Extraction of silicon dioxide from waste colored glasses by alkali fusion using potassium hydroxide*

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A process of extraction of SiO_2 from waste colored glasses by alkali fusion using KOH was investigated. In the present study, the waste colored bottles of green, blue, brown or black were selected as sample waste glasses. These colored bottles were qualitatively confirmed to contain the elements of Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe and Cu from energy dispersive X-ray spectroscopic analysis. The condition for alkali fusion of KOH and the waste glasses was optimized, i.e., for each bottle, the composition was KOH:crushed glass bottle = 90:10 wt%, melting temperature was 360°C and melting time was 2 h. For each waste colored bottle, the potassium silicate solution was prepared by using the potassium silicate obtained by alkali fusion. After mixing HCl with the obtained potassium silicate solution, $Si(OH)_4$ was then precipitated by boiling the solution which became to be a very strong acid. After drying the $Si(OH)_4$ separated from the solution, the SiO_2 powder with purity of 99.9% was obtained. The yield of $97.75 \pm 1.05\%$ for the SiO_2 powder extracted from the bottles was confirmed from quantitative analysis, indicating that the bottles selected in the present study contain about 60 wt%SiO_2. From the results of the yield and purity, the established process was found to have a potential applicability as a recycling process of waste glasses. Particularly, for alkali fusion of KOH, the melting temperature of 360°C was lower than those for alkali fusion of NaOH (500°C) and carbonate fusion of Na_2CO_3 (900°C). This suggested that the energy consumption during alkali fusion of KOH and the glasses in an electric furnace was lower than those for the fusions of NaOH and Na_2CO_3. In addition, ideal recycling and reusing processes of waste glasses and the final wastes produced after extracting SiO_2 from the waste glasses were also discussed. For the KCl solution which is obtained after extracting SiO_2, the KCl can be resolved into K and Cl by electrolysis (: $2KCl \rightarrow 2K^+ - 2Cl^-$ and $2K + 2H_2O \rightarrow 2KOH + H_2 \uparrow$) and the HCl can be also prepared by the chemical reaction of the H_2 and Cl_2 (: $H_2 + Cl_2 \rightarrow 2HCl$). These reactions suggested that the KOH and HCl can be reused as the alkali flux and acid solution, respectively. From these results and discussions, the established recycling process of waste glasses was expected that cost reduction would result from selection of KOH as an alkali flux and reuse of the final wastes. © *2003 Kluwer Academic Publishers*

1. Introduction

Recycling and reusing processes for waste glasses, such as cathode-ray tubes (CRTs), beverage and food containers, etc., have been widely studied [1–4]. Among these glasses, the processes for the CRTs were investigated for their thermal, chemical and optical properties, e.g., melting condition of the crushed CRT glasses and the influence of metal oxides (PbO, NiO, Co_3O_4, and Fe_2O_3) in the glasses on the optical property of the CRTs produced by using the glasses [1]. On the other

hand, the recycling process of the beverage containers has been already established. For example, in Japan, the glass bottles of beer, milk and sake (Japanese alcoholic beverage) were collected from consumers and utilized as a recycling bottle after washing the collected bottles, because colors and shapes of the bottles were standardized by Japanese beverage companies. Thus, the percentage of the collection was indicated to be 99% for the bottles of beer, i.e., 418.6×10^3 bottles were used as the bottle of beer and 415.6×10^3 bottles

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were collected from consumers (1997 data) [5]. In addition, for the bottles of milk and sake, their percentages were 97% (the collected bottles/the used bottles = $258.9 \times 10^3/267.5 \times 10^3$) and 89% (the collected bottles/the used bottles = $52.5 \times 10^3/58.8 \times 10^3$), respectively (1997 data) [5].

However, the other waste bottles, like the colored bottles of the imported alcoholic beverages, such as beer, whisky and wine, etc., have been difficult to be utilized as the recycling bottle, because these bottles have a variety of colors and shapes. Hence, these bottles were used as glass cullet after crushing the bottles. In Japan, glass bottles of 182.0×10^4 tons were produced by using the cullet of 141.6×10^4 tons (2000 data) [6], i.e., 77.8% on the components in the bottles was the cullet. In addition, the crushed waste bottles were also utilized as one of materials of road, because these waste bottles do not contain hazardous heavy metal ions, such as Cr, Cd, Pb, etc. Recently, solidification of hazardous heavy metal ions of Cr, Fe, Cu, Zn and Pb with soda-lime glass was investigated [2]. The result obtained from this investigation indicated that the glass was a medium for stable solidification of the hazardous heavy metal ions, suggesting that new reusing process of the waste glasses containing the soda-lime silicate (such as glass bottles, glass wares and window glasses) was established.

For the above waste glasses, it is known that silicon dioxide (SiO_2) is the main component in the glasses, e.g., 60–80 wt%SiO_2 for the colored glass bottles, lamps and laboratory glass wares [4, 7]. Silicon dioxide has been widely utilized as not only the traditional glasses, such as beverage and food containers and window glasses but also advanced glass materials, e.g., glass fibers for optical wave guides, flat CRTs, and optical glasses, which indicates that SiO_2 has been demanded from glass and ceramic industries. From this, it was expected that various utilizations of the waste glasses would result from extraction of SiO_2 from the glasses. With this background, the author has investigated a process of extraction of SiO_2 from waste colored bottles by alkali fusion using NaOH at 500°C [4]. From this investigation, the SiO_2 was extracted from waste colored bottles by this process, and the established process was revealed to have potential applicability as a recycling process of waste glasses. In addition, for this process, the waste bottles were melted by alkali fusion at the temperature which was lower than that for carbonate fusion, e.g., the temperature of Na_2CO_3 is 900°C [8]. This result indicates that the energy consumption (i.e., thermal energy applied by electric power during melting the glasses by alkali fusion using NaOH in an electronic furnace) was lower than that for the carbonate fusion, suggesting that this alkali fusion of NaOH results in cost reduction for the recycling process of waste glasses compared with that for carbonate fusion.

