Interfacial Reaction Design for
High-Purity Silica Production using
Wet-Chemical Processes

February 2016
Nobufumi MATSUO
Interfacial Reaction Design for High-Purity Silica
Production using Wet-Chemical Processes

界面反応設計による溶液処理を用いた
高純度シリカ生成プロセスの高度化

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Waseda University
Graduate School of Advanced Science and Engineering
Department of Nanoscience and Nanoengineering
Research on Nano Functional Surface Chemistry

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Chapter 1

General Introduction
1.1 Objective of this study

The production of solar-grade silicon (SOG-Si) is key in reducing the cost of Si photovoltaic devices, as the required purity of SOG-Si is 6N (99.9999%), i.e., less than that of semiconductor grade silicon (SEG-Si) by five orders of magnitude. To produce SOG-Si via inexpensive routes, the direct conversion of high-purity silica has attracted attention due to lower silica purification costs. Since amorphous silica can dissolve in alkaline solutions, an aqueous chemical purification process has been proposed, which purifies diatomaceous earth via an acid leaching process. Although heavy metals were eliminated using the acid leaching process, light elements, such as boron, remained in the silica. Thus, in the purification of silica, the efficient elimination of light elements is key due to their dopant activity and the higher solute partition coefficient to silicon.

To produce high-purity silica, an efficient and mass-productive purification method is required due to the high demand for SOG-Si. One promising device for this process is the microchannel device, which can shorten reaction time and precisely control the reaction through its short diffusion distance and large specific interfacial area. In addition, a sequential process can be carried out using the microchannel device, with the combination of unit operations such as mixing, extraction, and separation. The microchannel device is therefore an attractive device for the purification of silica followed by sequential elimination processes. The mass production design is also necessary for practical applications, as it maintains the efficiency of the microchannel devices. In this thesis, microchannel devices were applied in the purification of silica, and an optimized process aimed at mass production was proposed, focusing in particular on the solvent extraction of boron as a representative light element.

In Chapter 2, the application of the microchannel device is demonstrated using a typical y-type microchannel, employing 2-ethyl-1,3-hexanediol (EHD) as an extractant. To discuss the process quantitatively, a model sample composed of refined silica and trace amounts of boric acid and refined diatomaceous earth is utilized.

In Chapter 3, optimization of the microchannel device towards large scale production and the sequential process is reported. For the microchannel device, an increase in interfacial area with the horizontal liquid-liquid interface is demonstrated. In addition, the extraction reaction mechanism is investigated using theoretical calculations, employing 2,2,4-trimethyl-1,3-pentanediol (TMPD) as opposed to EHD. The combination of the updated microchannel with TMPD is also demonstrated.

In Chapter 4, the development of an efficient acid leaching process as a
preliminary purification process is described from the viewpoint of the chemical state of boron. An efficient and high yielding acid leaching process is investigated, controlling silica precipitation by adjusting ion strength, concentration, and/or pH.

1.2 Production of SOG-Si

1.2.1 Demand of SOG-Si

The demand for SOG-Si and the popularity of renewable energy have increased significantly in recent years.\textsuperscript{1-8} Originally, the main application of high-purity silicon was in integrated circuits (IC), where 11N purity (i.e., 99.999999999%) was required. Since the size of ICs has been drastically decreased according to Moore’s law, the demand for such high-purity silicon has not drastically increased. However, the advent of solar cells as renewable energy devices has changed the market for high-purity silicon once again. While the demand for SEG-Si has continued, the demand for solar cells has increased continuously due to the requirement of huge amounts of silicon for the generation of large quantities of electrical energy. When the market of solar cells was smaller, solar cell production was operated using off-grade SEG-Si. However, the demand for solar cells has increased to be significantly larger than that of SEG-Si. At present, the production of high-purity silicon for solar cells is independent from that of SEG-Si, although the production processes are similar.

The outlook for polysilicon demand for solar cells in 2014 was investigated by NPD Solarbuzz (Fig. 1.1),\textsuperscript{7} demonstrating a demand of over 250,000 tons, with 80\% of this demand being for SOG-Si. Thus, as the huge demand for SOG-Si continues to increase, production capacities have been increased. Although the global capacity is larger than demand, the capacities of GCL Poly, a Chinese company, and Wacker, a German company, were \textasciitilde50,000 tons/year in 2013. Furthermore, the capacities of OCI, a Korean company, and Hemlock, an American company, are \textasciitilde40,000 tons/year, with these companies planning to increase their capacities by 10,000 tons/year. When considering an alternative supply of SOG-Si, thousands of tons per year of production capacity would be required in one plant based on these predictions.
1.2.2 SOG-Si production method

The methodology for the production of high-purity silicon was originally developed in the semiconductor field, and is known as the Siemens process. This process begins with the carbothermal reduction of high-grade silica ore to produce metallurgical grade silicon (MG-Si). The MG-Si is then refined to SEG-Si (11N purity) through gasification, distillation, and re-crystallization processes. As the Siemens method was developed based on the semiconductor field, SOG-Si was conventionally produced from the off-grades of SEG-Si. However, with an increase in demand for and production of SOG-Si compared to SEG-Si, the Siemens process remains the mainstream production method, despite the distribution of high-grade silica ore being uneven and the refining of MG-Si requiring substantial energy input.

As the Siemens method was developed based on the semiconductor field, SOG-Si was conventionally produced from the off-grades of SEG-Si. However, with an increase in demand for and production of SOG-Si compared to SEG-Si, the Siemens process remains the mainstream production method, despite the distribution of high-grade silica ore being uneven and the refining of MG-Si requiring substantial energy input.

One of the most expensive processes in the Siemens method is the elimination of light-element impurities, such as boron and phosphorus, which are usually added as dopants to control the carrier density of p-type or n-type semiconductors. As the required purity of SOG-Si (>6N) is less than that of SEG-Si (>11N), a number of alternative approaches have been developed, as described below.
a) Metallurgical process\textsuperscript{11,12}

The solute partition coefficients of boron and phosphorus are significantly higher than those of heavy metals, and so the elimination of these elements by simple metallurgical processes is difficult. The application of a “metallurgical process” in the production of SOG-Si involves special treatment for the evaporation of boron and phosphorus. For phosphorus, an electron beam is utilized to preferentially evaporate phosphorus from the silicon surface. Directional solidification is then applied immediately to the refined silicon. For boron, a plasma source is utilized to achieve evaporation, with the furnace temperature increasing to 2027 °C. At this high temperature, boron oxide (e.g. BO, B\textsubscript{2}O, B\textsubscript{2}O\textsubscript{3}) with a relatively higher vapor pressure is formed. Boron is then eliminated in the form of boron oxides below the boiling point of silicon (2355 °C).

b) Zinc reduction process\textsuperscript{13,14}

The zinc reduction process uses silicon tetrachloride as outlined in Eq. 1.1:

\[
\text{SiCl}_4 (g) + 2\text{Zn} (g) \rightarrow \text{Si} (s) + 2\text{ZnCl}_2 (g) \quad (1.1)
\]

Since the reaction occurs in the gas phase, the production of silicon tends to be faster. The starting material, SiCl\textsubscript{4}, is a by-product of SiHCl\textsubscript{3} formation, which is utilized in the Siemens process, and requires less expensive treatment in the exhaust and unreacted gas. Although the reaction yield is estimated to be 80%, the treatment of zinc gas is difficult, and the reaction mechanism has not yet been elucidated.

c) Fluidized bed reactor\textsuperscript{15}

In the Siemens process, a fluidized bed reactor (FBR) is utilized instead of the conventional chemical vapor deposition (CVD) reactor. To fluidize the particles, the reactor is filled with silicon particles and gas. The fluidized particles behave like a liquid, maintaining a continuous movement within the reactor. In this process, silicon is deposited on the fluidized silicon particles by heating the reactor to the decomposition temperature. The fully grown particles are then extracted from the reactor and fresh particles are either injected or produced within the reactor itself.

d) Hydrogenation process\textsuperscript{16}

As a starting material, the hydrogenation process utilizes silane (SiH\textsubscript{4}) produced through the trichlorosilane production process, where trichlorosilane disproportionates into SiH\textsubscript{4} and SiCl\textsubscript{4} as follows:

\[
4\text{SiHCl}_3 \rightarrow \text{SiH}_4 + 3\text{SiCl}_4 \quad (1.2)
\]

The obtained silane is injected into a tube reactor to be heated at <900 °C. The injected silane is then decomposed and silicon powder is formed. The yield of this
decomposition is significantly higher than that of the Siemens process.

However, the processes outlined above require a substantial energy input for the fusion, gasification, and reduction of MG-Si. Furthermore, the majority of the refining process is carried out following the reduction of silica by carbothermal reduction, as many of these processes are modified versions of the Siemens method, where the refining process begins with MG-Si. The simplified procedure for the production of SEG and SOG-Si is shown in Fig. 1.2.

The direct reduction of high-purity silica to SOG-Si has also attracted attention because the purification of silica requires less energy input, and alternative resources can be applied. This process is described in further detail in Section 1.3.

![Diagram](image)

**Figure 1.2** The conventional production process of SEG-Si and SOG-Si.

### 1.2.3 Required purity of SOG-Si

As the impurities present in silicon strongly influence its performance as a semiconductor, the required purity of SEG silicon fabricated according to the Siemens process was specified as 11N. However, its influence on the performance of solar cells is lower, and so the required purity of SOG-Si is significantly lower than that required of SEG-Si. In general, the required purity of SOG-Si is 6N, with the total amount of impurities being less than 1 ppm. However, the specified purity varies between reports, due to the trade-off between purity and performance in terms of production costs.
In terms of impurities present, the elimination of boron and phosphorus is essential, as these elements are generally added as dopants, and thus their elimination via the conventional metallurgical refining process is difficult. Again, the required purities in terms of boron and phosphorus also vary between studies\textsuperscript{15, 18-20} for the same reasons outlined above. The representative targets for permissible impurities is shown in Table 1.1, while the solute partition coefficient of impurities is given in Table 1.2.

<table>
<thead>
<tr>
<th>Table 1.1 Target values of impurities for SOG-Si\textsuperscript{15}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>P</td>
</tr>
<tr>
<td>As</td>
</tr>
<tr>
<td>Fe, Al, Cr, Ni, Ti, Mo, V, Zn</td>
</tr>
<tr>
<td>Other Metals</td>
</tr>
</tbody>
</table>

For boron and phosphorus, the permissible content would be sub-ppm concentrations. Considering the subsequent process from high-purity silica, the level of impurities should ideally be $<0.1$ ppm. As the solute partition coefficients of boron and phosphorus are relatively high, the gasification and distillation steps are carried out in the Siemens process to eliminate these impurities.

In the case of metal impurities, their influence on the normalized efficiency of solar cells has been investigated in a number of studies.\textsuperscript{17,21,27-29} A representative plot is shown in Fig. 1.3, which demonstrates that a number of impurities influence the performance of solar cells. In the case of high-purity silica, however, the amount of other metal impurities is not important, as metal impurities can be eliminated using

<table>
<thead>
<tr>
<th>Table 1.2 Solute partition coefficients (equilibrium segregation coefficient)\textsuperscript{18, 20-26}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>Ta</td>
</tr>
<tr>
<td>P</td>
</tr>
</tbody>
</table>
a simple metallurgical process involving the conversion of silica to silicon.

![Figure 1.3](image)

Figure 1.3 Effect of metallic impurity content (in cm$^{-3}$) in single crystal silicon on the normalized efficiency of solar cells.\textsuperscript{29}

### 1.3 Application of high-purity silica for SOG-Si

#### 1.3.1 High-purity silica resources

Silicon is the second most abundant element after oxygen in the earth’s crust, with an abundance of 27%. Approximately 60\% of ore in the crust contains silicon, with the most common form being quartz. As quartz is chemically stable, it is resistant to weathering and erosion, thus resulting in its accumulation in rivers or seas as quartz sand. The grade of quartz sand is determined by the accumulation processes, as the composition of quartz accumulated from a number of different origins can vary significantly. To decrease refining costs, the high-grade quartz sand accumulated from a single origin is utilized as the source of MG-Si via carbothermal reduction. High-grade quartz sand is mined primarily in Brazil, India, and China. From the viewpoint of producing high-purity silica, crystalline silica resources cannot be utilized as these are chemically stable, and so the purification process at room temperature and atmospheric pressure cannot be applied.

In addition to crystalline silica ore, amorphous silica resources, such as opal, rice husk ash, and diatomaceous earth are also common. In particular, rice husk ash
and diatomaceous earth are candidates as resources for high-purity silica production because of their solubility in alkaline solutions, as the above chemical purification process at room temperature or under atmospheric pressure is necessary to reduce the SOG-Si production costs.

a) Rice husk ash
Rice husk ash is the waste obtained from the burning of rice husk as a fuel, and it contains ~60% silica, along with low quantities of Al, Mg, Ca, and Fe (~1%). The application of rice husk ash in the preparation of silica materials such as silica gels and powders has been investigated since the early 1990s, and its application as a source of silicon carbide has been also investigated. Purification mainly consists of an acid leaching process to give a desired purity of 3N. However, as the production of rice husk ash depends on the production of rice, its supply as a source of SOG-Si would be limited and unstable.

b) Diatomaceous earth
Diatomaceous earth is an abundant candidate for a high-purity silica source, as it forms through the accumulation of amorphous silica, the main component of the fossilized remains of diatoms, which is a type of hard-shelled algae. Applications of diatomaceous earth include filtration, catalyst carriers, and building materials. Diatomaceous earth exhibits a number of shapes, including spheres and needle rudders, among others. As these structures are microporous in nature (Fig. 1.4), diatomaceous earth is readily soluble in alkaline solutions.

![Figure 1.4 SEM image of diatomaceous earth.](image_url)

The worldwide production of diatomaceous earth is approximately two million tons per year, with 30% being produced in the United States, and 10% being produced in Japan. The origin of diatomaceous earth can be divided into sea origin and lake origin. In general, the purity of the lake-origin diatomaceous earth is higher
than that of the sea-origin material due to lesser quantities of impurities being present during accumulation.

