

New methods to prepare high-purity silica

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Two methods are described to prepare high-purity silica to be employed as a low-cost starting material for solar-grade silicon production. In the first process, abundantly available quartz sand is purified by fusing it with glass forming oxides to form a melt from which thin glass fibres are drawn. Subsequent treatment of the fibres with hot HCl leads to an ion exchange whereby all non-siliceous oxides are removed from the glass network leaving an insoluble matrix of high-purity silica. The second method employs sodium hexafluosilicate (Na_2SiF_6), prepared from fluosilic acid, a by-product of the fertilizer industry. The Na_2SiF_6 is thermally decomposed to yield gaseous SiF_4 which is subsequently hydrolysed in an ammonia solution. With both methods silica having a purity of $> 99.99\%$ was obtained.

1. Introduction

In recent years the use of high-purity silica as a raw material for the manufacturing of fused silica products, optical glasses and optical waveguides has steadily increased. Depending on the requirements to be met, two sources of silicon dioxide may be employed to produce such products: selected natural quartz crystals mined from various deposits in Brazil, the USA, Africa, etc., and synthetic amorphous silica prepared by flame hydrolysis of SiCl_4 or by hydrolysing derivatives of ortho silic acid. The two latter processes usually result in silicon dioxide of much higher purity compared to quartz, but because of its high price use is limited to special applications such as optical waveguides.

More recently a process has been developed [1], in which high-purity silica is employed as a starting material to produce silicon for solar cells by a carbothermic reduction process. This so-called solar-grade silicon must be both inexpensive ($10 \$ \text{kg}^{-1}$) and of high purity to permit production of solar cells with an efficiency of $> 10\%$ [2].

This means that neither of the available materials can be employed because pure synthetic silica is too expensive and the cheaper quartz lacks purity. It is important for the silica to be used to have a boron and phosphorus concentration below 1 ppm, because these impurities cannot be removed from the resulting silicon by conventional crystal-

lization techniques [2]. Furthermore, naturally occurring raw materials such as quartz are unsuitable because they may vary considerably in quality depending on their origin. What is needed, then, is a process that uses abundantly available raw materials and turns them into inexpensive, high-purity silica of consistent and well controlled quality. To this end, two processes have been studied, one using sand (fibre leaching (FL)-process) the other using hexafluosilicates as the starting material.

2. High-purity silica by fibre leaching (FL)-process

The principle of the FL-process is based on the fact that non-siliceous constituents can be removed from silicate glasses of a certain composition when treating them with acid. The solubility of silica under these conditions is negligible. This phenomenon, described extensively in the literature [3-5] is used commercially to produce high melting glass products of high SiO_2 -content from low melting glasses. In general the products obtained contain 96 to 98% SiO_2 , the remainder being constituents of the original glass composition such as B_2O_3 , Na_2O and various impurities such as iron, titanium, etc.

We decided to carry selective leaching of glass by acids one step further and to explore it as a new method for preparing high-purity silica.

2.1. Experimental details

The glasses used in this work were prepared by fusing sea sand or various quartz sands mined in Germany together with glass forming oxides in a Pt/Rh crucible. After the glass melt had been homogenized and fined, thin fibres ($\phi = 50$ to $100 \mu\text{m}$) were drawn through a hole in the bottom of the crucible [1]. The fibres obtained were leached with hot HCl and rinsed with water using a modified Soxhlet-apparatus.

Chemical analysis of the leaching solution and the silica obtained were performed by atomic emission spectroscopy using an inductively coupled plasma (ICP).

Reaction enthalpy during leaching of the fibres with HCl was measured using a DSC-2 Perkin Elmer differential scanning calorimeter. About 1 mg of glass fibres were filled into a gold crucible, $10 \mu\text{l}$ HCl were added, the leaching temperature was adjusted and the reaction enthalpy was measured as a function of time. Porosity and pore size distribution of the high-purity silica obtained were measured using the conventional N_2 -sorption method.