The purpose of the present study was to establish a process of extraction of SiO_2 from waste colored glasses by alkali fusion at the temperature which is lower than that for the alkali fusion of NaOH. In the present study, potassium hydroxide (KOH) was used as an alkali flux, because KOH has the melting point of

360°C. From this, it was expected that silicate glasses would be melted by alkali fusion using KOH at a lower temperature compared with that for the fusion using NaOH (500°C) [4]. The waste bottles of green, blue, brown or black color were selected as sample waste glasses. In addition, to discuss a potential applicability as a recycling process of waste glasses, yield and purity of the extracted SiO_2 were also analyzed.

## 2. Chemical reactions for process of extraction of SiO_2

The process of extraction consists of three chemical reactions. The first is preparation of potassium silicate (K_2SiO_3) by alkali fusion using KOH and the waste bottle containing SiO_2. This chemical reaction during alkali fusion is expressed by

$$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O. \qquad (1)$$
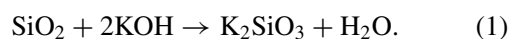
K_2SiO_3 is easily dissolved in water (H_2O) [9]. Thus, the potassium silicate solution can be obtained by mixing the potassium silicate with H_2O. The second is preparation of silicic acid ($Si(OH)_4$), i.e., after mixing hydrochloric acid (HCl) with the potassium silicate solution, $Si(OH)_4$ is precipitated by boiling the solution which became to be a very strong acid. This reaction is expressed by

$$K_2SiO_3 + 2HCl + H_2O \rightarrow Si(OH)_4 \downarrow + 2KCl. \quad (2)$$
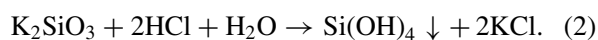
Because $Si(OH)_4$ does not dissolve in a very strong acid solutions, such as HCl, H_2SO_4, and HNO_3 [10], the precipitated $Si(OH)_4$ can be separated from the solution obtained by the above chemical reaction (Equation 2). The third is preparation of SiO_2 by heating the separated $Si(OH)_4$:

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \uparrow. \qquad (3)$$
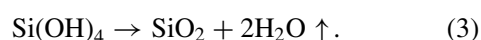
3. Experimental procedure
3.1. Preparation of potassium silicate solution and optimization of condition of alkali fusion

Before melting the waste colored bottles by alkali fusion, the condition of alkali fusion was clarified. Samples of potassium silicate [$(100 - X) SiO_2 \cdot X$ KOH ($X = 65, 80, 85, 88$ and 90 wt%)] were prepared by melting the crushed quartz (SiO_2) which the particle size was within 5 mm and regent grade KOH (purity of 85%, NACALAI TESQUE, INC. Kyoto, Japan). After mixing the crushed quartz and KOH in a nickel crucible with a capacity of 200 ml, a batch (10 g) was melted in the crucible in air in an electric furnace at 360°C which is the melting point of KOH. The melting times were 1, 2 and 3, respectively. After melting the samples of potassium silicate, the samples were then naturally cooled, and the samples were dissolved in H_2O (600 ml) in a beaker (a capacity of 1000 ml). Thus, potassium silicate solutions were obtained. From this preparation of the potassium silicate solutions, the condition of alkali

fusion was optimized by confirming the compositions of the potassium silicates which could completely dissolve in the H_2O.

3.2. Process of extraction of SiO_2 from waste colored bottles

For the waste colored bottles (green, blue, brown or black) selected in the present study, elements in the bottles were qualitatively confirmed by energy dispersive X-ray spectroscopic (EDX) analysis. A flow chart of the process of extraction of SiO_2 from the waste bottles by alkali fusion is shown in Fig. 1. This flow chart consists of five procedures: (1) crush of the bottles, (2) preparation of the potassium silicates by alkali fusion, (3) precipitation of $Si(OH)_4$ by boiling the potassium silicate solutions, (4) separation of $Si(OH)_4$ from the solution and (5) preparation of SiO_2 by heating the $Si(OH)_4$.

For each colored bottle, the crushed glass (5 g) and KOH (45 g) were mixed in the nickel crucible before melting by alkali fusion, i.e., crushed glass:KOH = 10:90 wt%, and a batch (50 g) was melted in air in the electric furnace at $360°C$ for 2 h (the composition and the melting time for the mixtures were optimized from the above experiment in Section 3.1, and the optimization for the condition of alkali fusion will be discussed in Section 4.1). After naturally cooling the mixtures, potassium silicate was prepared for each bottle, and the obtained potassium silicate was then dissolved in H_2O (600 ml). Thus, sample solutions which the potassium silicates dissolved in the H_2O were obtained.