Diatomaceous earth is initially refined for such practical applications. The process generally involves comminution, classification, and burning. Following treatment, lake-origin diatomaceous earth is sold for approximately $1 per kg in Japan. A representative composition of diatomaceous earth is shown in Table 1.3, which shows that the silica content is approximately 85%, and that a number of metal impurities are also present.

Considering its abundant quantities, reasonable price, and relatively high purity, diatomaceous earth is one of the most promising candidates for sourcing high-purity silica such as SOG-Si.

### Table 1.3 Representative impurities in diatomaceous earth, as determined by XRF

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>79400</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>25500</td>
</tr>
<tr>
<td>CaO</td>
<td>12000</td>
</tr>
<tr>
<td>Na₂O</td>
<td>6640</td>
</tr>
<tr>
<td>SO₃</td>
<td>4090</td>
</tr>
<tr>
<td>MgO</td>
<td>3120</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2910</td>
</tr>
<tr>
<td>SiO₂</td>
<td>85.6%</td>
</tr>
</tbody>
</table>

### 1.3.2 Reduction of silica to silicon

For the application of SOG-Si, silica reduction must first be carried out. In its basic form, this reduction reaction can be described according to Eq. 1.3:

$$\text{SiO}_2 + 4e^- \rightarrow \text{Si} + 2\text{O}^{2-} \quad (1.3)$$

However, this reduction step is a high-cost process in the Siemens method, and requires substantial energy input. In the Siemens process, carbothermal reduction is carried out in an electric arc furnace into which high-grade silica ore is fed, giving the reaction outlined in Eq. 1.4:

$$\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO} \quad (1.4)$$

However, the full reaction mechanism is complicated and has not yet been fully elucidated. Thus, to determine the reaction mechanism and reduce costs, carbothermal reduction with heating using a CO₂ laser has been reported. In this method, the reaction rate is significantly higher than that of the conventional carbothermal reduction. In addition, in situ observations of the carbothermal reaction can be carried out. This reaction will therefore be a promising method for the production of SOG-Si from high-purity silica when issues relating to cost and impurity incorporation are addressed upon elucidation of the reaction mechanism.

The direct reduction of silica to silicon via an electrochemical process has
also been proposed.\textsuperscript{40-42} As the reduction potential of silicon is lower than that of hydrogen, the reduction of silica in aqueous solution is not possible. Nohira reported that reduced silicon could be obtained in molten CaCl\textsubscript{2} by applying 0.5 V vs Ca\textsuperscript{2+}/Ca. This method has also been attempted to produce SOG-Si from SiO\textsubscript{2} pellets, powder, and granules, as depicted in Fig. 1.5.\textsuperscript{42}

\begin{center}
\textbf{Figure 1.5} Conceptual representation of the production of solar grade silicon by direct electrolytic reduction of solid SiO\textsubscript{2} in molten CaCl\textsubscript{2}.\textsuperscript{42}
\end{center}

In the direct electrolytic reduction method, SOG-Si production includes a directional solidification process, known as the floating zone (FZ) method. With the exception of boron and phosphorus, all other impurities could be removed using this method due to the low distribution coefficient of silicon. The proposed process for the production of SOG-Si using this method is outlined in Fig. 1.6.

\begin{center}
\textbf{Figure 1.6} Flowchart of the new production process for solar grade silicon\textsuperscript{42}
\end{center}
1.3.3 Other applications

High-purity silica can also be applied for a range of other applications, including as a source of high-grade quartz and crucibles. In addition, it can also be used as source of reduced material, since such materials require a lower purity than SEG-Si. For example, the main applications include a source of SiC and an anodic material for Li ion batteries.

a) SiC
SiC is a promising material for use in novel power devices due to its strength at high temperatures, good oxidation resistance, and wider band gap than silicon. The production of SiC has been conducted using the Acheson process, which involves the carbothermal reduction of SiO$_2$ by C at 1873–2373 K. However, this process requires a substantial energy input for the purification stage and suffers from a restriction of resources. A number of studies have focused on a decrease in production costs while developing an efficient reaction process.$^{43-45}$ For example, the use of high-purity silica for SiC production has been developed by Taiheiyo Cement Corporation. However, the purity of the utilized high-purity silica was $<$5N, and so to reduce the production costs of high-grade SiC, the purity of silica must be improved using a cost-effective process.

b) Anodic material for Li ion batteries
Silicon is an attractive material for use as the anodic material for Li ion batteries due to its large theoretical specific capacity (i.e., 4200 mAh g$^{-1}$) and its lithium insertion potential. Wang et al. reported the synthesis of porous silicon anodes from diatomaceous earth.$^{36}$ In addition, the morphology or composition of a silicon anode strongly influences its performance. Therefore, high-purity silica can be utilized to control the composition and structure with the optimization of reduction processes.
1.4 Silica refining process

1.4.1 Acid leaching

Leaching is a popular technique in the field of metallurgy, and is used to separate metals from solids by converting them into soluble salts. As microporous amorphous silica is soluble in alkaline solution but not in acidic solution, a purification process employing acid leaching has been utilized to eliminate heavy metal impurities. The procedure using diatomaceous earth as a starting material is depicted in Fig. 1.7.\textsuperscript{33}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{diagram.png}
\caption{Flow sheet representing the purification of diatomaceous earth using an acid leaching process.\textsuperscript{33}}
\end{figure}

Firstly, diatomaceous earth was dissolved in 2.5M NaOH solution and filtered, after which the pH was adjusted to 10.5 by the addition of HCl solution. The solubility of silica with varying pH along with the solubilities of representative impurities is shown in Fig. 1.8.
Figure 1.8 Dependence of the normalized dissolution ratio of (a) silica, and (b) Al, Fe, and B in the biogenic silica solutions. The dissolution of each element at pH 12 corresponds to a normalized dissolution ratio of 1.33.

While the dissolution ratio of silica was ~0.8 at pH 10.5, those of Al and Fe were <0.1. Thus, the majority of metal impurities, such as Fe and Al, precipitated when the pH was decreased to 10.5. Following filtration, the pH was decreased to 9, resulting in the precipitation of silica containing fewer metal impurities. Relatively pure silica was then precipitated by a further decrease in pH. In this phase, silica does not dissolve in the acidic solution, and so acidic leaching was carried out and repeated three times to eliminate any remaining metal impurities. Table 1.5 shows the contents of...
representative residual impurities in silica refined from diatomaceous earth. While the majority of impurities were successfully eliminated, boron and phosphorus remained present in the single ppm range.

**1.4.2 Solvent extraction**

Due to the high distribution coefficient of boron to silicon, the acid-leaching process cannot be easily applied, and so an alternative approach must be implemented.

Boron is a widely occurring element as it is present in boric acid and borate salts. It is an essential element for animals and plants, although in excess it can be toxic. The elimination and/or extraction of boron from aqueous phases such as drinking water has therefore been investigated.

One of the most cost-effective processes for boron removal is solvent extraction. This process utilizes the different distributions between two solvents, usually an aqueous and an organic solvent. In the case of boron extraction, boric acid is extracted from the aqueous phase to the organic phase using 1,3-diols as extractants. A representative example employing 2-ethyl-1,3-hexanediol (EHD) as the extractant is shown below, although the reaction mechanism has not yet been fully elucidated.

$$\text{EHD} + \text{B(OH)}_3 \rightarrow \text{EHD} - \text{BO} - \text{OH} + 2\text{H}_2\text{O}$$

EHD dissolves in organic solvents such as toluene, and reacts with boric acid at the organic/aqueous interface of the aqueous phase. The ester product is then distributed through the organic phase.

The application of this extraction reaction for the elimination of boron species in silica has indeed been reported. While boron was successfully eliminated from sodium silicate solution containing trace amounts of boric acid, the extraction efficiency must be improved further to achieve the desired SOG-Si purity.

**Table 1.5 Trace element content in silica refined from diatomaceous earth**

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (ppm)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.6</td>
<td>ICP-AES</td>
</tr>
<tr>
<td>Fe</td>
<td>4.2</td>
<td>ACP-AES</td>
</tr>
<tr>
<td>B</td>
<td>1.2</td>
<td>ICP-MS</td>
</tr>
<tr>
<td>P</td>
<td>&lt;7</td>
<td>XRF</td>
</tr>
<tr>
<td>U</td>
<td>0.06</td>
<td>TIMS</td>
</tr>
</tbody>
</table>
1.5 Microreactor

1.5.1 Microreactor features

When we consider a chemical reaction suitable for implementation in practical applications, the reactant quantity is important. If large amounts of chemicals A and B are prepared and mixed, the mixing conditions should differ between the addition of A to B or the addition of B to A. This often raises issues in industry in terms of engineering large scale chemical production in high yields. Thus, chemical reactions designed on the laboratory scale often cannot be applied to production on an industrial scale. Similarly, laboratory scale processes often cannot be applied when reducing the amount of reactant to the microliter scale, and this is the basis of the “microreactor” concept. Microreactors are promising devices in the design of efficient and precisely controlled reactions due to their large specific interfacial areas and short diffusion distances. The most common features of microreactors are outlined below.

a) Large specific surface area
In general, the specific interfacial area decreases with a decrease in volume. However, when this rule is applied to a reactor, the specific area of the interface within the reactor increases. This is the most important feature of a microreactor, and gives the following advantages with its application in chemical reactions.

b) Efficient reactions at the interface
Microreactors, which have large specific surface areas, also exhibit large specific interfacial areas for liquid-liquid, liquid-gas, and solid-liquid reactions. This feature enables efficient reactions and/or separation in microreactors.

c) Efficient mixing
Upon mixing two solutions, molecular diffusion is one of the most important factors. As the mixing time with molecular diffusion is proportional to the square of the diffusion distance, a decrease in diffusion distance when using a microreactor enables fast and efficient mixing, which cannot be achieved using conventional reactors.

d) Temperature control
Since microreactors have small volumes and large specific surface areas, the heat exchange efficiency is high. Temperature control can therefore be easily achieved using microreactors, and so reactions requiring high or low temperatures and/or
precise temperature control can be designed. This feature can be beneficial for industrial operations, where heat exchange problems based on scale-up often arise.

e) Application in flow processes
Industrial chemical processes are carried out mainly using batch-type reactors equipped with an impeller. While the batch process can handle a large volume of chemicals in one operation, long reaction times are generally required due to the poor diffusion of chemicals and heat. In contrast, microreactors have a shorter diffusion distance and large specific surface area, which can overcome the bottleneck encountered in flow-type reactors.

f) Numbering up for large-scale production
In general, the production of large quantities of chemicals is addressed based on scale-up, increasing the reactor size, using the numbering-up process, or increasing the number of reactors. Since the efficiency and controllability of microreactors originate from their reduced volume compared to batch-type reactors, the numbering-up process is utilized as a practical approach for the production of large amounts of chemicals using a microreactor. Numbering-up can be integrated without the scale-up restrictions relating to heat and mass transfer issues. Moreover, the numbering-up process maintains the efficiency and controllability of the microreactor from the laboratory scale to large scale production. Such an approach has been utilized mainly in the fine chemical field to maximize the reaction efficiency and controllability of microchannel devices.52, 53

1.5.2 Solvent extraction using the microreactor54

Solvent extraction is the separation of two solvents, typically water and an organic solvent (e.g., toluene). When a solvent containing the dissolved target chemical is mixed with a second solvent, the target chemical is transferred to the second solvent according to the distribution coefficient. When considering the efficiency of the solvent extraction, representative factors include the specific interfacial area, $A$ and diffusion time, $t$. With a microchannel, such as that shown in Fig.1.9, where $D$ represents the diffusion coefficient, these factors can be expressed as:

\[ A = \frac{H \times L}{W \times H \times \frac{L}{2}} = \frac{2}{W} \]  \hspace{1cm} (1.6)

\[ t \approx \frac{W^2}{D} \]  \hspace{1cm} (1.7)
When $W$ is 100 µm, the specific interfacial area is 20 cm$^{-1}$, which is comparable to that of a conventional separatory funnel. In addition, $t$ is 10 s when the diffusion coefficient is estimated as $10^{-9}$ m$^2$ s$^{-1}$, which is a typical value for a low molecular weight compound in water. This allows an efficient extraction to be operated in the microchannel without the requirement for agitation. Finally, the parallel flow is typically combined with other unit operations, such as those described in the following section.

![Figure 1.9 A schematic representation of a microchannel of width $W$, height $H$, and length $L$.](image)

1.5.3 Construction of a sequential process using the microreactor

Since the microreactor is a flow-type device capable of operating unit operations such as mixing, separation, and reaction, the construction of a complete chemical process is possible using a combination of microreactors. Kitamori et al. proposed a continuous flow chemical processing (CFCP) technique based on micro unit operations (MUOs). A schematic representation of CFCP is shown in Fig. 1.10. In this process, a reaction occurs upon mixing of two solutions in the first section of the microchannel. In the second section, the product formed in the first section is washed with a second solution. Thus, the formation of a parallel laminar flow (a flow pattern of multiphase microflows) is important for CFCP, including separation and multistage extraction. Since the microflow has a large surface/volume ratio, multiphase microflows are dominated by pressure, as proposed by Kitamori et al. in their model for controlling parallel laminar flow. In addition to these operations, a number of MUOs with microreactors exist, as depicted in the schematic representations shown in Fig. 1.11.
Figure 1.10 Schematic image of continuous flow chemical processing (CFCP).\textsuperscript{54}

Figure 1.11 Representative illustration of micro unit operation (MUO).\textsuperscript{54}
References

25. S. Kobayashi, R. Hull (Ed.), *Properties of Crystalline Silicon*, INSPEC – The
21


Chapter 2

Purification of Soluble Silica with Solvent Extraction using Microchannel Device
2.1 Introduction

Considering the purity of SOG-Si\(^1\),\(^2\) the elimination of impurities on the production of high-purity silica must be carried out efficiently. While metal impurities can be eliminated with acid leaching process, elimination of boron and phosphorus remained as an issue.\(^3\) In the case of phosphorus, the optimization of acid leaching process would be also effective since the recovery of phosphorus from soil and wastewater with acid or base treatment has been well studied.\(^4\)\(^6\) On the other hand, elimination of boron with acid leaching would be relatively difficult. While the solvent extractions have been applied for the recovery of boron,\(^7\)\(^8\) however, the sequential and efficient process is necessary to apply the refining to solar-grade purity.

