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MODIFICATION OF JAPANESE NATURAL DIATOMITE TO SUPPLY SILICA INTO ALKALI SOLUTION USING THERMAL TREATMENT AND ACID LEACHING

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ABSTRACT

Diatomite has different properties depending on the origin of the deposit and the collection site. In order to obtain a material suitable for silica supply, modification of diatomite using acid leaching after thermal treatment was investigated. Four types of diatomite, white and gray from deposits of marine origin in Takanosu, and white and yellow from lacustrine deposits in Shonai, were used. The samples were calcined at 300–1100 °C for 24 h, and then stirred in 5 M HCl solution at 80°C for 1 h. There are not notable changes of amorphous phase in diatomite at 300–900°C, while amorphous silica was transformed into cristobalite, which was low solubility in basic solution, after calcining at 1100°C. The removal of Al via acid leaching was the highest at 500–700°C, while those of Fe, Mg and Ca were almost constant at 300–900°C. The removal of Al from lacustrine diatomite was higher than that from marine one. Diatomites via acid leaching after calcination at 700°C contains higher Si and lower impurities than raw diatomite, and have the almost same solubility of silica into alkali solution.

Key words: Diatomite, Amorphous silica, Acid leaching, Calcination, Silica supply

INTRODUCTION

Diatomite is a fine-grained, biogenic, and siliceous sediment, and is available in large quantities at low cost (Kamigasa and Kato, 2000). Diatomite is an attractive and adequate material that offers a useful application in industry, owing to its unique properties of low bulk density, high porosity with strong adsorbability, chemically inert in most liquids, and gases and thermal resistance (Fukumizu et al., 2005; Martinovic et al., 2006; Rutherford and Coons, 2007). Diatomite is of sedimentary origin consisting of mainly an accumulation of the skeletons formed as a protective covering of the diatoms. The skeletons are essentially amorphous hydrated or opaline silica to easily dissolve in basic solutions. It is an important source of silica, with great potential for use as silica supplier, for example, in the synthesis of zeolites. Many researchers reported for the synthesis of zeolite from diatomite or the mixture of diatomite and ashes (Sanhueza et al., 2003, 2004; Chaisena and Rangsriwatananon, 2005; Jing et al., 2007; Wajima et al., 2006, 2008). However, sometimes the deposits consist of diatom shells only, but usually diatomite contains other sediments such as clay and fine sand. The properties of diatomite differ depending on the origin of the deposit and the collection site. It is necessary for stable utilization to design pre-treatment of diatomite for using various types of diatomite as silica supplier.

There are several patents and publications about the beneficiation and purification of diatomaceous earth (Kouloheris, 1971; Feinblum, 1994; Shiuh et al., 1997; Iosef, 1995), and one of the effective methods for beneficiation is the combination of thermal activation and acid leaching. The purification of Turkish diatomite was examined by way of the calcination at 600°C and leaching using hydrochloric acid (Remzi et al, 2002). Modification of Lampang diatomite, which was leached by sulfuric acid after the calcination at high temperature (900–1100°C) was investigated to synthesize zeolite (Rangsriwatananon et al., 2008). Littlie information can be available, however, on pre-treatment of Japanese natural diatomite using the combination of thermal activation and acid treatment.

The aim of this study was to develop the treatment of diatomite for stable utilization as silica supplier. The effect of the thermal activation on characteristic futures, mineralogi-

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cal structure, impurities leached into acid solution, and the solubility of silica into alkali solution were investigated, and modification of Japanese natural diatomite using calcination-acid leaching process was done to use as silica supplier.

EXPERIMENTAL

Diatomite

Diatomite naturally occurs in two types of geological environment, the marine and lacustrine. The samples used in this study were obtained from deposits located in Takanosu, Akita Prefecture, and in Shonai, Oita Prefecture, Japan. Takanosu and Shonai deposits were of marine and lacustrine origin, respectively. Samples collected from different sites in the same deposit differed in color. Four types of diatomite were used: white (T-W) and gray (T-G) from Takanosu, and white (S-W) and yellow (S-Y) from Shonai. The diatomite was ground to a size smaller than 30 mesh and dried at 60°C. The chemical composition of the dried samples as determined by a scanning electron microscope (SEM, S-2600H, Hitachi) equipped with an energy-dispersive X-ray spectrometer (EDS, E-MAX energy EX-200, Horiba) is shown in Table 1. The composition of the impurities in diatomite differed among four samples, but all samples have high Si content to use as silica source, and some minor elements, such as Al and Fe, to remove through the treatment.

