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# The increase in pH during aging of porous sol–gel silica spheres <sup>§</sup>

M.K. Titulaer <sup>a,\*</sup>, W.K. Kegel <sup>b</sup>, J.B.H. Jansen <sup>c</sup>, J.W. Geus <sup>b</sup>

<sup>a</sup> Department of Geochemistry, Institute for Earth Sciences, University of Utrecht, Budapestlaan 4, PO Box 80.021, 3508 TA Utrecht, The Netherlands

<sup>b</sup> Department of Inorganic Chemistry, University of Utrecht, Sorbonnelaan 16, PO Box 80.083, 3508 TB Utrecht, The Netherlands

<sup>c</sup> Bowagemi B.V., Prinses Beatrixlaan 20, 3972 AN Driebergen, The Netherlands

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## Abstract

The increase in pH in the hydrothermal fluid is studied after hydrothermal aging of porous silica gel spheres of 1–3 mm diameter. The porous silica spheres are formed by the sol–gel process from a supersaturated silica solution. The increase of the pH of the hydrothermal solution affects the silica solubility. A model to explain the increase in pH assumes condensation of sodium complexed silanol groups and the release of ionized monosilicic acid in the fluid. The existence of sodium complexed silanol groups is demonstrated by surface titration experiments.

## 1. Introduction

Porous silica is used to manufacture catalysts and catalyst supports. Porous silica can be obtained from supersaturated silica sol solutions in three ways, namely, (1) addition of a sodium silicate solution to a concentrated aqueous acid solution [1], (2) exchange of Na<sup>+</sup> for protons by an exchange resin column [2] and (3) removal of the Na<sup>+</sup> by electro-dialysis [3]. The spherical silica sol–gel bodies of 1–3 mm diameter in this paper are prepared according to the first of the above procedures. The porous silica gel spheres consist of a three-dimensional network of submicrometre colloidal silica particles. The prepara-

tion of the porous silica spheres has been described by Titulaer et al. [23] and in Ref. [1]. Variations in the conditions during preparation and in the hydrothermal treatment of the spheres enable one to control the porous structure of the spheres. Further, a catalyst precursor, for example, a transition metal oxide or a clay mineral, can be mixed with the silica sol before gelling. An excellent dispersion of the precursor within the gel can be obtained. The pore dimensions of the silica gel can be controlled subsequently by hydrothermal aging.

The cause of the increase of the pH level and the silica solubility in the hydrothermal fluid is the topic of the present work. An increase of the pH affects the solubility of silica and the ionization of surface silanol groups, and thus the ripening process of silica under hydrothermal conditions [4]. To explain the observed changes in the pH, the surface structure of the silica spheres is investigated by surface titration.

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\* Corresponding author. Tel: +31-30 534 969. Telefax: +31-30 535 030.

## 2. Materials and procedures

### 2.1. Preparation and hydrothermal treatment of the silica xerogel

Two solutions A and B were prepared. The stock sodium silicate solution A, 3M Si and 1.5M NaOH, was prepared by mixing commercially available waterglass (Merck Natronwasserglas, Art. 5621) with an equal volume of doubly distilled water. The nitric acid solution B, 2M HNO<sub>3</sub>, was prepared by diluting 65 wt% nitric acid (Merck, art. 456) with water. An aliquot of 76 ml of the sodium silicate solution A was slowly added to 50 ml of the stirred diluted solution B (present in a plastic beaker in an ice-water bath). The nitric acid solution B was kept at 273 K to avoid premature gelling. The rate of addition of A was kept constant at 60 ml/h with a Gilson Minipuls 2 pump. The resulting silica sol contained 13 wt% SiO<sub>2</sub> in salty solution. When a pH of 5 was reached, the sol was quickly introduced through a hollow vibrating needle into a double walled vessel (length 70 cm, diameter 9.5 cm) containing a cylinder of 5 l hot paraffin oil floating on water. The temperature of the oil was kept at 363 K by means of a water thermostatic bath (Tamson). The sol–gel conversion of the spherical sol droplets in the paraffin oil was accelerated by the high temperature. The spherical hydrogel bodies of few mm were caught in 2 l demineralized water under the paraffin cylinder and subsequently washed with 1.5 l demineralized water. After washing with demineralized water, several batches of hydrogel spheres were dried at 393 K, and calcined at 723 K for 24 h in air, forming porous xerogel spheres. The surface area of these spheres was measured by N<sub>2</sub> sorption on a Carlo Erba Sorptomatic 1800.