2.2 Selection of glass system

If high-purity silica is to be obtained by acid leaching of glass, the chemical composition of the glass must be carefully adjusted. In particular, the SiO_2 content plays an important role in the leaching process. Glasses with a high silica content, $> 75\%$ for instance, are only leached at the surface, because the resulting thin SiO_2 -rich layer acts as a barrier that substantially inhibits further leaching. If, on the other hand, the SiO_2 -content of the glass to be leached is too low, a gel-like product is obtained which is difficult to process and, more importantly, results in a poor SiO_2 yield. In addition to the SiO_2 content, the choice of the other glass constituents such as network modifiers like Na_2O , CaO , MgO and network formers like Al_2O_3 are also important parameters influencing the leaching process. Further requirements prospective glass systems have to meet include the use of inexpensive raw materials, good glass-forming properties and ready conversion into fibres. Conversion of bulk glass into fibres is particularly advantageous for the leaching process, because the large ratio of surface area to glass volume facilitates diffusion of ions present in the glass matrix into the surrounding acid solution.

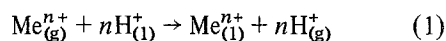
To satisfy all requirements mentioned above we

initially employed phase separable glasses from the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system which are known to be leachable in bulk form, resulting in a glass containing about 96% SiO_2 and 4% B_2O_3 [3]. By modifying the composition and employing fibres for the leaching process, silica of 99.99% purity was obtained. For solar-grade silicon application, however, the boron content of ≈ 100 ppm was still too high, although it was considerably lower compared to the conventional leaching process. Similar results were obtained by using E-glass fibres, which are known to be readily attacked by acids [5]. In this case not only the boron content but also the concentration of transition metals in the leached fibres was much too high for our applications.

Since it proved difficult with these two glass systems to achieve a boron level below 1 ppm, we decided to use boron oxide-free glasses. Best results were obtained with glasses from the $\text{Na}_2\text{O}-\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system which posed no problems with regard to melting or fibre drawings. The results obtained with this glass system are described in the following section.

2.3. Leaching of glass fibres

When glass fibres of our composition are exposed to hot HCl solution, an ion exchange reaction takes place at the solution/glass interface resulting in a rapid destruction of the glass network. This reaction may be described by the following simplified overall reaction:



In this equation Me^{n+} represents a metal ion of the glass constituents such as Na^+ , Ca^{2+} , Al^{3+} or an ion such as Fe^{3+} , Ti^{4+} , etc., originally present as an impurity in the SiO_2 starting material; H^+ or H_3O^+ represent the proton from the acid and the subscripts g and l refer to the location of ions in the glass and in the liquid, respectively; n the electric charge of the ions may vary from 1 to 4. On account of this ion exchange, non-siliceous oxides are removed from the glass network resulting first in a layer of pure silica on the fibre surface. For the glass composition chosen, this silica film is, in our case, highly porous and not sufficiently dense to protect the underlying glass from further attack by the acid.

Since the pores or channels formed in the SiO_2 layer are large enough to allow diffusion of protons to the glass surface and out diffusion of metal ions into the surrounding solution, the ion exchange

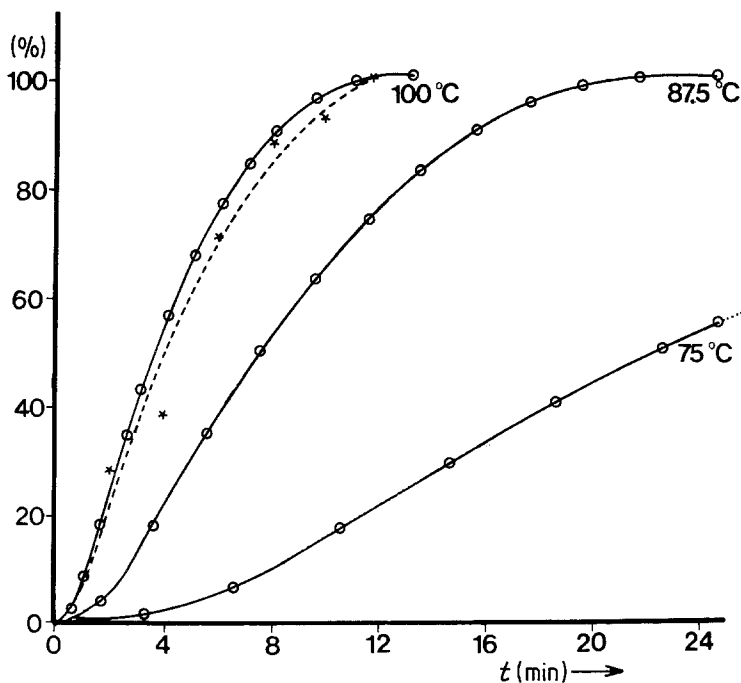


Figure 1 Leaching of glass fibres with hot HCl. Degree of leaching (%) as a function of temperature and time. * Determination from chemical analysis of leaching solution (ICP). \circ Determination from thermal analysis (DSC). At 75°C complete leaching in 72 min.