For sequential elimination of a number of impurities including light elements in the diatomaceous earth, flow-type reactors should be suitable rather than batch type reactors. However, the long contact period to reach equilibrium point is a kind of bottleneck of flow-type reactors. Since the efficiency of reaction in flow-type reactors is determined by the diffusion distance and the specific interfacial area in the channel, microchannel device can be one of the prime candidates for such efficient and sequential system due to its large specific interfacial area and short diffusion distance.\(^9\)\(^10\) In addition, chemical reactions in the microchannel can be precisely controlled by simply adjusting initial reaction conditions such as concentration, flow rate, and channel design. Compared to the conventional separatory funnel, extractions in microchannel device require significantly less time to reach the equilibrium point of the reaction and smaller amounts of organic solvents due to large specific interfacial area and short diffusion distance. In addition, flow-type reactor can incorporate the numbering-up process for large quantity processing.\(^11\)\(^12\) The production by numbering-up can be simply adjusted by increasing or decreasing of the number of microchannels without the scale-up consideration restriction deeply relating to the heat and mass transfer issues. Therefore, the construction of reaction systems using microchannels has advantages for silica purification from the viewpoint of sequential and efficient elimination of impurities. In the present chapter, the purification of silica and the elimination of boron via extraction from soluble silica samples using microchannel devices are described.
2.2 Experimental

2.2.1 Chemicals

A “model sample” composed of refined silica spiked with a trace amount of boric acid and a “real sample” composed of refined diatomaceous earth were prepared.

For the model sample, refined silica powder (> 3N) and boric acid (> 99.999 %) were purchased from Kanto Chemical and Aldrich, respectively. Then 1 g of the silica powder was dissolved in 50 mL of 2.5M NaOH aqueous solution, which contained 200 ppm boric acid. Decreasing the pH of the solution to be 10.5 by the addition of an 5M HCl aqueous solution led to the precipitation of silica gel. Following filtration, silica gel was leached using an aqueous solution of 5M HCl for 1 h at 100 °C.

For the real sample, diatomaceous earth was provided by Showa Chemical Industry Co. Ltd. The representative impurities of the diatomaceous earth are shown in Table I. Silica content in diatomaceous earth is approximately 85 %. Diatomaceous earth was refined via an aqueous chemical process according to a previous study. Subsequently, 1g of the obtained silica was added to an aqueous solution of HCl and stirred for 1 h at 100 °C.

2.2.2 Fabrication of microchannel reactor

A typical Y-shape microchannel was fabricated on Si(100) substrates using lithographic techniques. The microchannel had 100 µm width, 100 µm depth, and 10 mm length (Fig. 2.1).

![Figure 2.1](image.png)

*Figure 2.1* (a) Schematic image of microchannel (b) SEM image of microchannel.
The fabrication procedure is shown in Fig. 2.2. Inductively coupled plasma-reactive ion etching (ICP-RIE) was used for Si etching. The microchannel was covered with a glass substrate using anodic bonding.

![Diagram](gray part is silicon, slashed part is glass)

**Figure 2.2** A schematic image of the fabrication procedure of microchannel device

### 2.2.3 Extraction of boric acid

Removal of boron through solvent extraction using EHD was carried out in a conventional separatory funnel and microchannel device, respectively. The concentration of EHD in toluene solution is 0.5 M on both cases.

In the case of separatory funnel, 50 mL of silica solution and 50 mL of the EHD/toluene solution were agitated together in the funnel for 1 hour. Then the silica solution was separated after 30 min.

In the case of microchannel device, the two solutions were injected into the microchannel using a syringe pump with a continuous flow rate of 100 µL min⁻¹. Subsequently the silica solution was separated.
2.2.4 Evaluation method

The crystalline structure of model sample and diatomaceous earth was determined with X-ray diffraction (XRD).

Inductively coupled argon plasma atomic emission spectrometry (ICP-AES, ICAP-6300, Thermo Fisher Scientific) was used to determine boron content. Samples were dissolved into 48 % HF to form H$_2$SiF$_6$. Then, HF and H$_2$SiF$_6$ were evaporated and remaining impurities were dissolved in a 0.1 mol L$^{-1}$ aqueous solution of HNO$_3$ prior to the measurement.

2.3 Results and discussion

2.3.1 Characterization of model and real samples

The composition of refined diatomaceous earth (real sample) and refined amorphous silica (model sample) are shown in Table 2.1.

<table>
<thead>
<tr>
<th></th>
<th>Refined diatomaceous earth / ppm</th>
<th>Amorphous silica for the model sample / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>7.17</td>
<td>6.87</td>
</tr>
<tr>
<td>B</td>
<td>6.82</td>
<td>0.97</td>
</tr>
<tr>
<td>Ca</td>
<td>0.84</td>
<td>0.39</td>
</tr>
<tr>
<td>Co</td>
<td>0.25</td>
<td>0.24</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>3.21</td>
</tr>
<tr>
<td>Cu</td>
<td>0.6</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe</td>
<td>5.48</td>
<td>16.41</td>
</tr>
<tr>
<td>K</td>
<td>1.15</td>
<td>0.76</td>
</tr>
<tr>
<td>Mg</td>
<td>0.95</td>
<td>0.11</td>
</tr>
<tr>
<td>Mn</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>Na</td>
<td>0.7</td>
<td>24.36</td>
</tr>
<tr>
<td>Ni</td>
<td>0.55</td>
<td>1.51</td>
</tr>
<tr>
<td>P</td>
<td>9.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Ti</td>
<td>0</td>
<td>116.40</td>
</tr>
<tr>
<td>V</td>
<td>0.6</td>
<td>0.13</td>
</tr>
<tr>
<td>Zn</td>
<td>0.13</td>
<td>0.17</td>
</tr>
</tbody>
</table>
The purity of silica was calculated to be > 4N (99.99%), and the boron and phosphorus contents were 6.82 ppm and 9.01 ppm, respectively. The purity and composition of the refined amorphous silica were similar to the refined diatomaceous earth. In addition, the XRD pattern shows that both refined diatomaceous earth and refined silica are amorphous silica (Fig. 2.3). Thus, the refined silica was considered a reasonable and proper model sample. For boron extraction, the model sample was spiked with a trace amount of boric acid.

**Figure 2.3** XRD pattern of diatomaceous earth and refined amorphous silica.

Diatomaceous earth originally contains cristobalite and feldspar silica.

### 2.3.2 Extraction performance of EHD/toluene solution

In order to evaluate extraction efficiency, extraction of an aqueous solution of boric acid with EHD was carried out using a conventional separatory funnel. An aqueous solution of HCl containing 2 ppm of boron as boric acid was mixed with 0.5 mol L\(^{-1}\) EHD/toluene solution for 1 h. The aqueous layer was analyzed using ICP-AES. The boron content, shown in Fig. 2.4, decreased to 10% on each extraction stage and reached 0.014 ppm on the second stage. Since this residual boron content was comparable to the target value for SOG-Si, two extractions should be sufficient for silica purification.
2.3.3 Elimination of boron from silica sample with EHD using microchannel device

Elimination of boron species from silica samples with solvent extraction was conducted under the condition described in the previous section. In the case of the model sample, the refined silica was dissolved in an aqueous solution of NaOH spiked with 200 ppm of boric acid, which was equal to the boron content in the refined diatomaceous earth. Following the acid leaching process to eliminate the majority of metal and light element impurities, solvent extraction by EHD was carried out using both the microchannel device and separatory funnel. The boron content as determined by ICP-AES is shown in Tables 2.2 and 2.3.

Subsequent to the acid leaching process, the boron content decreased to 5.29 ppm, which was similar to the amount observed in the refined diatomaceous earth. When the separatory funnel was employed for the purification process (Table II), the boron content decreased to 0.53 ppm in the second stage. On the other hand, when the microchannel device was utilized, the boron content decreased to 0.51 ppm in the first stage, suggesting that the

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.29</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.95</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>0.53</td>
<td>44</td>
</tr>
</tbody>
</table>

Table 2.2 Boron extraction using separatory funnel from model sample

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.29</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.51</td>
<td>91.4</td>
</tr>
</tbody>
</table>

Table 2.3 Boron extraction using microchannel device from model sample
microchannel showed better extraction performance despite the shorter contact period of the reaction. However, the residual boron content of the model sample was higher than that of the boric acid solution although the extraction efficiency at the equilibrium point should be the same. This could suggest that the reaction did not achieve equilibrium following 1 h agitation in the separatory funnel. While boron extraction occurred under acidic conditions, silica formed a gel network during the acid leaching process. This gel network may contain boron as an aqueous solution of boric acid. Thus, the whole reaction did not consist of only the extraction of boric acid but also the dissolution of boron from the silica gel network. Since the reaction using the microchannel takes a smaller amount of time to reach the equilibrium point, those two reactions occurred efficiently to eliminate the boron at a higher extraction efficiency within the microchannel device. Although the microchannel showed much better extraction performance, the residual boron content should decrease further for 6N purity. Nevertheless, the boron content after solvent extraction via separatory funnel decreased at an exponential rate as depicted in both Fig. 2.4 and Fig. 2.5. Assuming equivalent extraction efficiency, the expected boron content after the second stage using the microchannel device is estimated to be less than 0.1 ppm.

![Figure 2.5](image)

**Figure 2.5** Change in residual boron content in the boric acid solution with extraction stage number. The point where stage number is zero indicates the initial boron content in the specimen.

Since the boron extraction process was effective for the model sample, we applied it to the refined diatomaceous earth, or real sample, using both the microchannel and separatory funnel. The results are shown in Tables 2.4 and 2.5. Similar to the model solution sample, boron content decreased to around 3 ppm after
the preliminary refinement using the aqueous chemical process. In the case of the separatory funnel, boron content decreased to 2.30 ppm, and the residual rate was 71.2 % on the second stage. On the other hand, boron content decreased to 2.27 ppm when the microchannel was utilized. Similar to the model sample, extraction using the microchannel device was equivalent to two stages of extraction using the separatory funnel (Fig. 2.6).

However, the residual boron in the refined diatomaceous earth was higher than that of the model sample and boric acid aqueous solution (Fig. 2.6). Additionally, there are some other possibilities concerning the lower extraction performance of the refined diatomaceous earth. One possibility is the influence of ionic strength on the formation of the silica network. Specifically, diatomaceous earth consists of fossilized diatoms, an alga with a silica frustule. In the refining procedure by the aqueous chemical process, silica was precipitated as silica gel to separate the metal impurities. During the precipitation process, the gel formation is influenced by solution conditions such as concentration, impurities and temperature, among others. In general, the size of the silica gel becomes larger in solutions of high ionic strength. In the case of diatomaceous earth, the amount of residual impurities at the refining process would be larger than that of the model sample. Thus, the size of the network would also become larger as the solvent and boric acid was incorporated into the network, where it was difficult to eliminate with solvent extraction. Another possibility for the lower extraction performance of the refined diatomaceous earth could be the difference in the chemical state of boron in the solution. The elimination of boron by EHD proceeds via the reaction of EHD and boric acid. If boron does not exist as boric acid in the solution, it would not be eliminated. In the model sample, boric acid was added as the boron component. Therefore, the boron was successfully eliminated via solvent extraction. In the case of the diatomaceous earth, it is possible that boron did not exist as boric acid but rather was incorporated as a Si-O-B bond within the silica network. Although the majority of Si-O-B bonds should be broken

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.72</td>
<td>15.8</td>
</tr>
<tr>
<td>2</td>
<td>2.30</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Table 2.5 Boron extraction using the microchannel device from refined diatomaceous earth

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.27</td>
<td>24.8</td>
</tr>
</tbody>
</table>

Table 2.4 Boron extraction using separatory funnel from refined diatomaceous earth
via the refining process and acid leaching, and subsequently eliminated as boric acid, it could be possible that some Si-O-B bonds remain in the refined diatomaceous earth samples. In summary, the conditions of the preliminary refining process has a strong influence on the extraction efficiency. If the diatomaceous earth was refined using the same conditions as the model sample, the elimination of boron via solvent extraction could be applied. Furthermore, the microchannel device requires a shorter period of time for the elimination of boron, which is present both as boric acid in solution and as a component of the silica network.

Figure 2.6 Change in residual boron content in the diatomaceous earth with extraction stage number.

2.3.4 Formation of stable laminar flow for sequential purification process

Considering the production of high-purity silica with aqueous chemical processes, the sequential process should be better than batch process since a number of impurities must be eliminated and the elimination may be conducted one by one. One of the sequential processes using microchannel device is formation of parallel flow. The automatic separation at the outlet enables the sequential elimination at the next microchannel. The formation of parallel flow was tried with controlling the flow rate of each solutions. A representative optical pictures are shown in Fig. 2.7. The channel design is same to that used in previous section, and flow rate of both solutions is 100 µL min⁻¹. From the figure, the interface between two solutions was not stable and two solutions were not separated at the outlet. In the case of different flow rate, the parallel flow was not observed in this microchannel.
Figure 2.7 Optical images of the microchannel with the height of 100 µm where silica sample and EHD/toluene solution were injected at (a) inlet, (b) middle of the channel, (c) outlet

The formation of parallel flow in the microchannel is strongly influenced by the balance of surface energy between two solutions and that between solution and wall of microchannel.\(^\text{14}\) In general, the parallel flow can easily form in the case of the smaller area of the interface between two solutions. Although the yield should be decreased with smaller interfacial area, the diffusion distance and specific interfacial area is not changed. Therefore, the height of microchannel was decreased to be 50 µm and 25 µm in order to form a stable parallel flow. The optical images of the flow are shown in Fig. 2.8. and 2.9. The flow rates of two solutions are same at 100 µL min\(^{-1}\).

