove the catechol from the germanium containing solution, solvent extraction using trioctylphosphine oxide was performed, demonstrating that 81% of catechol was removed. Compared with the initial percentage of germanium to silica, the concentration of silicate was 39 times higher in the germanium-concentrated solution, indicating that the proposed sequential process was very a powerful technique for the recovering germanium.

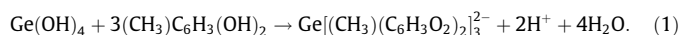
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### 1. Introduction

Germanium is a rare semi-metal and is used in semiconductors, catalysis, and optical apparatuses. Due to heightened interest in renewable energy sources, the production of solar panels has increased (Mark, 2009). In the production of solar panels, germanium is doped to a silicon compound so as to change the energy gap (Matéo-Vélez et al., 2012). Processing of solar panel production generates the mixed waste of germanium and silicon. When recycling this waste, germanium should be recovered from germanium-containing waste, as it is a rare metal.

Hydrometallurgy is the most important candidate for the recovery of germanium. In this process, the germanium-containing waste is dissolved into an alkaline or acid solution. Methods of hydrometallurgy include solvent extraction (Cote and Bauer, 1980), flotation (Hernández-Expósito et al., 2006), and adsorption (Caletka and Kotas, 1974). In adsorption, the adsorbent with the functional group *N*-methylglucamine is contacted with germanium-containing solution to capture germanium with the adsorbent (Yasida and Kawazu, 1991). The polymer brush with the functional group is introduced to the porous hollow-fiber membrane to permeate the germanium-containing solution, causing the germanium ion to be adsorbed via the transport of convection (Ozawa et al., 2000).

Germanium ion forms the anion complex with catechol in the solution (Pokrovski and Schott, 1998) as follows,



Ideally, the complexation with germanium and catechol forms a symmetric structure in three dimensions. In the solution the complex has an anionic charge. Compared with silica ion, germanium has the more stable complex with catechol.

The following process has been proposed for the recovery of germanium using catechol complexation; (1) germanium ion is complexed with catechol selectively in solution. (2) Anion complex of germanium is captured by quaternary-ammonium-group-introduced membrane in permeation mode (Nozoe et al., 2012). The original effects produced by this process include that the selectivity to the metal ion is dependent on the ligand, catechol in this study, and that the formed anion is captured by the membrane in convection. Moreover, this process does not require the preparation of material de novo and is assembled with the commercially-available molecules and materials easily. In the previous study, the selectivity of germanium ion against silicate ion was already found (Takemura et al., 2013; Nozoe et al., 2012).

In this study, germanium ions were recovered from actual waste solar panels using the process as shown in Fig. 1. The powder including germanium is dissolved in alkaline solution. In the selective complexation of germanium with catechol, the complex is concentrated using the membrane system in Fig. 1. Next, the adsorbed germanium-complex is eluted by the permeation of HCl

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solution. Finally, coexisting catechol with germanium is removed using trioctylphosphine oxide (TOPO) in a solvent extraction system. The remaining water phase includes the high concentration germanium. The concentration ratio of germanium in the solution of dissolving waste solar panel to the germanium concentration in the solution after the processing is determined to propose the treatment of actual germanium-containing waste.

## 2. Experimental

### 2.1. Materials

The waste of solar panel was a gift from NT Corporation, Japan. Catechol was obtained from Sigma-Aldrich. Germanium oxide was obtained from Wako Pure Chemical Industries, Ltd. Flat sheet anion-exchange membrane, RX-1, was purchased from Toray Industries, Inc. The properties of RX-1 are summarized in Table 1. The functional group density of the membrane was 2.1 mol/kg-membrane. Trioctylphosphine (TOPO) was used for the extractant and donated from Hokko Chemicals Co., Ltd. The other chemicals were of grade or higher.

### 2.2. Leaching of germanium from waste solar panels

The observation of the waste solar panels was performed using optical microscopy (Keyence VH-S5). The solid analysis of the waste solar panels was determined by X-ray fluorescence analysis (Phillips, Majix Pro). One gram of the waste solar panels was dissolved with the alkaline solution (0.1 M NaOH, 1 L). The qualitative and quantitative analysis of the existing metal ions was determined by ICP-AES (Shimadzu 8100 ICPS). The pH of the obtained waste-solar-panels solution was adjusted using 5 M HCl solution at the appropriate values.