Next, silicic acid ($Si(OH)_4$) was prepared by the chemical reaction (Equation 2) using the obtained sample solution and HCl. Fig. 2 shows a schematic diagram of an apparatus for the chemical reaction. After mixing guaranteed reagent grade HCl (NACALAI
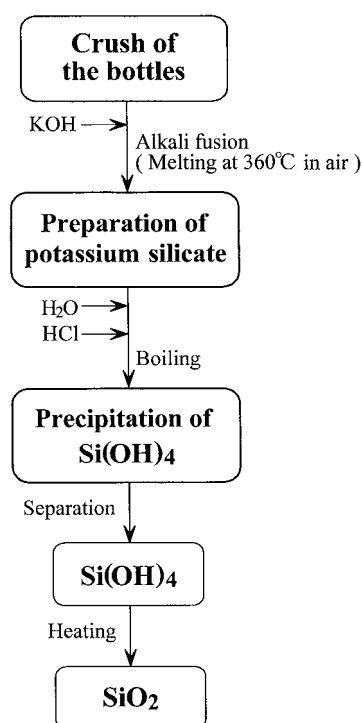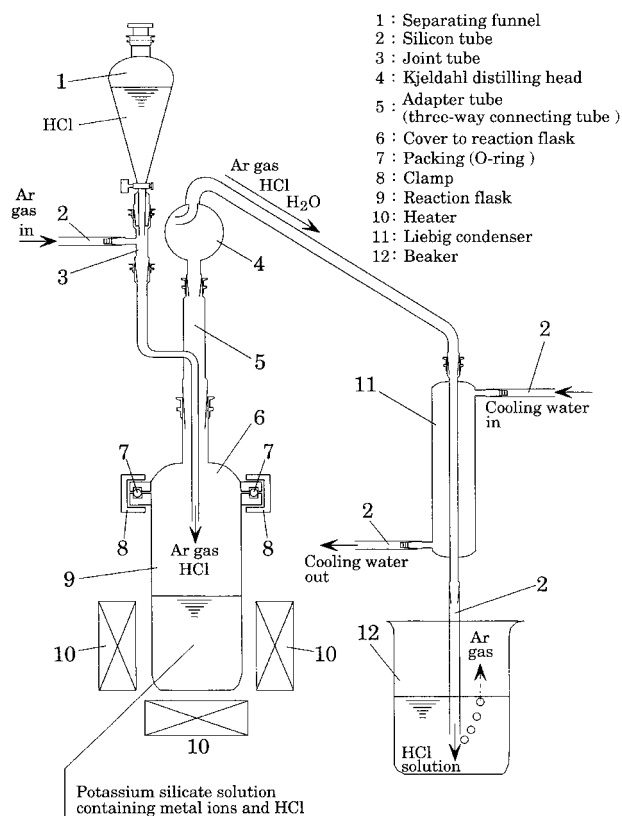
Figure 2 Schematic diagram of experimental apparatus for the chemical reaction $K_2SiO_3 + 2HCl + H_2O \rightarrow Si(OH)_4 \downarrow + 2KCl$ (Equation 2).

TESQUE, INC. Kyoto, Japan) (200 ml) in a separating funnel (1) with the sample solution in a reaction flask (9) with a capacity of 1000 ml, $Si(OH)_4$ was precipitated by boiling using heaters (10). By introducing Ar gas from a joint tube (3), HCl (gas) and H_2O (gas) in the flask were flowed through an adapter tube (5), a Kjeldahl distilling head (4) and a Liebig condenser (11), respectively, and these gases were then collected in a beaker with a capacity of 5000 ml (12) during boiling the solution in the flask. After boiling, the precipitated $Si(OH)_4$ was separated from the solution. Thus, SiO_2 was obtained by heating the separated $Si(OH)_4$ at $300°C$ for 3 h.

4. Results and discussion
4.1. Optimization of condition of alkali fusion

After naturally cooling the samples of potassium silicate $[(100 - X) SiO_2 \cdot X KOH (X = 65, 80, 85, 88$ and 90 wt%)$]$ prepared by alkali fusion at $360°C$, the potassium silicates with carbon powder (C) were obtained. This result was considered that the KOH in the samples absorbed carbon dioxide (CO_2) from the atmosphere in the furnace and the CO_2 was resolved into C and oxygen (O_2) during melting: $CO_2 \rightarrow C + O_2 \uparrow$. Because carbon does not react on H_2O, acid and alkali solutions [11], the C did not dissolve in the potassium silicate solutions obtained by mixing the potassium silicates with H_2O. Thus, the C was separated by filtering from the solutions. In addition, the crushed quartz (SiO_2), which was not completely melted by alkali fusion, was also confirmed by filtering, because the quartz could

Figure 1 Flow chart of the process of extraction of SiO_2 from the waste colored bottles by alkali fusion.
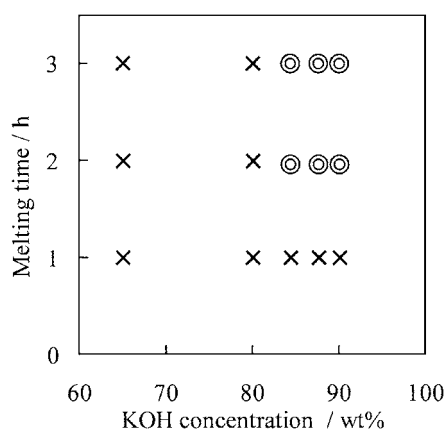
Figure 3 Effects of melting time and KOH concentration on preparation of the potassium silicate solutions. [Potassium silicates were obtained by alkali fusion of $(100 - X)\ SiO_2 \cdot X$ KOH system ($X = 65, 80, 85, 88$ and 90 wt%).]. ◎: potassium silicate was dissolved in water (H_2O). ×: SiO_2 was not completely melted.

not pass through the filter and was obtained together with the C. In this experiment, a glass micro fiber filter (Whatman, England), which can retain particle size of more than 0.7 μm by filtering, was used.