Figure 2.8 Optical images of the microchannel with the height of 50 µm where silica sample and EHD/toluene solution were injected at (a) inlet, (b) middle of the channel, (c) outlet
Figure 2.9 Optical images of the microchannel with the height of 25 µm where silica sample and EHD/toluene solution were injected at (a) inlet, (b) middle of the channel, (c) outlet.

In both cases, a parallel flow was observed at the inlet. In the case of the microchannel with the 50 µm height, the interface between two solutions moved to the side where silica solution flowed. It could cause the different pressure drop of silica solution and EHD/toluene solution. In addition, the separation of silica solution was not observed when the flow rates were changed. On the other hand, the silica solution was separated at the outlet in the case of the microchannel with 25 µm height although the silica solution slightly included the outlet on the other side. By controlling the flow rates to 70 µL min\(^{-1}\) for silica solution and 100 µL min\(^{-1}\) for EHD/toluene solution, the separation of silica solution at the outlet was successfully observed. The optical image at the outlet is shown in Fig. 2.10. The contact reaction period was calculated to 0.01 s.

Figure 2.10 Optical images of the outlet of the microchannel with the height of 25 µm where silica sample and EHD/toluene solution were injected.

In this condition, the residual boron content was determined by ICP-AES measurement. The result is shown in Table 2.6. The initial boron content in the model solution sample is relatively large since the incorporation of boron in silica sample...
could not been easily controlled. In addition, since the contact reaction period decreased and the condition of diffusion and mixing on parallel flows are different, the extraction efficiency could not be easily compared with the previous results, where parallel flow did not form. As a result, the boron content decreased to 4.66 ppm and efficiency is 55 % after the extraction. Considering the efficiency using a separatory funnel was 82 %, the extraction reaction did not reach the equilibrium in the case of microchannel device with 0.01 s of contact reaction period. Then a microchannel with longer channel length was fabricated. The width and depth were same at 100 µm and 25 µm, respectively. The length was 20 mm, which was two times larger. The schematic image of microchannel device is shown in Fig. 2.11. And the contact reaction period was calculated to 0.02 s. The separation at the outlet was observed on the same condition. The result of the boron extration is shown in Table 2.7. The efficiency was improved to be 83 % and comparable to the result with a conventional separatory funnel. Considering the sequential processes, the much shorter reaction period than that with separatory funnel is advantage for the elimination of a number of impurities. This result indicates that the elimination of boron species via solvent extraction using microchannel device, where parallel flow forms, can be utilized for the silica purification process toward the source of SOG-Si.

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.4</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>4.66</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 2.6 Boron extraction using the microchannel device from model solution sample (length:10mm)

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24.0</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>4.04</td>
<td>83</td>
</tr>
</tbody>
</table>

Table 2.7 Boron extraction using the microchannel device from model solution sample (length:20mm)

Figure 2.11 A Schematic image of microchannel with 100 µm width, 25 µm height, and 20 mm length
2.4 Conclusion

In the present chapter, boron extraction using microchannel devices was demonstrated for refining silica from diatomaceous earth to produce a high-purity silica source for SOG-Si. The microchannel device showed superior extraction performance, shorter reaction period and lower residual boron content, with both the model solution sample and refined diatomaceous earth. Specifically, for the model sample, residual boron content was less than 1 ppm when the microchannel device was utilized. It was estimated that multistage extraction with sequential microchannels would produce refined silica with less than 0.1 ppm boron content, the target value for SOG purity. On the other hand, the extraction rate for diatomaceous earth was lower than that found for the model sample, which can potentially be explained in terms of the preliminary refining process. If the diatomaceous earth was initially refined using the same conditions as the model sample, the elimination using the microchannel can be applied as well. In addition, the extraction condition in the parallel flow was also investigated toward a sequential purification process. A parallel flow, which enables an automatic separation at the outlet, was observed in the case of a microchannel, which had 25 μm height. And the extension of the channel length improved the elimination rate comparable to that of separatory funnel with the restriction of shorter contact duration. From these results, it can be concluded that the solvent extraction using a microchannel device is an attractive method to produce 6N grade silica for SOG-Si.
References

Chapter 3

Development of Scaled-up Microchannel Device for the Efficient and Mass-productive Process with Multistage Solvent Extraction
3.1 Introduction

To develop a novel approach for the production of high-purity silica for SOG-Si, the balance between quality and quantity in the purification process is important, especially for elimination of light elements. The application of microchannel device was proposed for the solvent extraction of boron with EHD as an efficient purification processes. While the short diffusion distance as well as the large specific interfacial area of the microchannel enabled a fast and efficient elimination of boron, however, improvement of throughput was required for the practical application. In order to take the advantage of microchannel device together with large productivity, further improvement of the elimination efficiency and increase in the liquid-liquid interfacial area with maintaining short diffusion distance comparable to the microchannel, is necessary.

Increase in the liquid-liquid interface on the parallel flow can be carried out with the formation of the horizontal interface along with the substrate surface. Since the formation of parallel flow is strongly influence of the surface energies among the sidewalls and interfacial liquids, a surface modification to one of the channels was needed in the case of glass channels to keep the stability of the interface. However, the modified surface could be damaged by the acid and base solution, which was utilized in the purification of silica with aqueous chemical process. Considering the stability of the surface, the channel fabricated of two different materials such as silicon and glass should be suitable. In the previous chapter, the silicon microchannel device covered with glass substrate was demonstrated. Adding to this, a microchannel device, which has another channel on the covered glass substrate, can keep the stable parallel flow and increase the interfacial area.

The optimization of extraction reaction is also important for practical application. Alkyldiol, such as EHD, is typically applied for boron extraction, although detailed reaction mechanism has not been elucidated yet. In addition, the extraction efficiency is different among the diols with different alkyl chain. For example, 2,2,4-trimethyl-1,3-pentanediol (TMPD) shows better extraction performance than EHD. Elucidation of the reaction mechanism is necessary for improvement of the purification efficiency.

In the present chapter, the optimization of the extraction reaction with a theoretical calculation and the channel design with silicon and glass substrates for increasing the throughput on the boron elimination from soluble silica via solvent extraction using the optimized microchannel is reported.
3.2 Experimental

3.2.1 Chemicals

A “model sample” composed of refined silica spiked with a trace amount of boric acid and a “real sample” composed of refined diatomaceous earth were prepared. For the model sample, refined silica powder (> 3N) and boric acid (> 99.999 %) were purchased from Kanto Chemical and Aldrich, respectively. Then 1 g of the silica powder was dissolved in 50 mL of 2.5M NaOH aqueous solution, which contained 200 ppm boric acid. Decreasing the pH of the solution to be 10.5 by the addition of an 5M HCl aqueous solution led to the precipitation of silica gel. Following filtration, silica gel was leached using an aqueous solution of 5M HCl for 1 h at 100 °C.

For the real sample, diatomaceous earth was provided by Showa Chemical Industry Co. Ltd. The representative impurities of the diatomaceous earth are shown in Table I. Silica content in diatomaceous earth is approximately 85 %. Diatomaceous earth was refined via an aqueous chemical process according to a previous study.5 Subsequently, 1 g of the obtained silica was added to an aqueous solution of HCl and stirred for 1 h at 100 °C. Note, the sample preparation process for both model and real samples would be updated for avoiding incorporation of impurities into the silica network.

3.2.2 Fabrication of microchannel reactor

A flow-type device was fabricated on Si (100) substrates and glass substrate using lithographic techniques. The channel had 1.0 mm width, 0.10 mm depth, and 10 mm length (Fig. 3.1). The interface between silica solution and extractant was designed to form horizontally. ICP-RIE and HF was used for Si and glass etching, respectively. Then, the Si and glass substrate was bonded with anodic bonding. The fabrication procedure is shown in Fig. 3.2 and 3.3.

Figure 3.1 Schematic image of microchannel device with horizontal interface
(a) top view (b) sectional view
Figure 3.2 a schematic image of the fabrication procedure of micarohcannel device (gray part is silicon, slashed part is glass)

Figure 3.3 a schematic image of the fabrication procedure of micarohcannel device (gray part is silicon, slashed part is glass)
For multi-stage extraction, the microchannel, which had 2 stages of extraction was fabricated through the same processes. One had 10 mm of each channel length, and another had 25 mm of each channel length. The latter was optimized channel length for sufficient contact duration to eliminate boron species to SOG grade. Schematic images of the microchannels were shown in Fig. 3.4.

**Figure 3.4** Schematic image of the microchannel with 2 stages of (a) 10 mm length and (b) 25 mm length.
3.2.3 Extraction of boric acid

Removal of boron through solvent extraction using EHD was carried out in a conventional separatory funnel and microchannel device, respectively. The concentration of EHD in toluene solution is 0.5 M on both cases.

In the case of separatory funnel, 50 mL of silica solution and 50 mL of the EHD/toluene solution were agitated together in the funnel for 1 hour. Then the silica solution was separated after 30 min.

In the case of microchannel device, the two solutions were injected into the microchannel using a syringe pump with a continuous flow rate.

3.2.4 Evaluation method

ICP-AES (ICAP-6300, Thermo Fisher Scientific) and ICP-MS (ICAP-Q, Thermo Fisher Scientific) were used to determine boron content. Samples were dissolved into 48 % HF to form H₂SiF₆. Then, HF and H₂SiF₆ were evaporated and remaining impurities were dissolved in a 0.1 mol L⁻¹ aqueous solution of HNO₃ prior to the measurement.

3.2.5 Theoretical calculation with density functional theory

Density functional theory (DFT) calculation, whose code was implemented in Gaussian09 package, was performed to calculate reaction energy of boric acid esters, supporting our choice of extractant. The exchange-correlation functional was B3LYP. Basis set for all atoms was 6-31++G**. Since we assume that both the extractant, di-ol, and the product, di-ester, are in the organic phase, toluene, in equilibrium, we set polarizable continuum as solvent model around reactant molecules, whose dielectric constant (ε) is 2.3741[-] (equal to the ε for toluene), using algorithm in Gaussian09. Note although boric acid is originally from water phase, it does not change the conclusion from comparison among reaction energy of esters.
3.3 Results and discussion

3.3.1 Influence of the interfacial area and sample preparation for the purification process

In order to increase the interfacial area, a microchannel with horizontal interface in combination of silicon and glass substrate was fabricated. A fundamental experiment of injecting the solutions with various flow rates was conducted for the formation of parallel flow and automatic separation using the microchannel device with 1.0 mm of the specific interfacial area. A model solution sample containing refined silica and boric acid was injected into the inlet (2). A toluene with 0.5 M EHD was injected into the inlet (1) as the extractant of boron. The component of the obtained solution is shown in Table 3.1.

<table>
<thead>
<tr>
<th>Flow rate / mL min⁻¹</th>
<th>Silica solution (Si)</th>
<th>EHD / toluene (Glass)</th>
<th>Separation condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>3.0</td>
<td></td>
<td>Reversed flow of silica solution</td>
</tr>
<tr>
<td>1.5</td>
<td>3.0</td>
<td></td>
<td>Outlet A: silica solution, B: silica solution + EHD / toluene</td>
</tr>
<tr>
<td>0.6</td>
<td>3.0</td>
<td></td>
<td>Outlet A: silica solution + EHD / toluene solution, B: EHD</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>toluene solution</td>
</tr>
</tbody>
</table>

In the case of the same flow rate at 3.0 mL min⁻¹, the silica solution sample flowed reversely to the inlet (2). That may cause the lower viscosity of toluene solution than water. When the flow rate of the silica solution was decreased to 1.5 mL min⁻¹, the silica solution was obtained at the outlet A. But the silica solution was included in the outlet B with EHD / toluene solution. When the flow rate decreased to 0.6 mL min⁻¹, the EHD / toluene solution was included in the silica solution; No automatic separation was observed in those conditions. Next, the inlets of two solutions were exchanged; the silica solution was injected into inlet (2), and the extractant was injected into Inlet (1). Then the relationship of flow rate and formation of parallel flow was also investigated in this condition. The result is shown in Table 3.2.
### Table 3.2 The separation at the outlet on the microchannel

<table>
<thead>
<tr>
<th>Flow rate / mL min⁻¹</th>
<th>Silica solution (Glass)</th>
<th>EHD / toluene (Si)</th>
<th>Condition of separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>3.0</td>
<td>No separation</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>1.5</td>
<td>Outlet A: silica solution, B: silica solution and EHD/ toluene solution</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.5</td>
<td>Outlet A: silica solution, B: silica solution and EHD / toluene solution</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.6</td>
<td>Outlet A: silica solution, B: silica solution and EHD / toluene solution</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>3.0</td>
<td>Outlet A: silica solution, B: EHD / toluene solution (slightly including silica solution)</td>
<td></td>
</tr>
</tbody>
</table>

In the case of the same flow rate at 3.0 mL min⁻¹, the silica solution was not obtained at the outlet due to larger flow rate of extractant solution. When the flow rate was decreased to be 1.5 mL min⁻¹, the result was almost same. On the other hand, separation of the silica solution was observed when the flow rate of silica solution was 1.5 mL min⁻¹ and that of extractant was 3.0 mL min⁻¹. Since the decrease of flow rate did not change the separation result, the 2 to 1 of the flow rate was the best condition for the formation of parallel flow and automatic separation. As a demonstration, the residual boron content was determined in the case of the flow rate at 1.5 mL min⁻¹ on silica solution. The result is shown in Table 3.3.