TABLE 1. Chemical compositions of diatomites.

	T-W	T-G	S-W	S-Y
Si	372	366	327	327
Al	27	17	21	34
Fe	11	12	6	11
Ca	2	2	2	5
Mg	3	3	1	1
K	4	4	1	2
Na	3	4	3	4
S	N.D.	2	N.D.	N.D.

N.D.: Not detected (mg/g)

Calcination and acid leaching

The natural diatomite was submitted to calcination at 300−1100°C to give the calcined diatomite. Calcination was carried out under an air atmosphere in a programmable furnace, with 1 h heating time from room temperature to the calcination temperature, and the samples were left in the furnace for 24 h at the calcination temperature. These solids were kept for characterization and one part of them was submitted to acid leaching. Five grams of the calcined samples were added into 25 mL of 5 M HCl solution, and stirred at 80°C for 1 h. After stirring, the suspension was filtered, and the residue was washed with distilled water, then dried at 110°C in a drying oven overnight. Raw diatomite, calcined diatomite, and calcined diatomite via acid leaching were characterized by powder X-ray diffraction (XRD, Rint-2200U/PC-LH, Rigaku), and calcined diatomites were analyzed by fourier transform infrared spectrometer (FT-IR, FTS-155, BIO-LAB Laboratories). The concentrations of Si, Al, Fe, Mg, and Ca in the filtrate were determined by an inductively coupled plasma method (ICP, SPS4000, SEIKO).

Solubility of Si from calcined diatomite

T-W, T-G, S-W and S-Y were used to investigate the effect of calcination temperature on solubility of Si into alkali solution. Five grams of diatomite calcined at various temperatures was added to 25 mL of 2.5 M NaOH solution, and stirred at 80°C for 1 h. After stirring, the suspension was filtered, and the residue was washed with distilled water, then dried at 110 °C in a drying oven overnight. These solids were characterized by XRD, and the concentrations of Si in the filtrate were determined by ICP.

Supply of Si into alkali solution

T-W and S-W were treated through the calcination-leaching process, and the extractions of Si into alkali solution from raw and treated diatomites were determined. The calcination-leaching process is that raw diatomites were leached by 5 M HCl at 80°C for 1 h after calcination at 700°C. Raw or treated diatomites (2.5 g) were added into 100 mL of 3 M NaOH solution, and stirred at 80°C for 90 min. During stirring, the aliquots were filtered, and the Si concentration in the filtrate was determined by ICP. Chemical compositions of T-W, S-W, treated T-W and treated S-W were analyzed by X-ray fluorescent spectrometry (XRF, ZSX101e, Rigaku).

RESULTS AND DISCUSSION

Calcination

Results for XRD and FT-IR were almost same among four types of diatomites used in this study. The typical X-ray diffraction patterns and FT-IR spectra of raw and the calcined diatomite samples (T-G) are shown in Fig. 1 and 2, respectively. The XRD patterns of raw diatomite indicate amorphous broad peak (20−40°) and the peaks of quartz as impurity, and those of calcined diatomite at 300−900°C are almost similar to that of raw diatomite, while new strong peaks, corresponded to crystals of cristobalite (Farmer, 1974), are appeared in the calcined diatomite at 1100°C. These spectra confirmed that the calcination at any conditions in this experiment produced dehydroxylation in the diatomite samples (Farmer, 1974). The bands at 3436, 3698 and 3621 cm^{-1} were assigned to OH stretching vibration, and a weak additional band, assigned to the H-O-H bending vibration mode of H_2O adsorbed molecules, can be seen at 1623−1635 cm^{-1}. These bands were eliminated in all samples with increasing the calcination temperature, and were not observable even after being calcined over 700°C. The bands at 798 cm^{-1} and 1099 cm^{-1} indicate Si-O-Si bending vibration and stretching vibration, respectively, and almost similar spectra were observable after calcination below 900°C. The appearance of a new band at 1095, 795, and 623 cm^{-1} when calcination at 1100°C showed the typical of cristobalite, which are in good accordance with XRD patterns as shown in Fig. 1.