Fig. 3 shows the effects of melting time and KOH concentration on preparation of the potassium silicate solutions. In this figure, ◎ indicates that potassium silicate was dissolved in H_2O. On the other hand, × means that the crushed quartz (SiO_2) was not completely melted. From this result, the condition of alkali fusion of the SiO_2 and KOH was optimized: $SiO_2 \leq 15$ wt%, KOH ≥ 85 wt% and the melting time of more than 2 h was confirmed to be necessary. In the previous report [4], the result of the optimized composition for alkali fusion using NaOH was obtained: $SiO_2 \leq 20$ wt% and KOH ≥ 80 wt%, indicating nearly the same as the result for alkali fusion using KOH. In the present study, the melting temperature for alkali fusion using KOH was 360°C, which indicated that the temperature was lower than those for the fusion of NaOH (500°C) and carbonate fusion of Na_2CO_3 (900°C). This result of the lower temperature suggested that the energy consumption (i.e., the applied thermal energy by electric power during alkali fusion using KOH in the furnace) was lower than those for the fusions of NaOH and Na_2CO_3, which was expected that cost reduction for the recycling process of waste glasses would result from selection of KOH as the alkali flux. From the result of the optimized condition (Fig. 3), the author will discuss extraction of SiO_2 from the colored bottles by alkali fusion using KOH in Section 4.2.

4.2. Extraction of SiO_2 from the colored bottles

For each sample bottle, the color and the measured weights of the crushed glass and KOH are given in Table I (sample no. 1–4). Fig. 4a shows a photograph of one of the sample bottles. This photograph is the blue bottle after crushing (the weight of 5 g was measured for the crushed bottle in the petri dish). From this photograph, the particle size of the glass was confirmed

TABLE I Weights of samples and results of extraction of SiO_2 from the waste colored bottles

Sample no	Color of bottle	Weight (g)		Extracted SiO_2	Purity (%)
		Crushed glass	KOH		
1	Green	5.0484	45.1332	2.9361	99.9
2	Blue	5.0278	45.2750	2.9407	99.9
3	Brown	5.0438	45.1462	3.1370	99.9
4	Black	5.0817	45.0645	3.0028	99.9

to be within 2 mm^1. In addition, the particle sizes of the glasses for the green, brown and black bottles were also within 2 mm, respectively[1]. From energy dispersive X-ray spectroscopic (EDX) analysis, the colored bottles selected in the present study were qualitatively confirmed to contain the elements of Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe and Cu.

After cooling the mixtures (the crushed glass (5 g) and KOH (45 g)) prepared by alkali fusion at 360°C for 2 h (the optimized condition of alkali fusion was clarified in Section 4.1), the potassium silicates with the C powder were obtained. For each sample (no. 1–4), the C did not dissolve in the potassium silicate solution ($>$pH 13.00) prepared by mixing the obtained potassium silicate with H_2O. In addition, metal hydroxides ($Mg(OH)_2$, $Mn(OH)_2$ and $Fe(OH)_3$), which do not dissolve in the solution with high KOH content, were also precipitated. Thus, the C and metal hydroxides were separated by filtering from the solutions (these metal elements (Mg, Mn and Fe) of the hydroxides were confirmed from EDX analysis after separating, which indicates that the metals are the coloring agents in the waste colored bottles). For this separation, the glass fiber filter (Whatman, England) retaining particle size of more than 0.7 μm was used.

Next, using the potassium silicate solutions, the $Si(OH)_4$ was prepared in the reaction flask (Fig. 2). The guaranteed reagent grade HCl was mixed with the solutions, and the solutions which became to be lower than pH 1.00 were then boiled by using the heaters up to 100°C. After boiling, the precipitate of $Si(OH)_4$ and KCl crystal were obtained in the solutions. From this result, it was confirmed that the chemical reaction of precipitation and crystallization obeyed Equation 2. On the other hand, the metals (Na, Al, Ca, Ti and Cu) dissolved in the solution, because the solutions were a very strong acid ($<$pH 1.00). Thus, the precipitated $Si(OH)_4$ and KCl crystal could be separated by filtering from the solutions. For the separation of the precipitate and crystal, the glass fiber filter (Whatman, England), which can retain particle size of more than 2.7 μm, was used. The separated $Si(OH)_4$ and KCl were heated on a hot plate at 100°C, and SiO_2 powder was then obtained, i.e., Equation 3. Because KCl can dissolve in H_2O, the