### Table 3.3 The boron content in boric acid solution on the extraction with microchannel device

<table>
<thead>
<tr>
<th>Before extraction</th>
<th>After extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron content / ppm</td>
<td>27.00</td>
</tr>
<tr>
<td>Boron content / ppm</td>
<td>2.78</td>
</tr>
</tbody>
</table>
From these results, the boron content decreased to half of the initial content in the both cases of initial boron content. Since the efficiency using a separatory funnel was approximately 90 %, the contact duration in the channel seemed to be shorter for equilibrium. In order to decrease boron to 0.1 ppm, multistage extraction and/or longer contact duration should be necessary. In addition, the preparation of silica sample should be improved to avoid the incorporation of impurities.

a) Multistage extraction using microchannel device

As a preliminary experiment for the multistage extraction, the extraction using the microchannel was conducted twice on the individual sample. Since the separation of silica solution sample subsequently follows the first extraction, the second stage of extraction might be influenced by the first stage of extraction. The flow rate of silica solution and extractant were set at 1.5 mL min$^{-1}$ and 3.0 mL min$^{-1}$, respectively. After the first extraction, the obtained silica sample was injected again into the microchannel with a fresh extractant. The result of each extraction was shown in Table 3.4.

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.68</td>
</tr>
<tr>
<td>1</td>
<td>5.88</td>
</tr>
<tr>
<td>2</td>
<td>2.34</td>
</tr>
</tbody>
</table>

From the result, the boron content in the each stage was decreased at the same efficiency; influence of the former extraction was not observed. Considering the efficiency in this case, the six or seven stages of extraction would be needed for 0.1 ppm of residual boron content. Thus the efficiency of each extraction stage should be improved to decrease the operation cost. Nevertheless, the multistage extraction can be utilized for the purification processes.

b) Improvement of sample preparation and optimization of contact duration

Considering the difference of extraction efficiency between boric acid solution and silica sample, the incorporation of boron into silica network is one of the most important issue for the efficient purification processes. In order to avoid the incorporation, the sample preparation was changed from previous study$^1$. In the previous study, the silica was precipitated at higher pH by adding HCl solution. On
the other hand the extraction of boric acid was operated at the acidic condition. Therefore the extraction was conducted at the condition, where silica was dispersed in the acidic solution. Focusing on solubility of silica, however, silica can be dissolved in acidic condition as metastable state. Thus, the alkaline solution dissolving silica was directly added into acidic solution in order to maintain the acidic condition. At the condition, the silica was not precipitated and the solution was still acidic condition, where the extraction with EHD can be operated. The detail of the procedure is shown in Fig. 3.5.

![Figure 3.5 Updated procedure for the preparation of model silica solution](image)

The boron extraction was conducted on the silica sample according to the improved preparation scheme. First, 50 mL of 2.5 M NaOH solution dissolving 2 g of silica and trace amount of boric acid was added to 50 mL of 4M HCl. Then the solution was agitated with the 0.5 M EHD/toluene solution using sepratory funnel for 1 hour. Then pH was adjusted by adding 2.5M NaOH solution to precipitate and filtrate purified silica. The boron content on this process is shown in Table 3.5. The boron content decreased with 90 % of efficiency. This result was comparable to the result on the solution only containing boric acid; the efficiency seemed to reach the equilibrium of boric acid and EHD. From this result, it is indicated that the pH decrease keeping silica dissolved can avoid the influence of incorporation into silica network and the existence of silica does not influence to the extraction reaction. Therefore, the sample preparation was upgraded and utilized in the following section and chapter.

Next, the optimization of contact duration was conducted by changing the flow rate. As model solution, boric acid aqueous solution was used and the concentration
was 10 ppm. Then the boric acid solution and 0.5M EHD/toluene solutions were injected into the microchannel device, respectively. The flow rates of silica solution were set to 1.5, 0.6, 0.3 mL min\(^{-1}\) and contact duration was calculated to 0.02, 0.05, and 0.10 s, respectively. The utilized microchannel had 1.0 mm width, 100 µm depth, and 10 mm channel length. The result was shown in Table 3.6.

Table 3.6  The influence of contact duration for the boron extraction

<table>
<thead>
<tr>
<th>Flow rate / mL min(^{-1}) (contact duration / s)</th>
<th>Boric acid solution Boron content /ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before extraction</td>
<td>9.88</td>
<td>—</td>
</tr>
<tr>
<td>1.5 (0.02)</td>
<td>1.27</td>
<td>87.2</td>
</tr>
<tr>
<td>0.6 (0.05)</td>
<td>1.24</td>
<td>87.5</td>
</tr>
<tr>
<td>0.3 (0.10)</td>
<td>1.27</td>
<td>87.2</td>
</tr>
</tbody>
</table>

When the flow rate of boric acid was 1.5 mL min\(^{-1}\), the boron content decreased to 1.27 ppm. This efficiency in this case almost reached the efficiency on the separatory funnel and the efficiency did not increase in the case of longer contact duration. Therefore, the contact duration is enough to 0.02 s where the reaction can reach equilibrium in the microchannel device.

Next, the same operation was applied for the silica sample prepared with the improved process. The dissolving silica was 2g in 50 mL of 2.5 M NaOH solution. The result is shown in Table 3.7. Similarly to the result on the boric acid solution, the extraction efficiency is almost same at approximately 90 %, regardless of longer contact duration than 0.02 s. From these results, the elimination of boron species can be operated by adjusting contact duration and optimization of initial sample treatment.

Table 3.7  The influence of contact duration for the boron extraction on the silica solution sample

<table>
<thead>
<tr>
<th>Flow rate / mL min(^{-1}) (contact duration / s)</th>
<th>Silica solution Boron content /ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before extraction</td>
<td>8.93</td>
<td>—</td>
</tr>
<tr>
<td>1.5 (0.02)</td>
<td>1.06</td>
<td>88.2</td>
</tr>
<tr>
<td>0.6 (0.05)</td>
<td>1.08</td>
<td>88.0</td>
</tr>
<tr>
<td>0.3 (0.10)</td>
<td>1.04</td>
<td>88.4</td>
</tr>
</tbody>
</table>
3.3.2 Fabrication of multi-stage microchannel device and its application for the boron elimination process

a) Fabrication of multistage microchannel

In order to further the purification procedure, the sequential elimination process is necessary. A microchannel having 2 stages was fabricated on the combination of silicon and glass substrate using the same lithography techniques. The schematic images are shown in Fig. 3.6.

![Microchannel Diagram](image)

Figure 3.6 A schematic image of multistage microchannel device (width: 1 mm, length: 10 mm, Depth: Si:50 μm-G:50 μm)

b) Formation of parallel flow and separation at the outlet

Prior to the application for the elimination process, the condition for the stable parallel flow was investigated. First, the separation from first stage to second stage was conducted by injecting ultra pure water and toluene. Water was injected into inlet 1 and toluene was injected into inlet 2, 3, and 4, respectively. The separation result is shown in Table 3.8. According to the result on the single stage microchannel, the flow rate was set at 1.5 mL min\(^{-1}\) for water and 3.0 mL min\(^{-1}\) for toluene, respectively. From the outlet 3 and 4, toluene with the same flow rate was injected. In this condition, the obtained solution at the outlet was not separated well. And the obtained amount of toluene from the first outlet was larger than that of water. Therefore, the flow rate of toluene was decreased to be 2.25 mL min\(^{-1}\), where the separation of water
and toluene was observed. Next, the flow rate of inlet 3 and 4 was adjusted for separation at the second stage of extraction. With decreasing the flow rate, the separation was observed when the flow rate of toluene was 0.33 mL min⁻¹. The optical images of obtained solutions at the each outlet were shown in Fig. 3.7. The solution obtained from outlet B was only water, although the solution obtained outlet A contained water slightly.

**Table 3.8 Separation condition of water and toluene in the multistage microchannel**

<table>
<thead>
<tr>
<th>Flow rate of inlet / mL min⁻¹</th>
<th>Separation condition at each outlet (W: water, T: toluene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 Water</td>
<td>A: W and T, B: W and T, C: T, D: T</td>
</tr>
<tr>
<td>1.5 Toluene</td>
<td>A: W and T, B: W and T, C: T, D: T</td>
</tr>
<tr>
<td>1.5 Toluene</td>
<td>A: W and T, B: W and T, C: W and T, D: W and T</td>
</tr>
<tr>
<td>1.5 Toluene</td>
<td>A: W and T, B: W, C: T, D: T</td>
</tr>
</tbody>
</table>

**Figure 3.7 Separation condition on the multi stage microchannel device**

(Flow rate: 1.5 mL min⁻¹)

c) Application for boron extraction

Using the condition optimized in the previous section (Inlet1 : 1.5 mL min⁻¹, Inlet2 : 2.25 mL min⁻¹, Inlet3 : 0.33 mL min⁻¹, Inlet4 : 0.33 mL min⁻¹), extraction of boron species was conducted. As a first step, boric acid solution and 0.5 M EHD toluene solution were injected into each inlet, respectively. For evaluating the efficiency of the second stage, the extraction efficiency on single stage microchannel was also
determined on individual sample by applying toluene solution, where no EHD was composed, as a quasi-extractant in the second stage. This meant no more extraction would occur after the first stage of extraction. The result is shown in Table 3.9. In the first stage of extraction, the boron content decreased from 6.24 ppm to 1.06 ppm with 91.1% of the efficiency. In the second stage, the boron content decreased to 0.55 ppm. Focusing on the second stage, the efficiency was calculated to 48.1% from the residual content of boron in the first stage. While the separation at the outlet was observed and boron was successfully eliminated, the issue of the lower extraction efficiency in the second stage remained.

Next, the extraction of boron species was applied for the model silica solution. The condition of flow was same to the previous experiment. The boron content of the obtained silica sample was determined with ICP-AES. The result is shown in Table 3.10. Similarly to the boric acid solution, the boron content decreased from 6.04 ppm to 1.10 ppm with the 81.8% of the extraction efficiency. In addition, the efficiency of second stage was also lower than that of the first stage. In addition, separation condition was also same to the case of boric acid solution. Hence, the multistage extraction can be utilized for the elimination of boron species from soluble silica solution sample. However, the issue of lower efficiency in the second stage remained.

d) Influence of the extraction in the second stage

In order to confirm the influence of the multistage extraction, the extraction using single-stage microchannel from silica solution sample was conducted. The microchannel has 1.0 mm width, 100 µm depth, and 10 mm channel length. The condition of flow was same at the previous experiment. The extraction was repeated two times to confirm the extraction efficiency at lower concentration. The result is shown in Table 3.11 and 3.12. When multistage extraction was conducted using single-stage microchannel, the boron content decreased from 1.54 ppm to 0.42 ppm in the second stage with the 72.7% of the extraction efficiency. Comparing the result on the multistage microchannel, the extraction efficiency was much higher. Since the

---

### Table 3.9 Boron extraction on the boric acid solution

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.24</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1.06</td>
<td>82.9</td>
</tr>
<tr>
<td>2</td>
<td>0.55</td>
<td>91.1</td>
</tr>
</tbody>
</table>

### Table 3.10 Boron extraction on the model silica solution using single-stage microchannel device

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.24</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1.54</td>
<td>81.8</td>
</tr>
<tr>
<td>2</td>
<td>0.42</td>
<td>89.6</td>
</tr>
</tbody>
</table>
difference between the experiments was the flow rate of extractant, the lower flow rate of extractant in the second stage could be on of the reason for the lower efficiency. The lower flow rate may cause the decrease of contact duration in unit volume; the freshness of extractant cannot be kept.

Next, the extraction under further low concentration sample was conducted to confirm the influence of concentration gradient for lower efficiency in the second stage. The boron content was set at around 1 ppm, which was almost same to the residual boron content in the first stage. The result is shown in Table 3.12. The boron content decreased from 0.92 to 0.16 ppm in the second stage with 82.6 % of total efficiency. While the efficiency on the higher concentration was 80 %, the efficiency on the lower concentration was 65.2 % in the first stage and 50 % from first stage to second stage. From the result, contact duration should be increased in the case of lower concentration, especially second stage of extraction due to lower concentration gradient.\(^9\)

Since the calculated contact duration on the above condition was 40 ms, the increase of contact duration by adjusting the flow rate could be effective. Thus, the flow rate of the silica solution sample was changed to 0.75 mL min\(^{-1}\). The flow rates of other solutions were also changed according to the flow rate of the silica solution sample. In this condition, the calculated contact duration was 80 ms. The each flow rate is shown in Table 3.13. The result of extraction is shown in Table 3.14. When the flow rate decreased to half, the residual boron content in the first stage was 0.23 ppm with 75.0 % of the efficiency. In the second stage, the boron content

<table>
<thead>
<tr>
<th>Inlet</th>
<th>Type of solution</th>
<th>Flow rate / mL min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silica solution</td>
<td>0.75</td>
</tr>
<tr>
<td>2</td>
<td>Extractant</td>
<td>1.20</td>
</tr>
<tr>
<td>3</td>
<td>Extractant</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>0.20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stage</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.04</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1.10</td>
<td>81.8</td>
</tr>
<tr>
<td>2</td>
<td>0.63</td>
<td>89.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stage</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.92</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.32</td>
<td>65.2</td>
</tr>
<tr>
<td>2</td>
<td>0.16</td>
<td>82.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stage</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.92</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.23</td>
<td>75.0</td>
</tr>
<tr>
<td>2</td>
<td>0.07</td>
<td>92.4</td>
</tr>
</tbody>
</table>

Table 3.11 Boron extraction on the model silica solution

Table 3.12 Boron extraction on the boric acid solution

Table 3.13 Flow rate on the extraction

Table 3.14 Boron extraction on the model silica solution
decreased to 0.07 ppm with 92.4 % of the total efficiency. Focusing on the second stage the efficiency was increased to be 70 %, which was comparable to that in the first stage. From this result, increase of the contact duration in the second stage of extraction can further the purification process using microchannel device. In order to utilize the longer contact duration with the reasonable productivity, the microchannel with longer channel length with the same contact duration was required.