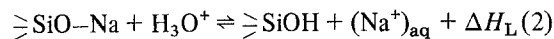
proceeds unhindered until all metal ions are removed to leave a structure of pure silica.

Fig. 1 (dashed line) shows the percentage of all leached glass constituents (Na^+ , Mg^{2+} , Ca^{2+} , Al^{3+}) as a function of temperature. As is apparent, leaching is completed after ≈ 13 min. When the ions leached from the glass at 100°C are plotted individually as a function of time, the plot reveals that the leaching rate is the same for all ions, i.e. no preferential leaching takes place under these conditions. Thus leaching may be compared to a dissolution process [6] in which acid soluble oxides (Na_2O , CaO , etc.) are removed from an acid-resistant matrix (SiO_2). This situation is typical for glasses with SiO_2 concentrations too low to screen metal cations [7]. Since ion exchange takes place at a temperature below the glass transition temperature, the glass network cannot contract sufficiently to accommodate H^+ ions having a much smaller partial molar volume than cations of the glass constituents. This results in considerable tensile forces in the leached layer leading to the propagation of microcracks induced during fibre drawing.

Fig. 2a shows the scanning electron micrograph of a fibre immersed in hot HCl for 4 min. The leached surface layer is seen to be cracked and partly peeled, resulting in new surfaces for acid attack. Microcrack propagation not only occurs

parallel to the fibre axis as seen in the SEM micrograph, but perpendicular to it as well so that long fibres break up into pieces a few millimetres long thus facilitating the leaching process. Fig. 2b shows a SEM micrograph at high magnification of a completely leached glass fibre surface. The figure reveals an apparently continuous matrix of silica full of pores (dark areas) which correspond to a large specific surface area (see Section 2.4).

In the course of our leaching experiments we noticed that an exothermic reaction took place when fibres were immersed in hot HCl. The heat evolved is apparently due to hydration of metal cations (Me^+_{aq}) and the formation of SiOH groups; e.g.



The reaction enthalpy for the leaching process ΔH_{L} may be represented in a simplified way as

$$\Delta H_{\text{L}} = \Delta H_{\text{G}} - \Delta H_{\text{H}} - \Delta H_{\text{OH}} \quad (3)$$

where ΔH_{G} is the "lattice energy" of the cation in the glass network, ΔH_{H} is its hydration enthalpy, and ΔH_{OH} is the reaction enthalpy for Si-OH formation. In HCl used in our experiments most cations in solution will form aquo-chloro complexes. The exact nature of these complexes will depend on the type and concentration of cation (Na^+ , Ca^{2+} , Al^{3+} , Fe^{3+} , etc.) and on the temper-