The solubility of Si from raw and the calcined diatomites into alkali solution is shown in Fig. 3. The solubility of Si from raw and the calcined diatomites below 900°C was almost constant, while that from the calcined diatomites at 1100°C was low. The low solubility may result from the transforma-

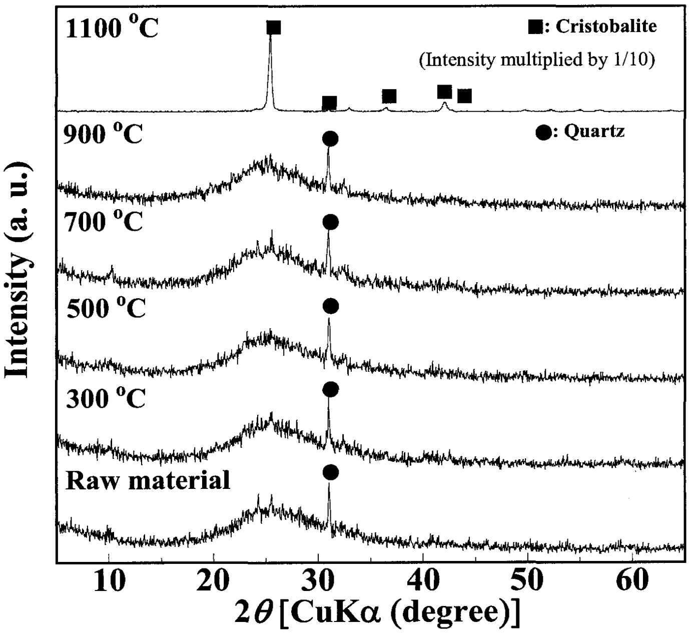

FIG. 1. Typical XRD patterns of raw and the calcined diatomites (T-G).

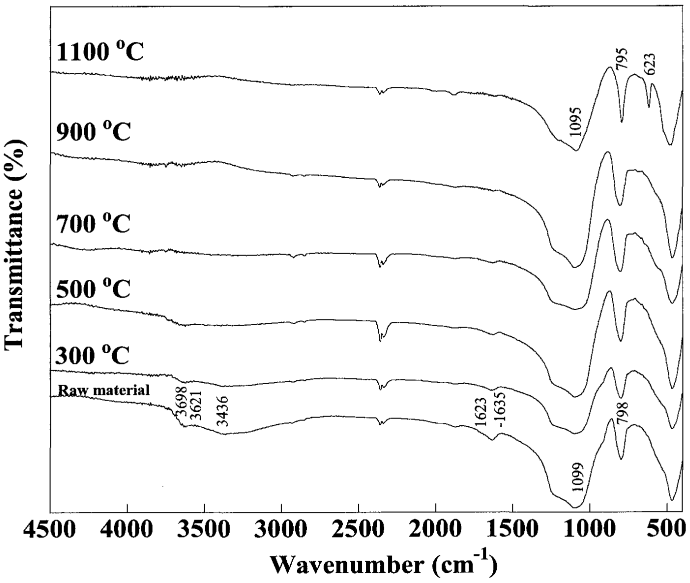

FIG. 2. Typical FT-IR spectra of raw and the calcined diatomites (T-G).