[1]In the present study, the crushed bottle (5 g) which particle size was larger than 5 mm was not completely melted by alkali fusion using KOH (45 g) at 360°C for 2 h; in this experiment, the crushed glasses, which the maximum particle size was 2 mm and minimum size was 0.1 mm (i.e., 0.1 mm $\leq$ particle size $\leq$ 2 mm), were selected as the sample for each bottle. The particle sizes were measured by using a micrometer.
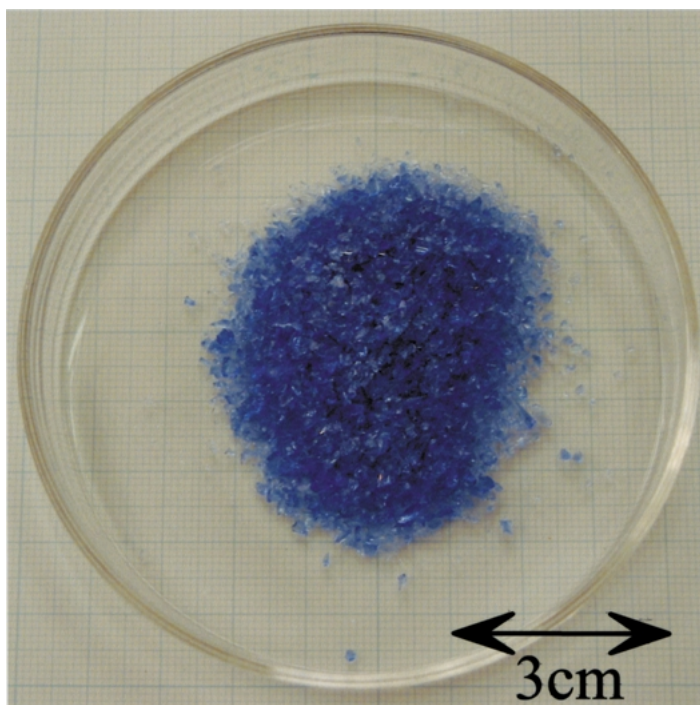
(a)
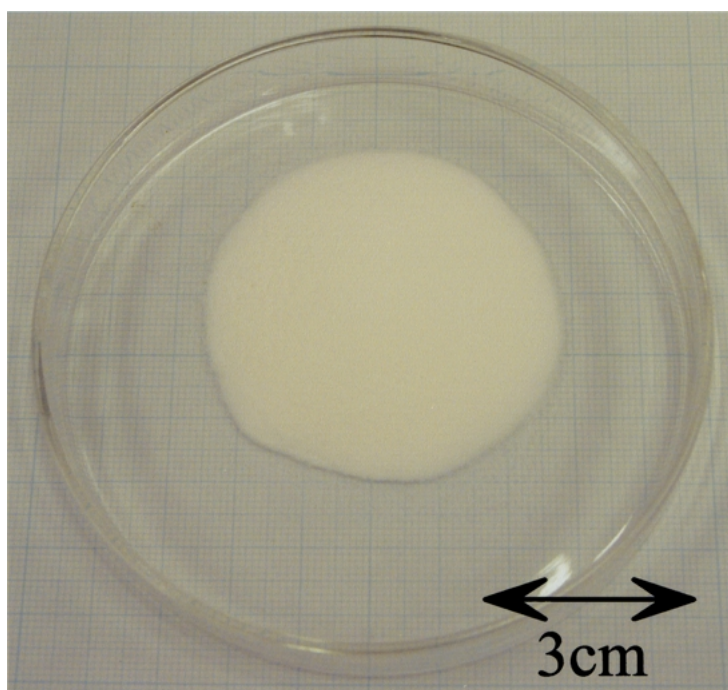
(b)

Figure 4 (a) Photograph of the crushed blue bottle before melting by alkali fusion. (The weight of 5 g was measured for the crushed bottle in this petri dish. The particle size of the crushed bottle is within 2 mm.) (b) Photograph of the SiO_2 powder extracted from the crushed blue bottle. (The weight of about 3 g was measured for the extracted SiO_2.)

SiO_2 powder was separated from the KCl solution after mixing H_2O with the SiO_2 and KCl. In addition, the SiO_2 powder was dried at 300°C for 3 h in air in the furnace after rinsing the separated SiO_2 powder using the HCl and H_2O. From this process, the dried SiO_2 powder was obtained. The weights of the SiO_2 for the samples (no. 1–4) were measured, and the results are given in Table I. The weight of the SiO_2 was about 3 g for each sample. Fig. 4b shows a photograph of one of results after extracting SiO_2 from the bottles. This photograph is the result of the sample of the crushed blue bottle (sample no. 2). From this photograph, it was confirmed that the SiO_2 powder with color of white was extracted from the blue bottle (5 g). In addition, the purity of the SiO_2 was also analyzed by the following chemical reaction using hydrofluoric acid (HF) [12].

$$SiO_2 + 4HF \rightarrow SiF_4 \uparrow + 2H_2O. \qquad (4)$$
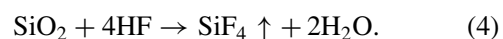
The results of the purity are also given in Table I. From the analysis, the extracted SiO_2 (about 3 g) was confirmed to be purity of 99.9% for all these samples,

similar to the previous result of the purity and weight for the SiO₂ extracted from the same bottles by alkali fusion using NaOH [4].