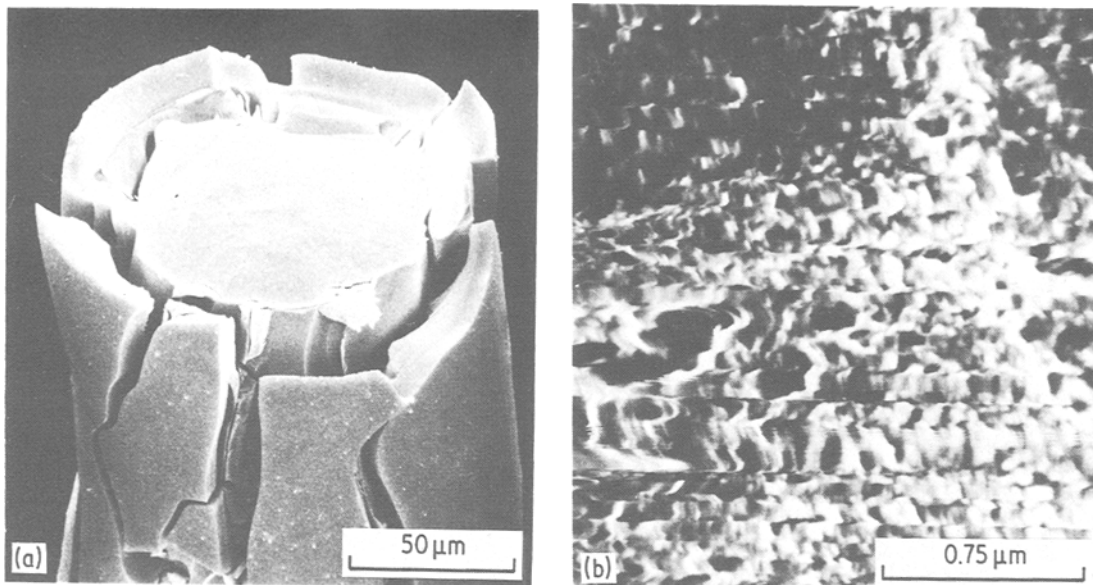


Figure 2 SEM micrograph of a (a) glass fibre leached with hot HCl for 4 min, and (b) completely leached glass fibre surface.

ature of the leaching solution. To examine the thermodynamic aspect of the FL-process in more detail, ΔH_L was measured as a function of time using a differential scanning calorimeter (DSC). Fig. 1 shows that at a leaching temperature of 100°C , the reaction is completed after approximately 13 min. Furthermore, the shape of the DSC curve is nearly identical to the dashed curve obtained by determining the total amount of cation removed from the glass with the ICP. This close correlation can be expected, since as was pointed out before the major glass constituents are leached out at nearly the same rate. The relative contribution of the various cations to ΔH_L ($= 921\text{ J g}^{-1}$ glass fibre) is presently not known.

The DSC curves of Fig. 1 also show leaching to be temperature dependent; at 87.5°C the reaction is completed after 25 min, while at 75°C 72 min are required. This latter curve also reveals that the leaching rate is much slower in the first few minutes than later on. This is due to the fact that in the initial phase the macroscopic structure of the fibre is still unchanged. At 75°C cracking of leached fibre surface and breakage of long fibres into smaller pieces begins after ≈ 5 min leading to an increase in surface area which in turn leads to an increasing leaching rate. This increase in surface area with the concurrent increase in leaching rate continues to $\approx 60\%$ of the total time needed to

complete the reaction. At this point the macroscopic surface area remains nearly constant. This result was gleaned by comparing the leaching rate of long fibres with that for fibres that were finely powdered by grinding prior to acid exposure.

As is apparent from Equation 1 the reaction must be shifted to the right hand side to obtain high-purity SiO_2 . This is accomplished by continuously removing leached out cations from the equilibrium and by maintaining a high concentration of H^+ ions in the leaching solution.

When glass fibres are contacted with hot HCl two processes take place simultaneously: the formation of new surfaces due to microcrack propagation and chemical reactions at new generated surface sites. A number of solid state reactions are known where — similar to the leaching process — the reaction products formed lead to the propagation of microcracks in the starting material, which in turn create new reaction centers. According to Prout and Tompkins [12] such reactions may be described by the following equation:

$$\ln\left(\frac{\alpha}{1-\alpha}\right) = kt + C \quad (4)$$

where α is the conversion of starting material to reaction products and the other symbols have their usual meaning. Fig. 3 shows the results obtained when Equation 4 is applied to the leach-