3.3.3 Fabrication of microchannel device with longer contact duration

In order to optimize the contact duration for the extraction, extraction on longer contact duration was compared. The boron extraction using the 2-stage microchannel was conducted with 80 ms and 120 ms of contact duration on an individual sample, respectively. The result is shown in Table 3.15 and 3.16. In the case of longer contact duration, the boron content was decreased from 1.12 ppm to 0.22 ppm with 80.4 % of efficiency. In the second stage, the boron content was decreased to 0.06 ppm with 94.6 % of total efficiency. Comparing the two results, the increase of contact duration from 80 to 120 ms had less influence for the residual boron content and efficiency than that from 40ms to 80 ms. That may be caused by the lower concentration of boric acid in the second stage, which almost reached the equilibrium. From the result, the multi-stage microchannel with two longer channels was designed. The schematic image of channel is shown in Fig. 3.8.

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.12</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.27</td>
<td>75.8</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>92.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.12</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.22</td>
<td>80.4</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>94.6</td>
</tr>
</tbody>
</table>
The designed microchannel had two channels with 25 mm length and contact duration was calculated to 100 ms at 1.5 mL min\(^{-1}\) of flow rate. Compared to the previous design, the flow direction was changed and curved at the separating area. This was due to the restriction of fabrication and operation of the laboratory. While the stability of parallel flow was decreased by the curve in the channel such as Dean vortex\(^{10}\), mixing condition could be increased in general. When the flow condition for the separation was determined, the extraction efficiency may be improved. The microchannel was fabricated through the same lithography processes with 50 \(\mu\)m depth of silicon and glass, respectively. Then the silicon and glass substrate were bonded with anodic bonding.

Next, the separation condition in the channel was investigated. The standard of flow rate was set to 1.5 mL min\(^{-1}\) for silica solution sample since the contact duration would be proper in this condition. Following the adjustment of each flow rate of extractant, the separation condition was determined as shown in Table 3.17. At this condition, silica solution was separated and obtained from outlet C, while the silica solution was slightly included in the solution obtained from outlet A. The optical images of the solution obtained from each outlet were shown in Fig. 3.9.

**Table 3.17** Flow rate on the extraction

<table>
<thead>
<tr>
<th>Inlet Type of solution</th>
<th>Flow rate / mL min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Extractant</td>
<td>3.0</td>
</tr>
<tr>
<td>2 Silica solution</td>
<td>1.5</td>
</tr>
<tr>
<td>3 Extractant</td>
<td>0.6</td>
</tr>
</tbody>
</table>

![Figure 3.8 A schematic image of updated microchannel device](Width: 1.0 mm, Length: 25 mm, Depth Si:50 \(\mu\)m-G:50 \(\mu\)m)
3.3.4 Application of the updated microchannel device for purification process

The fabricated microchannel device was applied for the boron extraction from boric acid solution. The initial content of boric acid was 1 ppm and the two-stage extraction was carried out in the flow condition shown in Table 3.17. The result is shown in Table 3.18. In the first stage of the extraction, boron content decreased from 1.09 ppm to 0.22 ppm with 79.8 % of efficiency. In the second stage, boron content was decreased to 0.07 ppm with 94.3 % of total efficiency. The efficiency from the first to the second stage was calculated to 71.8 %. This result was comparable to the previous result using the shorter microchannel device with lower flow rate and almost same contact duration. Thus, the contact duration for boron extraction using the microchannel device would be proper.

Next, the extraction was applied to model solution sample and refined diatomaceous earth as a real sample. Following the preliminary acid leaching process in order to remove heavy metal elements, solvent extraction of boron with EHD toluene solution was carried out. The flow rate is same as shown in Table 3.16. The condition was adjusted to form stable parallel flow and separate the extractant from the silica solution at the outlet. The boron contents of the model sample on each stage of the extraction are shown in Table 3.19. The boron content decreased to 0.07 ppm and the elimination rate was 94%. The boron content on the second stage was less than the target value of the SOG-Si, 0.1 ppm. In addition, this value was

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.09</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.22</td>
<td>79.8</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>94.3</td>
</tr>
</tbody>
</table>

Table 3.18 Boron extraction on boric acid solution
comparable to that reaching to equilibrium point of the reaction with a conventional separatory funnel, even though the contact duration was estimated to be less than 100 ms.

This procedure was applied to the real sample, diatomaceous earth. Diatomaceous earth was preliminary refined with the acid leaching process according to the previous study and sample preparation of previous chapter and boron content decreased to 1.03 ppm before the solvent extraction. The flow rate, at which the parallel flow was stable, was same to the model solution. The boron content on the solvent extraction is shown in Table 3.20. The results are almost similar to the model solution sample. It could be due to sample preparation and acid leaching condition. In the previous study\(^1\), the chemical state of boron and condition of silica solution were different between model and real sample. The influence of silica network on the acid leaching process was investigated. Then, the condition of silica solution on the real sample was similarly prepared to that on the model sample. This is the reason why the elimination efficiency is almost same between model and real samples. This result may suggest that the solvent extraction itself is not significantly influenced by the other impurities and can be applied to real samples.

### Table 3.19 Residual boron content after the solvent extraction with EHD on a model sample

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Elimination rate / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.16</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>78.4</td>
</tr>
<tr>
<td>2</td>
<td>0.07</td>
<td>94</td>
</tr>
</tbody>
</table>

### Table 3.20 Residual boron content after the solvent extraction on a real sample

<table>
<thead>
<tr>
<th>Stage number</th>
<th>Boron content / ppm</th>
<th>Elimination rate / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.03</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.24</td>
<td>78.4</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>91.8</td>
</tr>
</tbody>
</table>
3.3.5 Elucidation of the reaction mechanism of 1,3-diols on boron extraction and optimization of extractant

In order to improve the productivity of high-purity silica for SOG-Si, the efficiency of each solvent extraction is also important. While the extraction mechanism has not been elucidated, 1,3-diols such as EHD are popular boron extractant. When we consider the extraction performance, most important factor is partition coefficient. In the case of the boron extraction, the partition coefficient of extractant and/or produced boron ester should be important. However, the extraction efficiency has low relationship with the partition coefficient on the boron extraction with 1,3-diols\(^5\). For instance, 2,2-diphenyl-1,3-propanediol has larger partition coefficient, but has lower extraction efficiency than EHD. In addition, TMPD is one of the better extractant than EHD (Table 3.21), while both EHD and TMPD is alkyldiol with same molecular weight and the difference is the side chain and the number of carbon neighbors. In order to elucidate the difference of reactivity for these extractants, DFT calculation was carried out.

As a model reaction scheme, the initial and final formations of the reaction of boric acid with EHD or TMPD were analyzed. As shown in Table 3.22, reaction energy of TMPD was estimated to be 1.3 times lower than that of EHD. In this case, the reaction energy was mostly influenced by the stability of the final product. Since the reaction produced two new B-O-C bonds, the stability of this bond could be a key for the reactivity of whole reaction. Focusing on the electron population of B-O-C region, that of the final product with TMPD is also larger than that with EHD. From this result, the difference in number of electron population may be important for the difference in extraction reactivity. For this, the reaction energy of diols with the different number of carbon neighbors was analyzed. The representative reaction scheme is shown in Fig. 3.10 and result is shown in Table 3.23. As the number of carbon neighbors increases, the reaction energy became more negative; the final product became more stable. Since EHD is tertiary and TMPD is quaternary, the reactivity of the extraction reaction can be explained with this hypothesis. In addition, the number of carbon neighbors of other carbon may be also important. The discussion here should provide theoretical background of higher extraction efficiency of TMPD. Moreover, these results indicate the possibility to propose another extractant, which is more efficient than TMPD.
Table 3.21 Residual boron content with solvent extraction using separatory funnel

<table>
<thead>
<tr>
<th>C_{extractant} (mol·L⁻¹)</th>
<th>Before extraction / ppm</th>
<th>After extraction / ppm (EHD)</th>
<th>After extraction / ppm (TMPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.14</td>
<td>0.12 (89.4%)</td>
<td>0.07 (93.9%)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.96</td>
<td>0.06 (93.8%)</td>
<td>0.02 (97.9%)</td>
</tr>
</tbody>
</table>

Table 3.22 Reaction energy of the extraction reaction with EHD and TMPD

<table>
<thead>
<tr>
<th>Electron population in B-O-C region / -</th>
<th>Reaction energy / kJ·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>EHD</td>
<td>0.775 -23.71</td>
</tr>
<tr>
<td>TMPD</td>
<td>0.998 -31.69</td>
</tr>
</tbody>
</table>

Figure 3.10 (a) Representative reaction scheme of boric acid with secondary diol (b) structure of tertiary diol (c) structure of quaternary diol

Table 3.23 Reaction energy of the extraction reaction on different number of carbon neighbors

<table>
<thead>
<tr>
<th>Type of diol</th>
<th>ΔG / kJ·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary</td>
<td>-21.94</td>
</tr>
<tr>
<td>Tertiary</td>
<td>-23.1</td>
</tr>
<tr>
<td>Quaternary</td>
<td>-25.42</td>
</tr>
</tbody>
</table>
Finally, TMPD was applied to the extraction using the flow–type device on both the model and real samples. The flow rate was adjusted as described in Table 3.17. Under this condition, the silica solution was separated at the outlet. The result is shown in Table 3.24. In both the model and real samples, the residual boron content was 0.06 ppm. It is lower than that with EHD shown in Table 3.19 and 3.20 although the difference is not so large as expected from the result in Table 3.21. This table indicates that the optimization of extraction condition such as the contact duration or concentration of the extractant can further improve the productivity and efficiency for the cost-effective processes.

**Table 3.24** The condition of solvent extraction using the flow-type device with TMPD

<table>
<thead>
<tr>
<th></th>
<th>Flow rate / mL·min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica solution</td>
<td>1.5</td>
</tr>
<tr>
<td>Extractant (1st stage)</td>
<td>3.0</td>
</tr>
<tr>
<td>Extractant (2nd stage)</td>
<td>0.75</td>
</tr>
</tbody>
</table>

**Table 3.24** Residual boron content after the solvent extraction with TMPD

<table>
<thead>
<tr>
<th></th>
<th>Before extraction / ppm</th>
<th>After extraction / ppm</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model sample</td>
<td>0.99</td>
<td>0.06</td>
<td>94</td>
</tr>
<tr>
<td>Real sample</td>
<td>1.1</td>
<td>0.06</td>
<td>95</td>
</tr>
</tbody>
</table>
3.4 Conclusion

To develop a cost-effective process for the production of high-purity silica as a resource for SOG-Si, the elimination procedure of boron species from diatomaceous earth by solvent extraction with a scaled-up microchannel device was demonstrated. As an efficient elimination method, a flow-type device, which have larger liquid-liquid interface with maintaining short diffusion distance comparable to the microchannel, was fabricated in combination of lithography techniques on silicon and glass substrate. Then, multistage micorchannel device was applied for the boron elimination process maintaining the specific interfacial area and productivity. Following the optimization of flow condition and contact duration for the separation at the outlet, the updated microchannel device showed better extraction performance and productivity than the microchannel device described in the previous chapter. Although the productivity was still required for thousands tons production, the increase the interfacial area with horizontal interface would be a guideline for the further increase of the throughput. In addition, DFT calculation was conducted to elucidate the extraction mechanism of boron with diols, especially focusing on the difference between EHD and TMPD. The theoretical calculation revealed that the number of carbon neighbors of the central carbon and electron population of B-O-C region were keys for the reactivity of the extractant, i.e. the reason TMPD showed better extraction performance than EHD. Finally, the boron elimination from the preliminary refined diatomaceous earth was improved by the combination of the flow-type device and TMPD and the residual boron content in SOG-purity, 0.1 ppm, was achieved. From these results, it is concluded that multistage extraction with the flow-type device can be utilized for the production of the high-purity silica as a resource of SOG-Si, and the increase of the throughput of one device would decrease the cost of numbering-up process.
References

Chapter 4

Influence of Solvation on the Preliminary Acid-Leaching Process of Silica toward High-purity Starting Material
4.1 Introduction

In order to improve the efficiency of the solvent extraction in the purification process of silica, the incorporation of boron into silica network should be prevented as described in the previous chapter. The incorporation of the impurities mainly occurs in the acid-leaching process. The acid-leaching process was mainly separation of solid and liquid phase on filtration and leaching. When silica was separated as solid phase from liquid phase including impurities, silica should incorporate impurities such as boron. Considering the solubility of silica and boron in acidic solution, however, the amount of the incorporated impurities can be further decreased with controlling silica precipitation. While the elimination of boron in sub-ppm level would be operated with microchannel devices, the acid-leaching process would have a potential to decrease the residual boron content in single ppm level with optimization of such simple operations. In addition, the improvement of the efficiency should decrease the cost of the purification process with microchannel devices.

The production of silica has been well developed such as glass and silica gel. When precipitation of silica occurs from alkaline solution, the precipitation would be influenced by a number of conditions such as concentration of silica, ion strength, pH, temperature and so on. However, there are few report to apply these process for production of high-purity silica from amorphous silica resource such as diatomaceous earth. Among the impurities in diatomaceous earth and/or refined silica, sodium would be a key in addition to boron and phosphorus since the purification process utilized NaOH solution, which contained huge amount of sodium. In order to prevent the incorporation of sodium, development of a sodium-free or controlled process is necessary. One of the sodium-free alkaline reagents is tetramethylammonium hydroxide (TMAH), which are widely utilized in semiconductor field as developing agent on lithography process. By adding sodium ion as NaCl to TMAH solution, the influence of sodium ion for the acid leaching process can be quantitatively investigated.

In the present chapter, the development of efficient acid leaching process aiming for combination with the solvent extraction process and an investigation of the influence of sodium ion was reported.
4.2 Experimental

4.2.1 Chemicals

A “model sample” composed of refined silica spiked with a trace amount of boric acid and a “real sample” composed of refined diatomaceous earth were prepared.