4.3. Yield of SiO₂ and potential applicability of recycling process

The yield of the SiO_2 extracted from the colored bottles is discussed. In order to confirm the yield, sample solutions were prepared by considering the result of EDX analysis using raw materials (SiO_2, Al, $CaCO_3$, Fe_2O_3, MnO_2 and KOH)[2], i.e., for each sample, the HCl solution (200 ml) containing Al, Ca, Fe and Mn ions was mixed with potassium silicate solution (600 ml). The potassium silicate solutions were prepared by mixing the potassium silicates (obtained by alkali fusion of 10 wt%SiO_2 and 90 wt%KOH at 360°C for 2 h in air in the furnace) with H_2O. The composition of materials (SiO_2:Al:$CaCO_3$:Fe_2O_3:MnO_2) was 70:10:10:5:5 (wt%) for each sample. The measured weights of each material are given in Table II. The mixed solutions (pH 0.50 ± 0.40) were boiled in the reaction flask (Fig. 2), and the precipitate of $Si(OH)_4$ and KCl crystal were then obtained. Thus, the SiO_2 was prepared by the same process of extraction (Fig. 1) using the $Si(OH)_4$ separated from the solutions.

Fig. 5 shows the relationship between the amounts of SiO_2 in the solutions and the extracted SiO_2. The solid line in this figure is the theoretical value. For example, this line indicates that the SiO_2 of 7 g should

TABLE II Weights of raw materials

Sample no	Weight (g)					
	SiO₂	Al	CaCO₃	Fe₂O₃	MnO₂	KOH
5	4.0190	0.5717	0.5718	0.2857	0.2855	36.1166
6	6.0179	0.8572	0.8570	0.4295	0.4289	54.0645
7	7.0145	1.0700	1.0798	0.5024	0.5009	63.0045

For each sample, the compositions are SiO_2:Al:$CaCO_3$:Fe_2O_3:MnO_2 = 70:10:10:5:5 (wt%) and SiO_2:KOH = 10:90 (wt%), respectively.
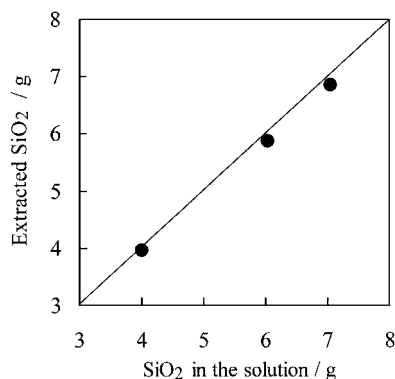

Figure 5 Relationship between the amounts of SiO_2 in the solutions and the extracted SiO_2. The solid line is the theoretical value.

[2]The raw materials produced by NACALAI TESQUE, INC. were used in this experiment. For each material, grade and purity are indicated as follows: reagent grade SiO_2 (guaranteed reagent), reagent grade Al (purity of 99.9%), reagent grade $CaCO_3$ (purity of 99.5%), reagent grade Fe_2O_3 (for chemical experiment), and reagent grade MnO_2 (purity of 99%).

TABLE III Weight of the extracted SiO₂ and results of yield and purity for the SiO₂

Sample no	Weight (g) Extracted SiO₂	Yield (%)	Purity (%)
5	3.8863	96.7	99.9
6	5.8805	97.7	99.8
7	6.9296	98.8	99.9

be extracted from the sample solution dissolving the SiO_2 of 7 g. For all these samples (no. 5–7), the experimental plots and the theoretical values in Fig. 5 agree satisfactorily. The measured weights of the extracted SiO_2 and the yields are also given in Table III. In addition, the results of yields were $97.75 \pm 1.05\%$ for the samples (no. 5–7), confirming again good agreements between the amounts of SiO_2 in the solutions and the extracted SiO_2. From these results obtained in the present study, the bottles were concluded to contain about 60 wt% SiO_2, because: for each waste glass bottle (sample no. 1–4),

$$\frac{\text{The extracted } SiO_2 \text{ (about 3 g and purity of 99.9\%)}}{\text{The crushed glass (5 g)}}$$

$$\times 100 \fallingdotseq 60 \, (\text{wt\%}).$$

In addition, for the extracted SiO_2, the purity was also analyzed by using the chemical reaction (Equation 4). The results were $99.85 \pm 0.05\%$ as given in Table III. From the above discussions on the yield and purity of the extracted SiO_2, the process established in the present study was found to have a potential applicability as a recycling process of waste glasses.

Next, the author discuss ideal recycling and reusing processes for waste glasses based on the established process of the waste colored bottles. Fig. 6 shows ideal recycling and reusing processes of waste glasses. In this figure, the area of gray color indicates the process established in the present study (this process was represented based on the results of the yield and purity). For the KCl solution which is obtained after separating $Si(OH)_4$ and metals, such as Al, Ca, Fe, and Mn, etc., the KCl can be resolved into K and Cl by electrolysis,
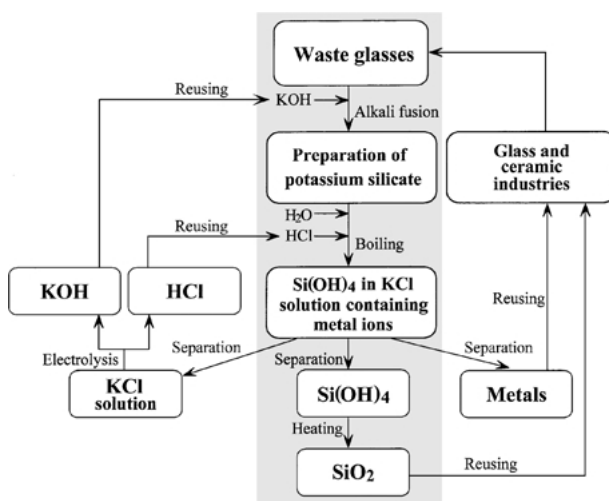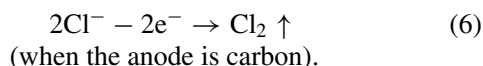