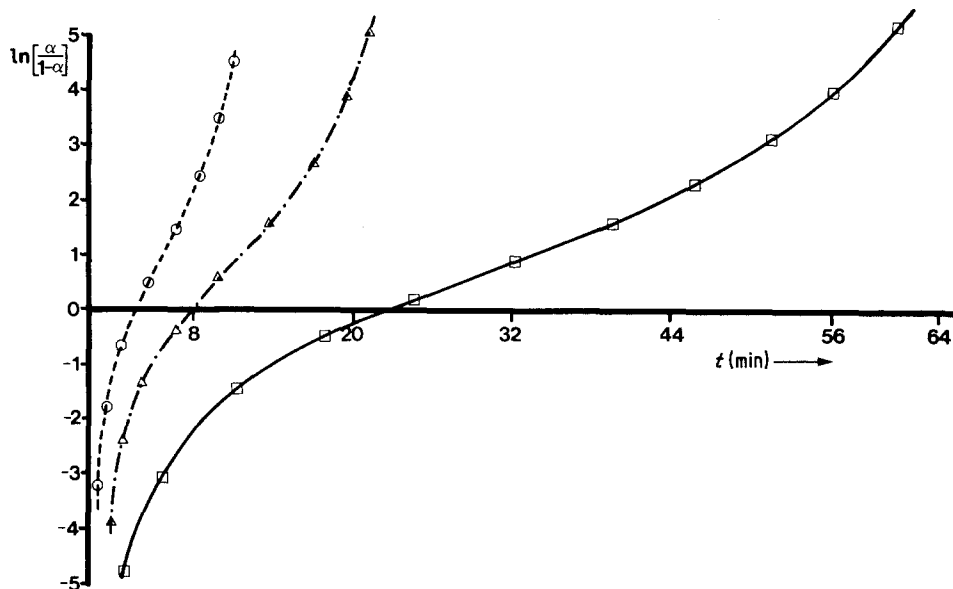


Figure 3 Presentation of leaching reaction at various temperatures using the Prout-Tompkins equation [12]. α = fraction of cations leached from the glass: - - - - $T = 100^\circ \text{C}$, - · - · - $T = 87.5^\circ \text{C}$, and — $T = 75.0^\circ \text{C}$.

ing of glass fibres. As is apparent, only the middle section of the three curves shown may be represented by a straight line, at short and long leaching times smaller to larger $[\ln(\alpha/1-\alpha)]$ values, respectively, than would be predicted by Equation 4 are observed. Presumably, for the straight line section reaction rate for formation of new surface sites is comparable to the chemical reaction rate, while for short leaching times the chemical reaction is inhibited by a slower surface formation rate. For longer leaching periods ($t \geq 0.6t_{\text{total}}$) the surface area remains nearly constant and leaching is determined by chemical reaction only, resulting in larger $[\ln(\alpha/1-\alpha)]$ values. From the experimental results we conclude the formation of new surfaces to be the rate determining step. Furthermore, the leaching reaction is not diffusion controlled and cannot be described by a simple reaction order.

2.4. Characterization of SiO_2

Table I shows the chemical analysis of SiO_2 prepared by the FL-process together with the composition of sea sand which had been chosen as a starting material because of its particularly high impurity content to demonstrate the capability of the FL-process. As can be seen, impurities such as boron, phosphorus and transition metals especially harmful for solar-grade silicon applications can be drastically lowered by the FL-process.

N_2 -sorption measurements were performed to determine the surface area and pore size distribution of the silica obtained. Fig. 4 shows the sorption isotherm of N_2 on SiO_2 dried at 500°C before being used. According to international convention this isotherm is classified as type IV [8], characterized by a pronounced hysteresis caused by capillary condensation in mesopores and saturation behaviour at high relative pressure. The shape of the hysteresis is of type II [8] which is characteristic for amorphous silica. Evaluation of the data results in a BET surface of $216 \text{ m}^2 \text{ g}^{-1}$, a

TABLE I Impurity concentration in sea sand and SiO_2 purified with the fibre leaching (FL)-process

Impurity	Starting material sea sand concentration (ppmw)	SiO_2 after FL-process concentration (ppmw)
B	3.2	< 0.2
P	14	< 1
Na	10^3 to 10^4	< 5
Mg	10^3 to 10^4	< 0.5
Ca	10^3 to 10^4	< 0.5
Al	10^4 to 10^5	< 10
Fe	10^3 to 10^4	< 0.1
Ti	10^2 to 10^3	< 1
Zr	10^2 to 10^3	< 5
V, Cr, Mn, Co,		
Ni, Cu	1 to 10	< 1
Nb, Mo, Ta, W	1 to 10	< 0.1