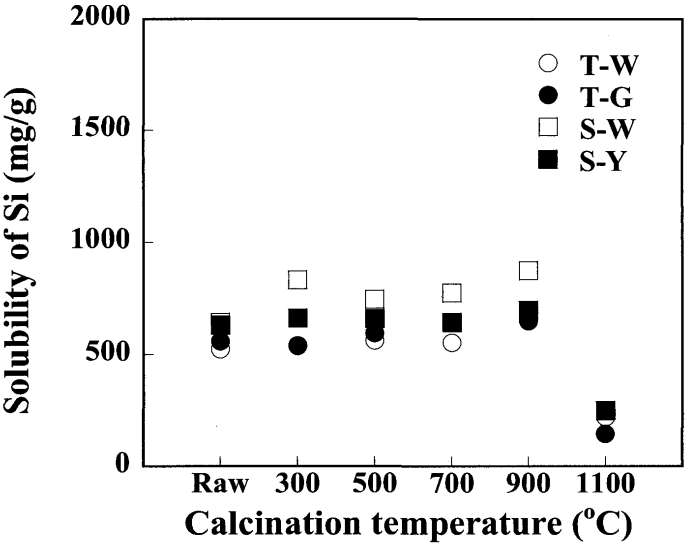

FIG. 3. The solubility of silica from raw and the calcined diatomite into alkali solution.

tion of high reactive amorphous silica into low reactive cristobalite crystal after calcination at 1100°C.

From these results, solubility of diatomite was almost constant after calcination below 900°C.

Acid leaching

The amounts of elements leached from calcined diatomite are shown in Fig. 4. The percentages of leached elements were calculated by each element contents leached into the solution after leaching compared to their original contents in raw diatomite as shown in Table 1. Little amount of silica can be leached from all samples, because of high stability of silica to acid solution. Almost impurities, such as Al, Fe, Mg and Ca, in raw diatomite can be leached through the calcination-leaching process. The trend in the extents of leached Fe, Mg and Ca is similar, except for leached Al. The extents of leached Fe, Mg and Ca are almost constant below 700–900°C, and decrease at 900–1100°C. On the other hand, the extent of leached Al increases at 500–700°C, and decreases above 900 °C. In the range of 500–700°C, the extents of Al leached from lacustrine diatomites (S-W and S-Y) indicated more highly than those from marine diatomites (T-W and T-G). Diatomite samples composed of opaline silica and surrounding rocks, such as sand and clay. Typical clay minerals in diatomite would be kaolinite, aluminium hydroxide, ferric hydroxide, calcite and dolomite. Although aluminium hydroxide, ferric hydroxide, calcite and dolomite could easily dissolve in hydrochloric acid after calcination at 300–1100°C, the solubility of kaolinite is changeable at calcination temperature. Kaolinite is transformed into metakaolin at > 500°C, and the solubility increases. When kaolinite is heated to higher temperatures (> 900°C) new crystalline phases develop to react with Fe, Mg and Ca. Hence the solubility of the Al, Fe, Mg and Ca decreases. Therefore, the maximum extents of leached elements can be obtained from calcined diatomite at 700°C.

The typical X-ray diffraction patterns of raw and the calcined diatomite samples (T-G) after acid leaching are shown in Fig. 5. The XRD patterns of calcined diatomite after acid leaching are almost similar to those of calcined diatomite, as shown in Fig. 1, and impurities, such as kaolinite etc., could not detected by XRD due to the minor. This suggests that the acid leaching does not change amorphous phases in diatomite and quartz.

From these results, the process of impurities removal for using silica supplier is that diatomite was calcined at 700°C, and then treated with HCl.