### 2.3. Germanium concentration and elution with catechol complexation and membrane

Germanium-containing solution from waste solar panels and catechol solution (1.5 mM) were mixed in a glass beaker at 150 rpm and 303 K for 6 h. The volume of the solutions was set at 10 mL. Three sheets of the membrane were packed in the folder of the membrane. The total volume of the membrane was 1.5 mL. The stirred germanium-catechol solution was flown through the anion-exchange membrane (RX-1) using the peristaltic pump (Perista bio-mini pump Atto, AC-2120) at the flow rate of 60 mL/h. The eluate through the membrane was collected using fraction collector (Advantec, CHF-161 RA). The concentration of germanium ion and silica ion was determined by ICP-AES. The concentration of

**Table 1**  
Properties of anion-exchange membrane (RX-1).

Matrix	Polystyrene
Functional group	Quaternary amine
Functional group density	2.1 mol/kg
Diameter of membrane	47 mm
Thickness of membrane	242 $\mu\text{m}$
Pore diameter of membrane	0.74 $\mu\text{m}$

catechol was determined by UV-vis (JASCO, V-630 BIO). The wavelength of UV-vis was set at 278 nm. The amount of the metal ions and catechol adsorbed to the membrane, bed volume (B. V.), and residence time were calculated using the following equation,

The amount of metal ions or catechol adsorbed (mol/kg)

$$= \int_0^v (C_i - C_e) dv / W \quad (2)$$

$$B.V. [-] = (\text{volume of the eluate}) / (\text{membrane volume in the folder}) \quad (3)$$

$$\text{Residence time [second]} = (\text{membrane volume packed}) / (\text{flow rate of germanium-containing solution}) \quad (4)$$

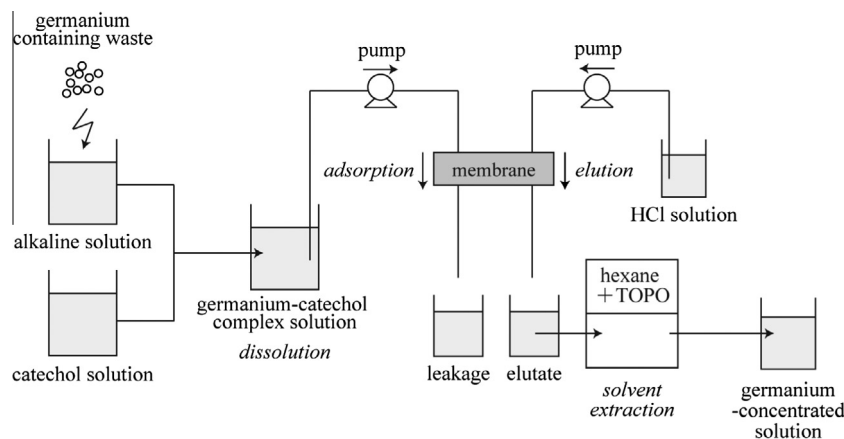
where  $V$ ,  $C_i$ ,  $C_e$  and  $W$  were volume of the eluate, the initial concentration of metal ion or catechol, the concentration of metal ion and catechol in each eluate, and the membrane weight, respectively.

The metal ions and catechol adsorbed to the membrane were eluted in permeating 0.1 M HCl solution at 60 mL/h. The elution was performed in only the case of pH 3.0-adjusted germanium-containing solution. The eluted fractions were collected and the concentration of metal ions and catechol was determined. The elution percentage was determined as the following equation,

$$\text{Elution percentage [\%]} = 100(\text{the amount of metal ions or catechol eluted}) / (\text{the amount of metal or catechol adsorbed}). \quad (5)$$

### 2.4. Solvent extraction of catechol using TOPO

The eluted germanium solution in each fraction was gathered to one solution. Ten mL of the solution was mixed with 100 mM of TOPO dissolved to hexane (10 mL). The two-phase solution was stirred for three hours at 150 rpm and at 303 K. The concentration of germanium ions, silicate ions, and catechol in water phase was



**Fig. 1.** Germanium recovery system using catechol complexation, membrane permeation, and solvent extraction.

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