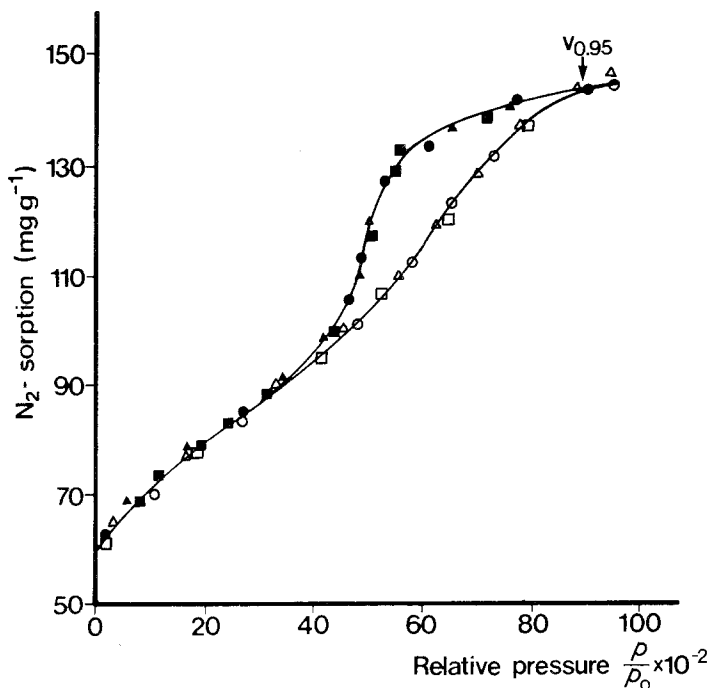


Figure 4 Adsorption and desorption isotherm of N_2 (77 K) at SiO_2 prepared by FL-process. Closed symbols: Desorption. Open symbols: Adsorption.

C constant of 187 and a total pore volume of $0.177 \text{ cm}^3 N_2 g^{-1}$.

Using these results the mesopore size distribution was determined, assuming that pores are rigid and of cylindrical shape. Fig. 5 shows that the distribution peaks at a mean pore radius

$r_p \approx 1.60 \text{ nm}$ and that most pores have a mean radius $< 6.0 \text{ nm}$.

Comparing these results with those obtained using leached sodium borosilicate glass [9] clearly shows that FL- SiO_2 has a much smaller r_p and a larger BET surface. In $Na_2O-B_2O_3-SiO_2$ glasses,

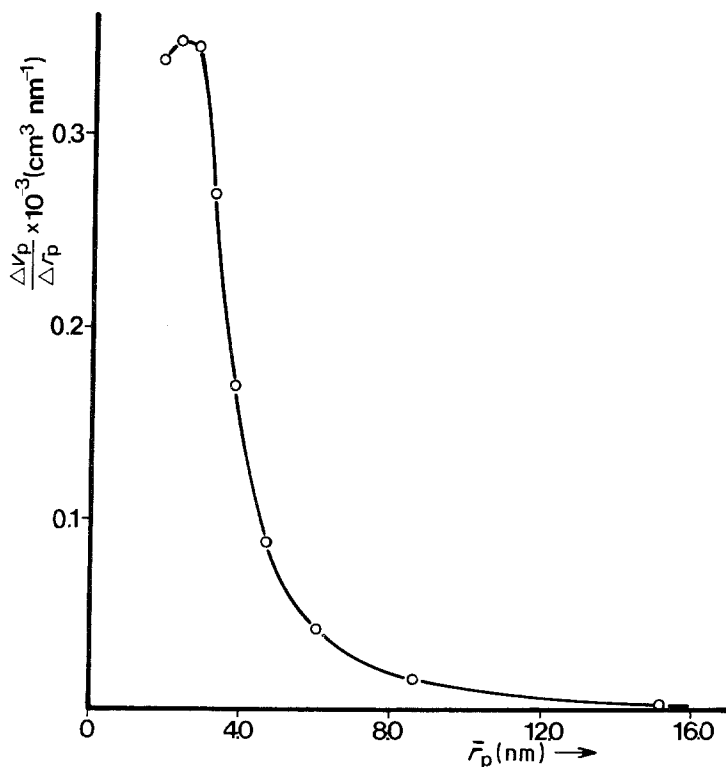


Figure 5 Mesopore size distribution (r_p) of SiO_2 prepared by FL-process.

the acid soluble $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ phase ($r \approx 30 \text{ nm}$) induced by tempering apparently gives rise to much larger pores after leaching compared to our glass system, where acid soluble cations are distributed throughout the glass network in clusters of much smaller dimensions.