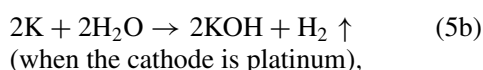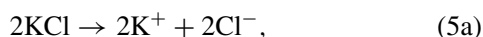*Figure 6* Ideal recycling and reusing processes of waste glasses.

and KOH solution is then obtained. These chemical reactions express as follows:

$$2KCl \rightarrow 2K^+ + 2Cl^-, \tag{5a}$$

$$2K + 2H_2O \rightarrow 2KOH + H_2 \uparrow \tag{5b}$$
(when the cathode is platinum),

$$2KOH \rightarrow 2K^+ + 2OH^-, \tag{5c}$$

$$2Cl^- - 2e^- \rightarrow Cl_2 \uparrow \tag{6}$$
(when the anode is carbon).

Thus, the KOH can be reused as the alkali flux after evaporating the H_2O in the KOH solution. HCl can be also prepared by the following chemical reaction of the H_2 and Cl_2:

$$H_2 + Cl_2 \rightarrow 2HCl. \tag{7}$$

The HCl can be reused as the acid solution, when the HCl is mixed with the potassium silicate obtained by alkali fusion.

In addition, the metals of Al, Ca, Fe, and Mn, etc., in the final waste solution (i.e., the KCl solution containing metal ions) can be also reused as a metal in a glass or ceramic material after separating the metal ions from the solution by redox reactions or electrolysis. For example, the atomic composition analyzed by EDX for the brown bottle was confirmed and each concentration was 21.2 at%Si, 7.58 at%Na, 1.48 at%Mg, 1.09 at%Al, 2.76 at%Ca, 0.04 at%Mn, 0.24 at%Fe and 65.6 at%O; the weight percentage was 29.6 wt%Si[3], 8.67 wt%Na, 1.79 wt%Mg, 1.46 wt%Al, 5.50 wt%Ca, 0.10 wt%Mn, 0.67 wt%Fe and 52.2 wt%O (see Appendix). This result suggests that the metals of 0.10–5.50 wt% can be extracted by the ideal recycling and reusing processes. Particularly, it is expected that Mn and Fe will be reused as coloring agents in glasses or ceramics and Mg, Al and Ca will be also utilized as components of a transparent glass (e.g., SiO_2-MgO-Al_2O_3-CaO system), such as window glass, beverage and food containers, etc. This indicates that the reuse of the final waste produced by the processes in Fig. 6 contributes the cost reduction for the recycling process for waste glasses. Thus, the author shall investigate experimentally these recycling and reusing processes (Fig. 6) elsewhere in the near future.

5. Conclusion

The process of extraction of SiO_2 from waste colored bottles (green, blue, brown or black) by alkali fusion using KOH was investigated. The colored bottles selected in the present study were qualitatively confirmed to contain the elements of Na, Mg, Al, Si, K,

Ca, Ti, Mn, Fe and Cu from energy dispersive X-ray spectroscopic analysis.

The optimized condition for alkali fusion of KOH and the bottles containing the above elements was clarified, i.e., for each bottle, the composition was KOH:crushed glass bottle = 90:10 wt%, melting temperature was 360°C and melting time was 2 h. This melting temperature of 360°C was lower than those for alkali fusion of NaOH (500°C) and carbonate fusion of Na_2CO_3 (900°C), suggesting that the energy consumption during alkali fusion of KOH and the glasses in an electric furnace was lower than those for the fusions of NaOH and Na_2CO_3. From this, it was expected that cost reduction for the recycling process of the waste glasses would result from selection of KOH as the alkali flux, compared with those for the processes using NaOH and Na_2CO_3.

For the waste colored bottles, the potassium silicate solutions were prepared by using the potassium silicates obtained by alkali fusion of the KOH and the crushed bottles. The prepared potassium silicate solutions which became to be lower than pH 1.00 were boiled after mixing HCl with the solutions, and the precipitates of $Si(OH)_4$ were then obtained. After drying the precipitates separated from the solutions by filtering, the SiO_2 powder with purity of 99.9% was extracted. The yield of the extracted SiO_2 was confirmed to be $97.75 \pm 1.05\%$ from quantitative analysis, indicating that the bottles contain about 60 wt%SiO_2. From the results of the yield and purity of the extracted SiO_2, the process established in the present study was found to have a potential applicability as a recycling process of waste glasses; various utilizations of the waste glasses were expected by extracting SiO_2 which is the main component in the glasses.

In addition, throughout the discussion on the ideal recycling and reusing processes of waste glasses, it was also expected that all final wastes (the KCl solution containing metal ions, such as Al, Ca, Fe and Mn, etc.) produced after extracting SiO_2 from the waste glasses would be reused by redox reactions or electrolysis as the recyclable materials, i.e., the alkali flux (KOH), the acid solution (HCl), and coloring agents in glasses or ceramics. Thus, the author shall investigate experimentally the processes elsewhere in the near future.