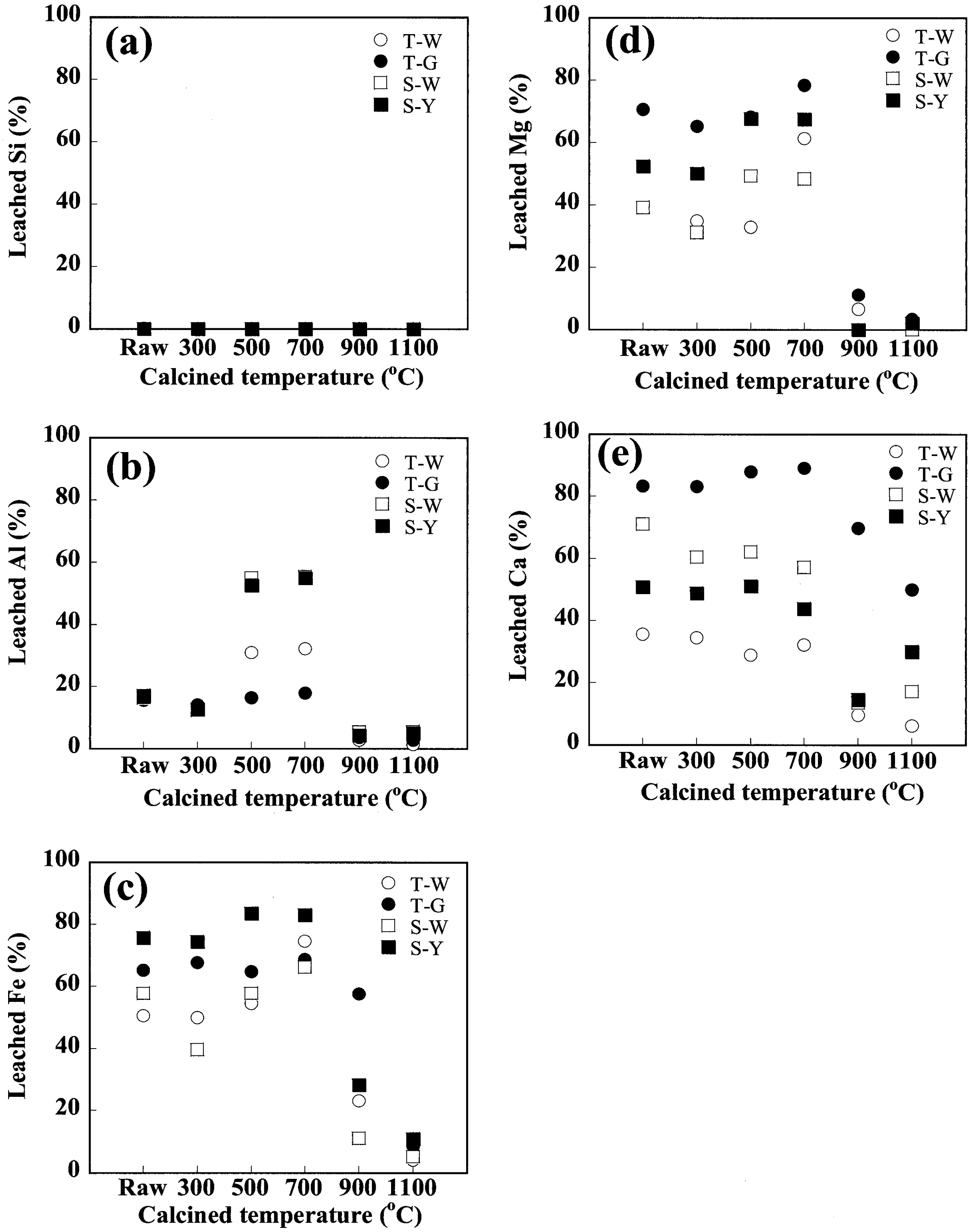

FIG. 4. The leached contents of (a) Si, (b) Al, (c) Fe, (d) Mg, (e) Ca into leachant from calcined diatomite via acid leaching compared to their original content in raw diatomites.

Supply of Si into alkali solution

The suggested process was applied to T-W and S-W, and the extracted amounts of Si from raw and treated diatomites are examined. The result for extraction of Si was shown in Fig. 6. The extractions of Si from all samples are saturated after heating of 45–60 min. In the case of raw diatomite, the extraction of Si from T-W was lower than that from S-W. After the treatment, the extraction of Si from treated T-W increases, and tendency of extraction of Si from treated T-W is similar to that from S-W and treated S-W. Chemical compositions of T-W, S-W, treated T-W and treated S-W were shown in Table 2. Treated samples are higher SiO_2 contents and lower impuri-