3. High-purity silica from hexafluosilicates

In addition to the FL-process a second method was investigated as to its potential to prepare high-purity silica. This process relies on the use of fluosilic acid (H_2SiF_6) as a starting material, which is abundantly available as a by-product of the phosphate fertilizer industry. As a first purification step, H_2SiF_6 is converted into the sodium salt which in turn is thermally decomposed to yield gaseous SiF_4 . This SiF_4 is then hydrolyzed in an alkaline solution to obtain high-purity silica.

3.1. Experimental details

Commercially available H_2SiF_6 (31% aqueous solution) and Na_2SiF_6 from various suppliers were used. Since these materials were produced on an industrial scale, their purity varied considerably with respect to the various vendors. Na_2SiF_6 was decomposed in a reaction vessel made from quartz glass or from a Ni-Co-Cu alloy at a temperature between 700 and 800°C using a resistance furnace. The SiF_4 produced was transported with an argon carrier gas into a hydrolyser made from quartz glass, equipped with a stirrer, a glass electrode to measure the pH of the solution and an inlet for liquid ammonia solution. Hydrolysis of SiF_4 was carried out at 80 to 90°C and the pH of the solution was maintained at ≈ 7 by adding the appropriate amount of ammonia solution (Fa. Merck Suprapur). The silica obtained was filtered off and washed with distilled water before being analysed for impurities.

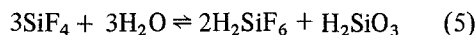
3.2. Results and discussion

Commercially available H_2SiF_6 contains a high concentration of impurities such as aluminium (100 to 1000 ppm), boron (10 to 100 ppm), magnesium, calcium (100 to 1000 ppm), iron, titanium, chromium, arsenic (100 to 1000 ppm) and phosphorus (≥ 1000 ppm). These impurities will be present in the solution as fluorocomplexes and cannot be removed simply by addition of a base to form SiO_2 . Under these conditions, impurities forming insoluble hydroxides such as titanium, iron, etc., would coprecipitate with SiO_2

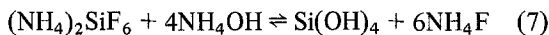
while impurities remaining in solution such as boron, phosphorus will partly be adsorbed on the submicron fine silica particles. A pronounced purification of H_2SiF_6 is obtained, however, by reacting NaCl solution with H_2SiF_6 solution to form the sparingly soluble Na_2SiF_6 . Analytical results show the concentration of impurities in Na_2SiF_6 to be lower by a factor of more than 100 compared to H_2SiF_6 .

When thermally decomposing Na_2SiF_6 to gaseous SiF_4 and solid NaF a further purification takes place since most of the impurities still present will form non-volatile fluorides and will remain in the NaF residue. The resulting SiF_4 is of high purity when reacted with liquid sodium [10].

For our application the SiF_4 is hydrolysed according to the following reaction:



Since the SiF_6^{2-} anion is stable up to a pH value of ≈ 3 the pH is further increased to ≈ 7 by adding ammonia solution:



Ammonia is used as a base because of the high solubility of NH_4F in aqueous solution. The reaction with ammonia is carried out at $\approx 90^\circ \text{C}$ to form polymeric silic acid of higher molecular weight, thereby reducing the solubility of amorphous silica in NH_4F solution [11]. Under these conditions the SiO_2 yield was found to be 92%. The resulting silic acid is gel-like and after drying yields a submicron fine high-purity silica product having the following impurity concentrations in ppmw: Mg: 0.1 to 1; Ca < 10; B < 1; Al 1 to 10; Fe, Cu, Ti, Cr, Cu < 0.1. Preconditions for obtaining SiO_2 of such purity is to establish high-purity conditions (ammonia, water, reaction vessel) for SiF_4 hydrolysis. This is necessary because, on account of the high surface area of silic acid produced, impurities present in solution will be adsorbed and cannot be removed by subsequent washing procedures.

4. Conclusions

Both the FL-process and the thermal decomposition of Na_2SiF_6 yield silicon dioxide of high purity that can be employed for the carbothermic production of solar-grade silicon. Whether the silica obtained can advantageously be used for

other applications depends not only on the purity and the cost of the material but on other parameters as well, such as surface area, porosity, surface composition and reactivity, to name just a few.

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