For the model sample, refined silica powder (> 3N) and boric acid (> 99.999 %) were purchased from Kanto Chemical and Aldrich, respectively. As one of the sodium-free solvent, 25wt% TMAH solution was purchased from Kanto Chemical. The chemical formula of TMAH is shown in Fig. 4.1

![Figure 4.1 The structure of TMAH](image)

4.2.2 Acid leaching process from alkaline solution

- SiO$_2$ 1.0 g
- $\leftarrow$ 0.5, 13, 2.5, 5.0 M NaOH solution 50 mL
- $\leftarrow$ 10000 ppm boric acid 120 μL
- Agitation at 100 °C
- $\leftarrow$ 5.0 M HCl
- pH adjustment
- Filtration
- $\leftarrow$ 5.0 M HCl 50 mL
- Agitation at 100 °C
- Filtration
- Dry at 80 °C
4.2.3 Acid leaching process from acidic solution

SiO₂ 1.0 g
← 2.5 M NaOH solution 50 mL
← 10000 ppm boric acid 120 mL

Agitation at 100 °C ・・・ (A)

5.0 M HCl 30 mL
← (A)

pH = -0.9
← 2.5 M NaOH solution

pH adjustment

Filtration
← 5.0 M HCl 50 mL

Agitation at 100 °C

Filtration

Dry at 80 °C
4.2.4 Acid leaching process from TMAH solution

<table>
<thead>
<tr>
<th>1.4M TMAH solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>← SiO₂ 1 g</td>
</tr>
<tr>
<td>← 10000 ppm boric acid 120 mL</td>
</tr>
<tr>
<td>← 10000 ppm phosphoric acid 40 mL</td>
</tr>
<tr>
<td>← NaCl</td>
</tr>
</tbody>
</table>

Agitation at 100 °C

<table>
<thead>
<tr>
<th>pH Adjustment</th>
</tr>
</thead>
</table>

Filtration

Dry at 80 °C

<table>
<thead>
<tr>
<th>5.0 M HCl 50 mL</th>
</tr>
</thead>
</table>

Agitation at 100 °C

<table>
<thead>
<tr>
<th>Filtration</th>
</tr>
</thead>
</table>

Dry at 80 °C

4.2.5 Determination of amount of impurities with ICP-MS

ICP-AES (ICAP-6300, Thermo Fisher Scientific) and ICP-MS (ICAP-Q, Thermo Fisher Scientific) were used to determine boron content. Samples were dissolved into 48 % HF to form H₂SiF₆. Then, HF and H₂SiF₆ were evaporated and remaining impurities were dissolved in a 0.1 mol L⁻¹ aqueous solution of HNO₃ prior to the measurement.
4.2.6 Dynamic light scattering (DLS)

Sample tube

← 1 mL sample solution
← UPW 24 mL

Agitation ・・・ (*)

Cell

← (*) 2 mL

DLS measurement

4.3 Results and discussion

4.3.1 Chemical state of boron species on the purification processes

The elimination mechanism of boron with acid leaching process is dissolution of boron species from precipitated silica to acidic solution. The reaction would occur at the interface between silica (solid phase) and acidic solution (liquid phase). In order to confirm the chemical state of boron at the surface of precipitated silica on the acid leaching process, measurement with X-ray photoelectron spectroscopy (XPS) was carried out. Due to the restriction of the resolution of XPS, the trace amount of boric acid was 1.5 g, which was approximately 10000 times larger than that in diatomaceous earth. The result is shown in Fig. 4.2 and 4.3. In the figures, the chemical state of boron was determined as boric acid and the boron at the surface of silica was eliminated through the acid leaching. This result indicated that the increase of surface area of silica to expose the boron species at the surface could enhance the elimination efficiency of the acid leaching process.
4.3.2 Acid leaching process from alkaline solution

In the acid-leaching process, the dissolution of silica is a process, where impurities should be released from silica to the solution, and the precipitation of silica is a solid-liquid separation, where the incorporation of impurities should be prevented. Thus, the specific surface area of the precipitated silica should mainly influence the efficiency of the acid leaching process. Since the silica easily dissolves into the sodium hydroxide solution, the influence of the precipitation and leaching process
was firstly investigated. The concentration of NaOH aqueous solution to dissolve silica was changed to 0.5, 1.3, 2.5 M, respectively. Then HCl acidic solution was added to the solution dissolving silica until the precipitation of silica was observed. The pH of precipitation and its conditions is shown in Table 4.1

<table>
<thead>
<tr>
<th>Precipitation pH</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺ 0.5 M, OH⁻ 0.5 M</td>
<td>7.8  Gel</td>
</tr>
<tr>
<td>Na⁺ 1.3 M, OH⁻ 1.3 M</td>
<td>9.9  Gel</td>
</tr>
<tr>
<td>Na⁺ 2.5 M, OH⁻ 2.5 M</td>
<td>10.2 Precipitation</td>
</tr>
</tbody>
</table>

From the result, the color of precipitated silica became white with increasing the concentration of NaOH. This would be due to the diameter of precipitated silica. The result of DLS measurement was shown in Fig. 4.4. In this figure, the order of diameter did not follow the result of Table 4.1. In the case of 0.5 and 1.3 M of NaOH, the peak around 3500 nm was observed. Since gelation was observed in these conditions, the observed would be secondary particle. The acid leaching process was carried out in those conditions, respectively. The residual boron content is shown in Table 4.2. The initial boron content was set at 200 ppm by adding boric acid. The boron content was determined with ICP-MS.

<table>
<thead>
<tr>
<th>Concentration of NaOH /M</th>
<th>Boron content before acid leaching /ppm</th>
<th>Boron content after acid leaching /ppm</th>
<th>Yield of silica /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>42.8</td>
<td>7.23</td>
<td>93</td>
</tr>
<tr>
<td>1.3</td>
<td>15.2</td>
<td>5.49</td>
<td>81</td>
</tr>
<tr>
<td>2.5</td>
<td>6.67</td>
<td>0.0713</td>
<td>66</td>
</tr>
</tbody>
</table>
Figure 4.4 The diameter profile of silica sample determined with DLS dissolved in (a) 2.5 M, (b) 1.3 M, and (c) 0.5 M NaOH
From the table, the residual boron content of the precipitated silica (before acid leaching) was larger in the case of lower NaOH concentration. This would be caused by the difference of precipitation condition with incorporation of boron species. When the lower concentration of sodium ion such as 0.5 M, nucleation of silica would occur rather than its growth due to lower surface potential. Then gelation would occur with incorporation of aqueous solvent including boron species. The network of the gel would be so strong that the boron within the network was not easily to remove with acid leaching process; the acid could not attack the inner part of network. On the other hand, in the case of the higher concentration, the growth would occur rather than nucleation due to thinner electric double layer of silica by sodium ion. That would also cause the physical aggregation. Thus, the precipitation would avoid the including the aqueous solvent. However, the yield in the case of 2.5 M was lowest. This would be due to the difference of precipitated pH. If the pH was decreased to where gelation occurs, the yield would be increased but the purity would be decreased.

4.3.3 Acid leaching process from acidic solution

As described in the previous chapter, the preparation of silica solution sample for the solvent extraction was changed from alkaline condition to acidic condition in order to avoid incorporation of boron species into silica network. Therefore the precipitation from acidic condition could be effective for the acid leaching process and separation of silica.

First, the precipitation condition and efficiency of acid leaching process was investigated. As model solution sample, 1g of silica and trace amount of boric acid were added into 50mL of 2.5 M NaOH aqueous solution. Then the solution was added to 30 mL of 5.0 M HCl aqueous solution to adjust the pH to -0.9. In this condition, silica seemed to maintain as dissolved observed by human eyes. However, the solubility of silica strongly decreases when pH is below 10. Thus the silica particle should be grown in this condition. The result of DLS measurement is shown in Fig. 4.5.
From the figure, the peak was observed around 400 nm, which would be secondary particle of silica. When the alkaline and acidic solutions were mixed, the mixing condition should influence the growth of silica particle. In this case, the solution was just added to beaker with the acidic solution like simple batch process. If the mixing condition was improved, the particle should be smaller and prevent the incorporation as well.

Then, 2.5 M NaOH solution was added to the solution sample to increase the pH for gelation. When the pH of the solution reached to 6, the gelation of silica was observed. The optical image of obtained silica gel is shown in Fig. 4.6. Due to lower concentration of silica along with the operation, where some solutions were added for pH adjustment, the silica gel was not covered whole solution in the beaker. Then the obtained silica was purified with acid leaching process. The result is shown in Table 4.3.

![Figure 4.5](image.png) Diameter profile of silica sample prepared acidic condition

![Figure 4.6](image.png) Optical image of silica gel obtained at pH=6
(a) as deposited  (b) after filtration
Table 4.3 Boron content and yield of silica on the acid leaching process

<table>
<thead>
<tr>
<th>Boron content before acid leaching /ppm</th>
<th>Boron content after acid leaching /ppm</th>
<th>Yield of silica /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.6</td>
<td>1.34</td>
<td>93</td>
</tr>
</tbody>
</table>

From the result, the residual boron content was almost similar to the result of 0.5 M in Table 4.2; the residual boron content was relatively higher and yield was high. The boron content after acid leaching reached around 1 ppm, from which the solvent extraction with microchannel devices could decrease to the target level of SOG-Si. This silica gel was so friable that the acid leaching would be more effective than that in the case of 0.5 M NaOH. That would be why the residual boron content before and after acid leaching was lower in the case of precipitation in acidic condition. The diameter was determined with DLS. The result is shown in Fig. 4.7. From the result comparing the case of 0.5 M NaOH, the peak over 1000 was not observed in the case of acidic condition. This would be because friability. The efficiency of acid leaching was strongly influenced by the specific interfacial area of silica. Since the structure of the silica gel prepared in acidic condition was sparse structure, the residual boron content was lower.
Figure 4.7 Diameter profile of silica sample prepared acidic condition and alkaline condition
Since the friable gel was obtained due to lower concentration of silica in solution, the silica amount was increased to 2.0 g to confirm the influence. The amount and concentration of other solutions were same. The Optical image is shown in Fig. 4.8. As a result, silica gel was obtained around pH 5 and whole of solution became gel at pH 6. In this condition, the acid leaching process was conducted. The residual boron content and result of DLS are shown in Table 4.4 and Fig. 4.9.

**Figure 4.8** Optical image of silica gel obtained at pH=6 (Silica was 2 g)

**Table 4.4** Boron content and yield of silica on the acid leaching process (Silica was 2 g)

<table>
<thead>
<tr>
<th>Boron content before acid leaching /ppm</th>
<th>Boron content after acid leaching /ppm</th>
<th>Yield of silica /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.8</td>
<td>9.40</td>
<td>115</td>
</tr>
</tbody>
</table>

**Figure 4.9** Diameter profile of silica sample prepared acidic condition
From the result, the amount of residual boron content was larger than that in the case of lower silica concentration. This would be due to the incorporation of solvent with the gelation. The result that the yield of silica was higher than 100 % and the gelation, which contained whole of solvent, indicated the incorporation of impurities with aqueous solvent. In addition, the DLS result revealed that the frequency of the particle with larger diameter was higher than that prepared with alkaline condition with 0.5 M NaOH solution. This result also indicated the amount of the incorporated impurities would be larger. From these results, the acid leaching process prepared with acidic condition was high yield but relatively lower elimination efficiency. Nevertheless, the residual boron content would be enough to apply next purification process, the solvent extraction, since the starting content studied in the solvent extraction was around 1 ppm.

4.3.4 Influence of the concentration of sodium ion

a) Acid Leaching process using TMAH

One of the important issues on the acid leaching process is incorporation of sodium ion in the precipitated silica. On the other hand, the sodium ion helps the dissolution of silica. In order to apply sodium-free process, TMAH was attempted. TMAH has no sodium ion but tetramethylamine. Using TMAH and NaCl, quantitative investigation of the influence of sodium ion and the acid leaching process using TMAH was carried out.

First, the dissolution of silica to TMAH aqueous solution was investigated. The concentration of TMAH was set at 2.8, 1.4, and 0.7 M. Then 1.0 g of silica was added into the solution and agitated at 100 °C. While silica was not dissolved in the case of 2.8 M, dissolution was observed in the case of 1.4 and 0.7 M. Since the etching of silicon using TMAH was applied at lower concentration due to adsorption of TMA ion to prevent the attack by hydroxide ion at high concentration, the dissolution of silica would follow same mechanism. For 0.7 and 1.4 M sample, DLS measurement was conducted. The results are shown in Fig. 4.10 and 4.11.
While 1.0 g of the silica easily dissolved in NaOH solution; the mean diameter was less than 1 nm, the diameter in the case of TMAH was approximately 170 nm. Focusing on pH, the pH of 1.4 M TMAH solution was 13.4 and 2.5 M NaOH was 12.4. pH was almost same but dissolution in the case of NaOH was better. This result indicated that the cations in the solution would more influence than anion.

Following the dissolution process, the acid leaching process was conducted. The amount of silica was 1.0 g and trace amount of boron and phosphorus was added as boric acid and phosphoric acid, respectively. The result is shown in Table 4.5.

From the table, the incorporation of sodium was not observed in the result on TMAH in contrast to that on NaOH. While the incorporation of sodium was prevented, the residual boron content and phosphorus content before acid leaching was larger in the case of TMAH. This would be due to the precipitation condition in pH adjustment. In the case of NaOH, silica aggregated when pH was decreased to be 11 and gelation occurred. On the other hand, aggregation was not observed in the case of TMAH. The
silica particle was just dispersed in the solution. Therefore, the separation of filtration was not easy due to small particle size compared to the filter. In addition, the lower concentration of TMAH showed better efficiency of acid leaching process. This would be also due to the influence of TMA ion as described above.