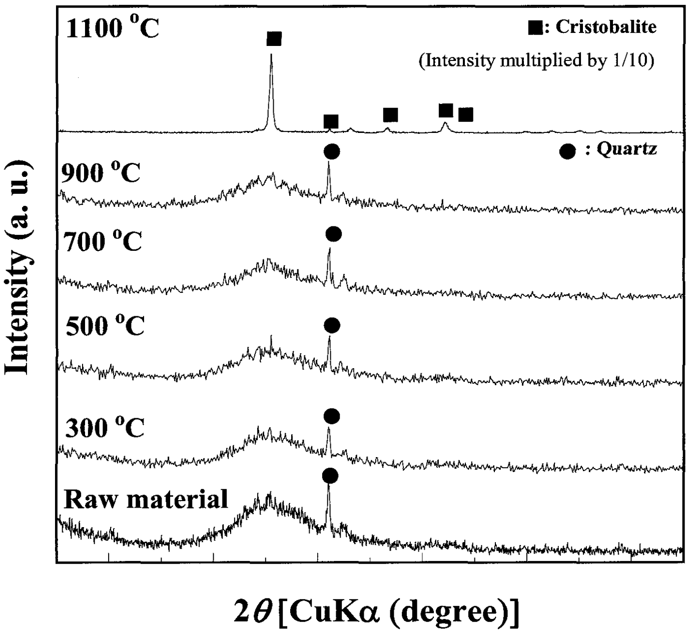

Fig. 5. Typical XRD patterns of raw and the calcined diatomites after leaching (T-G).

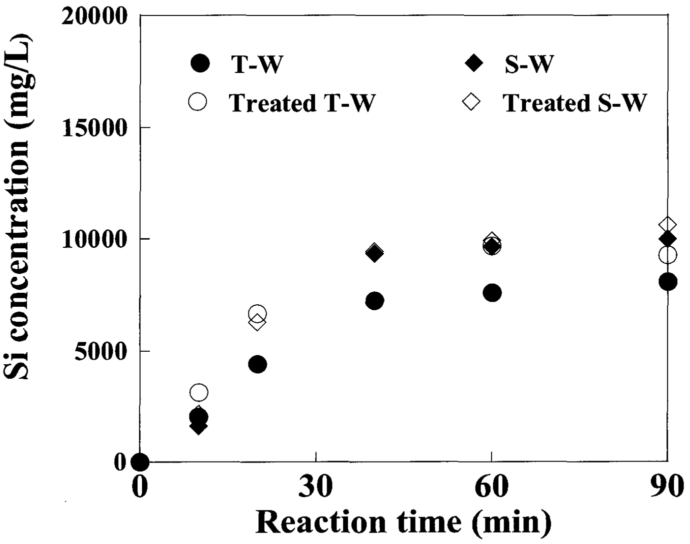

Fig. 6. The extraction of Si from raw and treated diatomite into alkali solution.

ties than raw diatomites. It is considered that diatomite treated through the suggested process could supply high Si content stably into alkali solution.

CONCLUSION

The type of silica presented in natural diatomite is amorphous silica and a small amount of quartz. When the natural diatomite was calcined with different temperatures in the range of 300–1100°C, amorphous phases of the natural diatomite did not change in the calcination temperature range of 300–900°C, and was transformed into crystalline structure of cristobalite at 1100°C. The solubility of Si from calcined diatomite at 300–900°C was almost constant, but that from calcined diatomite at 1100°C was low. The Si content in calcined diatomite was not leached via HCl acid leaching. The extents of Fe, Mg and Ca leached from calcined diatomite at 300–700°C was almost constant and decreased above 700 °C, while that of Al from calcined diatomite at 500–700°C indicated maximum values. The removal of Al from lacustrine diatomite was higher than that from marine one. The process that diatomite was calcined at 700°C and then treated with 5 M HCl at 80°C for 1 h was applied to diatomite samples, and the improvement for extraction of Si from diatomite was succeeded.

Table 2. Chemical compositions of T-W, S-W, treated T-W and treated S-W.

	T-W	S-W	Treated T-W	Treated S-W
SiO_2	88.4	93.7	93.2	95.7
Fe_2O_3	3.8	1.9	2.0	0.7
Al_2O_3	4.8	2.6	2.9	2.1
K_2O	1.4	0.5	0.9	0.3
CaO	0.7	1.4	0.5	0.9
MgO	0.6			
TiO_2	0.5		0.5	0.3
Total	100.0	100.0	100.0	100.0

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