Appendix

The atomic composition of the brown bottle (sample no. 3) was confirmed from EDX analysis. Each atomic concentration in the bottle was 21.2 at%Si, 7.58 at%Na, 1.48 at%Mg, 1.09 at%Al, 2.76 at%Ca, 0.04 at%Mn, 0.24 at%Fe and 65.6 at%O, respectively. Based on this result, the weight percentage of the bottle was determined by the following equations.

$$
\begin{aligned}
Si_{weight} &= \text{atomic weight of Si} \\
&\quad \times \text{atomic concentration of Si} \\
&= 28.0855 \, (g) \times 21.2 \, (at\%) \\
&= 594.57 \, (g),
\end{aligned}
$$

where Si_{weight} is the weight of Si,

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[3]From the weight concentration of Si (29.6 wt%), good agreements between the weights of Si for the EDX-analyzed value and the experimental data re-confirmed, because the analyzed value (29.6 wt%) indicated that Si of 1.48 g should be obtained from the sample of 5 g (i.e., 1.48 g/5 g × 100 = 29.6 wt%) and the extracted SiO_2 of sample no. 3 (the brown bottle) contains Si of 1.4650 g (=3.137 g × 0.467, and 0.467 = atomic weight of Si/molecular weight of SiO_2 = 28.0855/60.0843; SiO_2 contains 46.7 wt%Si) which is the same weight determined from EDX analysis (1.48 g).

$$\mathrm{Na_{weight}} = \text{atomic weight of Na}$$
$$\times \text{atomic concentration of Na}$$
$$= 22.98977\,(\mathrm{g}) \times 7.58\,(\mathrm{at\%})$$
$$= 174.26\,(\mathrm{g}),$$

where $\mathrm{Na_{weight}}$ is the weight of Na,

$$\mathrm{Mg_{weight}} = \text{atomic weight of Mg}$$
$$\times \text{atomic concentration of Mg}$$
$$= 24.3050\,(\mathrm{g}) \times 1.48\,(\mathrm{at\%})$$
$$= 35.971\,(\mathrm{g}),$$

where $\mathrm{Mg_{weight}}$ is the weight of Mg,

$$\mathrm{Al_{weight}} = \text{atomic weight of Al}$$
$$\times \text{atomic concentration of Al}$$
$$= 26.98154\,(\mathrm{g}) \times 1.09\,(\mathrm{at\%})$$
$$= 29.410\,(\mathrm{g}),$$

where $\mathrm{Al_{weight}}$ is the weight of Al,

$$\mathrm{Ca_{weight}} = \text{atomic weight of Ca}$$
$$\times \text{atomic concentration of Ca}$$
$$= 40.08\,(\mathrm{g}) \times 2.76\,(\mathrm{at\%})$$
$$= 110.62\,(\mathrm{g}),$$

where $\mathrm{Ca_{weight}}$ is the weight of Ca,

$$\mathrm{Mn_{weight}} = \text{atomic weight of Mn}$$
$$\times \text{atomic concentration of Mn}$$
$$= 54.93805\,(\mathrm{g}) \times 0.04\,(\mathrm{at\%})$$
$$= 2.1975\,(\mathrm{g}),$$

where $\mathrm{Mn_{weight}}$ is the weight of Mn,

$$\mathrm{Fe_{weight}} = \text{atomic weight of Fe}$$
$$\times \text{atomic concentration of Fe}$$
$$= 55.847\,(\mathrm{g}) \times 0.24\,(\mathrm{at\%})$$
$$= 13.403\,(\mathrm{g}),$$

where $\mathrm{Fe_{weight}}$ is the weight of Fe, and

$$\mathrm{O_{weight}} = \text{atomic weight of O}$$
$$\times \text{atomic concentration of O}$$
$$= 15.9994\,(\mathrm{g}) \times 65.6\,(\mathrm{at\%})$$
$$= 1050.0\,(\mathrm{g}),$$

where $\mathrm{O_{weight}}$ is the weight of O.

$$\text{The total weight} = \mathrm{Si_{weight}} + \mathrm{Na_{weight}} + \mathrm{Mg_{weight}}$$
$$+ \mathrm{Al_{weight}} + \mathrm{Ca_{weight}} + \mathrm{Mn_{weight}}$$
$$+ \mathrm{Fe_{weight}} + \mathrm{O_{weight}}$$
$$= 2010.5\,(\mathrm{g}).$$

Thus, each weight concentration of the bottle was obtained as follows:

$$\mathrm{Si} = \mathrm{Si_{weight}}/\text{the total weight} \times 100 = 29.6\,(\mathrm{wt\%}),$$
$$\mathrm{Na} = \mathrm{Na_{weight}}/\text{the total weight} \times 100 = 8.67\,(\mathrm{wt\%}),$$
$$\mathrm{Mg} = \mathrm{Mg_{weight}}/\text{the total weight} \times 100 = 1.79\,(\mathrm{wt\%}),$$
$$\mathrm{Al} = \mathrm{Al_{weight}}/\text{the total weight} \times 100 = 1.46\,(\mathrm{wt\%}),$$
$$\mathrm{Ca} = \mathrm{Ca_{weight}}/\text{the total weight} \times 100 = 5.50\,(\mathrm{wt\%}),$$
$$\mathrm{Mn} = \mathrm{Mn_{weight}}/\text{the total weight} \times 100 = 0.10\,(\mathrm{wt\%}),$$
$$\mathrm{Fe} = \mathrm{Fe_{weight}}/\text{the total weight} \times 100 = 0.67\,(\mathrm{wt\%}),$$
$$\mathrm{O} = \mathrm{O_{weight}}/\text{the total weight} \times 100 = 52.2\,(\mathrm{wt\%}).$$

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