**Table 4.5** Residual content of impurities on the acid leaching process

<table>
<thead>
<tr>
<th></th>
<th>2.5M NaOH /ppm Before acid leaching</th>
<th>After acid leaching</th>
<th>1.4M TMAH /ppm Before acid leaching</th>
<th>After acid leaching</th>
<th>0.7M TMAH /ppm Before acid leaching</th>
<th>After acid leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>11.00</td>
<td>0.60</td>
<td>72.60</td>
<td>22.91</td>
<td>39.80</td>
<td>0.55</td>
</tr>
<tr>
<td>Na</td>
<td>97621</td>
<td>591.91</td>
<td>13.97</td>
<td>10.04</td>
<td>5.25</td>
<td>4.77</td>
</tr>
<tr>
<td>P</td>
<td>4.412</td>
<td>0.17</td>
<td>31.00</td>
<td>0.40</td>
<td>13.10</td>
<td>0.80</td>
</tr>
</tbody>
</table>

**b) Addition of sodium ion to TMAH solution**

As described in the previous section, the existence of sodium ion is important to dissolve silica in alkaline solution. In order to control the incorporation of sodium into silica maintaining efficient purification process, 1.4 M TMAH solution with NaCl as sodium agent was attempted.

First, the solubility of silica in the sodium-added TMAH solution was investigated. The amount of NaCl was 2.5 M, 1.3 M, 0.60 M, respectively. Then 1g of silica was added to the solution and the solution was agitated for 1 hour at 100 °C. Then DLS was conducted to each sample. The results are shown in Fig. 4.12, 4.13, and 4.14.

From the figures, the mean diameter was decreased with increasing the NaCl amount and the mean diameter in the case of 2.5 M NaCl was comparable to that used 2.5M NaOH solution. Since the time of agitation was constant at 1 hour, the dissolution rate would be increased along with the sodium ion concentration. From the viewpoint of the chemical state in the solution, silica would exist as mono-silicic acid, \((\text{HO})_2\text{SiO}_2^-\), when the ratio of Na/Si is higher than 3.\(^5\) When the ration is between 2 and 3, silica would exist as poly-silicic acid, \((\text{HO})_n\text{Si}_n\text{O}_{2n}^-\). In the all experiments, the ratio was higher than 3. However, the mean diameter of silica particle was different among the samples. This would be caused because the TMA ion would adsorb to the surface of silica and prevent the dissolution. The dissolution occurs through hydrolytic cleavage of Si-O-Si by hydroxide ion. Since the surface of silica have negative charge, the charge should be canceled with cations to attack hydroxide ion.\(^9,10\) Both sodium and TMA ions would adsorb to the silica surface but TMA would prevent the attack of hydroxide ion due to its bulky structure. Thus the
silica could not dissolved well whether the ratio of Na/Si was higher than 3. In addition, the existence of sodium ion can improve the solubility although sodium would be incorporated as impurities.

**Figure 4.12** Diameter profile of silica sample prepared using 1.4 M TMAH with 2.5 M NaCl

**Figure 4.13** Diameter profile of silica sample prepared using 1.4 M TMAH with 1.3 M NaCl

**Figure 4.14** Diameter profile of silica sample prepared using 1.4 M TMAH with 0.60 M NaCl

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Since the solubility of silica is one of the important steps on the acid leaching process to release the impurities into the solution, the optimization should be needed both for dissolution and precipitation of silica using sodium-added TMAH solution. The incorporation of the impurities and efficiency of acid leaching process was investigated on sodium-added TMAH solution. The concentration of TMAH was 1.4 M and trace amount of boron and phosphorus was added as boric acid and phosphoric acid, respectively. The concentration of NaCl was set as previous section. The residual content of impurities was determined ICP-MS. The result is shown in Table 4.6.

**Table 4.6 Residual content of impurities on the acid leaching process**

<table>
<thead>
<tr>
<th></th>
<th>Without NaCl /ppm</th>
<th>2.5M NaCl /ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before acid leaching</td>
<td>After acid leaching</td>
</tr>
<tr>
<td>B</td>
<td>72.60</td>
<td>22.91</td>
</tr>
<tr>
<td>Na</td>
<td>13.97</td>
<td>10.04</td>
</tr>
<tr>
<td>P</td>
<td>31.00</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**Table 4.6 Residual content of impurities on the acid leaching process (continuous)**

<table>
<thead>
<tr>
<th></th>
<th>1.25M NaCl /ppm</th>
<th>0.6M NaCl /ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before acid leaching</td>
<td>After acid leaching</td>
</tr>
<tr>
<td>B</td>
<td>24.53</td>
<td>0.40</td>
</tr>
<tr>
<td>Na</td>
<td>94815.28</td>
<td>464.41</td>
</tr>
<tr>
<td>P</td>
<td>10.46</td>
<td>1.52</td>
</tr>
</tbody>
</table>

From the result, sodium-added TMAH solution showed higher efficiency of the acid leaching process. As described the previous section, the precipitation condition was different whether sodium exits or not. In the case of TMAH solution without sodium ion, aggregation of silica was not observed. It would prevent incorporation of solvent dissolving the impurities. But it also induced the filter clogging at the separation. As existence of sodium ion, the growth of particle would occur rather than the aggregation of particle with incorporation of solvent. On the other hand, the amount of sodium was larger when sodium was present.

Comparing the efficiency of the acid leaching among NaOH, TMAH, and sodium-added TMAH solution, the residual boron content was almost same. The result from each experiment previously shown is shown in Table 4.7. Although the boron content before acid leaching process was different, the boron content decreased to be less than 1 ppm after the acid leaching. Since 0.7 M TMAH solution did not
contain sodium and showed comparable efficiency of acid leaching process, the process using TMAH solution would be effective.

**Table 4.7** Residual content of impurities on the various acid leaching process

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Na content / ppm</th>
<th>B content / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before acid leaching</td>
<td>After acid leaching</td>
<td>Before acid leaching</td>
</tr>
<tr>
<td>2.5 M NaOH</td>
<td>$9.8 \times 10^4$</td>
<td>5.9 $\times 10^2$</td>
</tr>
<tr>
<td>0.7 M TMAH</td>
<td>5.3</td>
<td>4.8</td>
</tr>
<tr>
<td>1.4 M TMAH + 1.25 M NaCl</td>
<td>$9.5 \times 10^4$</td>
<td>4.6 $\times 10^2$</td>
</tr>
</tbody>
</table>
4.4 Conclusion

In the present chapter, the influence of the condition of acid leaching process for the production high-purity silica was investigated. XPS revealed the chemical state of boron would be boric acid at the surface of silica and boron could be removed with acid leaching process. In order to develop efficient refining process, efficiency of separation and leaching process of silica was investigated from the viewpoint of precipitation condition.

In the case of alkaline solution, the boron content was decreased to be 0.07 ppm from 6.7 ppm on 2.5 M NaOH solution although the yield of silica was not high due to the precipitation condition. In the case of acidic condition, a friable gel was obtained at the pH 6. The boron content of the gel was decreased with acid leaching process from 37.6 to 1.34 ppm and the yield was 93 %. The residual boron content would be enough to apply next purification process with the solvent extraction, which could reduce the boron content to 0.1 ppm from 1 ppm.

In order to investigate the influence of sodium ion for the incorporation of impurities into silica, TMAH was utilized. The solubility of silica in TMAH solution was not better compared with NaOH solution. In addition, the incorporation of impurities was observed in the case of TMAH solution as well as NaOH solution although the sample did not contain much sodium as impurities. NaCl was added to the TMAH solution as sodium agent for quantitative investigation of the influence of sodium ion. With increasing the concentration of NaCl, the solubility of silica was improved. This result indicated the bulky structure of TMA ion prevent the dissolution of silica. From the viewpoint of residual sodium content and boron content, the optimization of sodium concentration would be effective for efficient purification process with acid leaching process.

From these results, it was indicated that controlling the silica precipitation could improve the efficiency of acid leaching process and that in acidic condition would be effective. In addition, TMAH was also effective to eliminate sodium from refined silica as final step of acid leaching process.
References

Chapter 5

General Conclusion
This thesis has shown a novel approach for the production of high-purity silica toward the alternative source for SOG-Si focusing on the interfacial reactions on solvent extraction with microchannel device and acid leaching process. As an impurity for elimination, boron was selected due to the strong influence for the semiconductor performance and high solute partition coefficient to silicon. In chapter 2 and 3, the application of microchannel device for the elimination of boron was investigated from the fundamental studies such as theoretical calculation and evaluation of the efficiency of microchannel device to practical applications such as optimization of channel design and extractant toward large-scale production. In chapter 4, elimination of boron species with the acid leaching process was investigated toward the total purification process of silica, especially on the influence of sodium ion to the precipitation condition.

As described in chapter 2, boron extraction using microchannel with EHD was demonstrated and showed superior extraction performance, shorter reaction period and lower residual boron content, with both the model solution sample and refined diatomaceous earth. Specifically, for the model sample, residual boron content was less than 1 ppm when the microchannel device was utilized. It was estimated that multistage extraction with sequential microchannels would produce refined silica with less than 0.1 ppm boron content. In addition, A parallel flow, which enables an automatic separation at the outlet toward a sequential purification process, was observed in the case of a microchannel, which had 25 µm height.

In chapter 3, a flow-type device, which have larger liquid-liquid interface with maintaining short diffusion distance comparable to the microchannel, was fabricated in order to increase the throughput of the production. Then, multistage micorchannel device was applied for the boron elimination process showed extraction performance comparable to the microchannel device and better productivity than the microchannel device described in chapter 2. In addition, DFT calculation revealed that the number of carbon neighbors of the central carbon and electron population of B-O-C region were keys for the reactivity of the extractant. Then TMPD was applied instead of EHD and the boron elimination from the preliminary refined diatomaceous earth was improved by the combination of the flow-type device and TMPD to be solar grade level; boron content was less than 0.1 ppm.

In chapter 4, the influence of the condition of acid leaching process, which were conducted as a pre-refining process for the production high-purity silica, was investigated especially focusing on the influence of sodium ion. By adjusting the pH at the precipitation of silica, the yield and efficiency on the acid leaching process was improved and can be applied for the real sample, diatomaceous earth. In addition, TMAH, a sodium free alkaline solvent, was utilized. The solubility of silica in TMAH
solution was not better compared with NaOH solution and the incorporation of impurities was observed in the case of TMAH solution as well as NaOH solution. From the viewpoint of residual sodium content and boron content, the optimization of sodium concentration would be effective for efficient purification process with acid leaching process.

In this thesis, a novel approach for the purification process of silica especially with microchannel device was described. While the main target of impurity in this thesis was boron, the process can be practically applied for other impurities including phosphorus, metals, and/or carbon. In addition, the sequential process, which can eliminate each impurity one by one, can be operated in combination of such microchannel devices. This concept has a potential to produce high-purity silica with one unit of microchannel device with much lower cost than conventional metallurgical process such as Siemens process. The results in this thesis can be also useful for the production of other high-purity source with wet-chemical process and the all processes with microchannel devices toward high-efficiency and large-scale production.
List of Achievements
Original articles


“Elimination of Boron from Soluble Silica via Solvent Extraction with 2,2,4-Trimethyl-1,3-Pentanediol using a Multistage Flow-Type Reactor” Nobufumi Matsuo, Takafumi Ishihara, Takahiro Oyanagi, Kazuki Nakajima, Masahiro Kunimoto, Yasuhiro Fukunaka, Takayuki Homma, *ECS Trans.*, **64**, 91 (2015).

Presentations

International conference
“Solvent Extraction using Microchannel System for High Purification of Silica” 
Nobufumi Matsuo, Yuki Matsui, Yasuhiro Fukunaka, Takayuki Homma, PRiME 2012, 2012.10

Nobufumi Matsuo, Yuki Matsui, Takafumi Ishihara, Yasuhiro Fukunaka, Takayuki Homma, 224th Meeting of the Electrochemical Society (ECS), 2013.10

“Elimination of Incorporated Boron in Silica with Precipitation Control and Solvent Extraction using a Microchannel Device for High-purity Source of Solar-Grade Silicon”,
Nobufumi Matsuo, Yuki Matsui, Takafumi Ishihara, Yasuhiro Fukunaka, Takayuki Homma, International Symposium on Integration of Chemistry and Bioscience, 2014.1

“Elimination of Boron from Silica with Solvent Extraction Using a Multistage Microchannel Device for High-Purity Source for Solar-Grade Silicon”
Nobufumi Matsuo, Yuki Matsui, Takafumi Ishihara, Yasuhiro Fukunaka and Takayuki Homma, The 5th NIMS/MANA-Waseda University International Symposium, 2014.3

“Elimination of Boron from Soluble Silica via Solvent Extraction with 2,2,4-Trimethyl-1,3-Pentanediol using a Multistage Flow-Type Reactor”
Nobufumi Matsuo, Takafumi Ishihara, Takahiro Oyanagi, Kazuki Nakajima, Yasuhiro Fukunaka, Takayuki Homma, 226th Meeting of the Electrochemical Society (ECS), 2014.10

“Elimination of Light Elements from Soluble Silica via Solvent Extraction using Flow-Type Reactor toward High-Purity Source for Solar-Grade Silicon”
Domestic conference
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松井雄希, 松尾伸史, 福中康博, 本間敬之，
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“マイクロ流路を用いた 2-ethyl-hexanediol によるシリカからのホウ素抽出プロセスの検討”，
石原貴史, 松井雄希, 松尾伸史, 福中康博, 本間敬之，
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“流路型デバイスを用いたシリカ中からの軽元素除去プロセスの高効率化”，
松井雄希, 石原貴史, 松尾伸史, 福中康博, 本間敬之，
2013 年電気化学会秋季大会, 2013.9

“流路型デバイスを用いた 2,2,4-Trimethyl-1,3-pentanediol によるシリカからの高効率ホウ素除去の検討”
小柳高宏, 松井雄希, 松尾伸史, 福中康博, 本間敬之
電気化学会第 81 回大会, 2014.3

“高純度シリカ生成に向けた溶液処理による軽元素除去プロセスの検討”
石原貴史, 中嶋一輝, 松尾伸史, 福中康博, 本間敬之，
第 4 回 CSJ 化学フェスタ 2014, 2014.10
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