In the hydrothermal experiments, 3.15 g of xerogel spheres were treated with 20.85 ml of 1M NaCl in rotating Teflon cups (48 ml) contained in steel pressure vessels. The initial pH of the solution was 6. All the hydrothermal experiments were performed at the vapour saturation pressure.

The xerogel spheres dried at 393 K were divided into fractions for hydrothermal treatment

for periods of time between 2 and 47 h at 473 K. Second, the temperature was varied in intervals between 373 and 523 K at a fixed duration of 24 h. Third, NaCl concentrations were varied with intervals between 0 and 6M with hydrothermal treatment at a constant duration of 24 h and temperature of 473 K.

After hydrothermal treatment, the spheres were separated from the hydrothermal fluid by filtration, and dried at 393 K. The pH of the filtered fluid was measured. Finally, the xerogel spheres were thoroughly washed, dried at 393 K for a period of 24 h and subsequently calcined at 723 K for 24 h. The pore radius, pore volume and internal surface area were assessed by Hg penetration (Carlo Erba 2000). Only the intrusion of Hg was measured. The pore size distribution and pore volume were calculated with the Washburn equation and the volume of Hg intruded at different pressures. The internal surface area was estimated from the pore radius and pore volume, assuming a cylindrical pore shape.

### 2.2. The solubility of silica in the hydrothermal fluid

The silica solubility in the hydrothermal fluid after aging of silica spheres was measured. Since the filtered fluid does not contain solids, the silica solubility could be assessed by measuring the silica concentration in the solution. Two different solubilities could be measured, namely, (1) the monosilicic acid (MSA) solubility, and (2) the ‘true’ solubility, comprising both MSA and colloidal forms of silica. The MSA solubility is usually determined by using the reaction of the silicate ion with an acidified ammonium heptamolybdate solution, followed by colorimetric determination of the resulting yellow silicomolybdate complex [5,6]. A reagent (A) was prepared having an acidity of 1.5M. Reagent (B) of pH = 7 contained 0.56M MoO<sub>4</sub><sup>2-</sup>, 1.16M NH<sub>4</sub><sup>+</sup> and 6.7 × 10<sup>-3</sup>M NH<sub>3</sub>. An unstable reagent (C) was prepared by adding 200 ml of reagent (A) and 100 ml of reagent (B) to 500 ml distilled water [7]. An aliquot of 50 ml of solution (C) was added to 1 ml of the filtered hydrothermal fluid (D). After 2 min, the absorption of the yellow silicomolybdate

complex at 410 nm was measured in a 1 cm quartz-glass cuvette on a spectrophotometer (Perkin–Elmer Lambda 1 UV/VIS).

The ‘true’ silica solubility in solution was established by inductively coupled plasma atomic emission spectrophotometry (ICP-AES) on a 30 channel simultaneous instrument (type 34000, Applied Research Laboratories, Valencia, USA). The colloidal forms of silica in solution were estimated by subtracting the  $\beta$ -silicomolybdate solubility from the ‘true’ solubility. The hydrothermal fluids of the various samples were diluted ten times to reduce the expected interference of Na on the silicon determination by ICP-AES.

### 2.3. Spheres added to solutions of different pH

An amount of 1 g of hydrothermal treated xerogel spheres, having a pore radius 8 nm and a surface area of 156 m<sup>2</sup>/g as determined by Hg intrusion, was added to 50 ml of either (1) distilled water or (2) 1M NaCl or (3) 3M NaCl. The maximal adsorption of hydroxyl ions was measured after 20 h as a function of the pH. Different pH values, ranging from 1 to 12, were established by addition of a few drops diluted 27 wt% ammonia or 37 wt% HCl to the solution. The exchanged [Na] after addition of the spheres was measured by atomic emission spectroscopy (AES).

## 3. Results

### 3.1. Increase in pH with hydrothermal aging

Fig. 1 shows the pH of the 20.85 ml hydrothermal fluid as a function of the specific surface area of the xerogel spheres after hydrothermal treatment as measured by Hg intrusion. The initial pH of the 1M NaCl solution, in which the spheres have been suspended, was 6. The specific surface area of the untreated spheres was 455 m<sup>2</sup>/g, as determined by N<sub>2</sub> sorption. The pore volume of the xerogel spheres remained constant on 0.8 ml/g with aging. The final pH of the hydrothermal fluid increases as the surface area of the spheres decreased by the treatment. This process

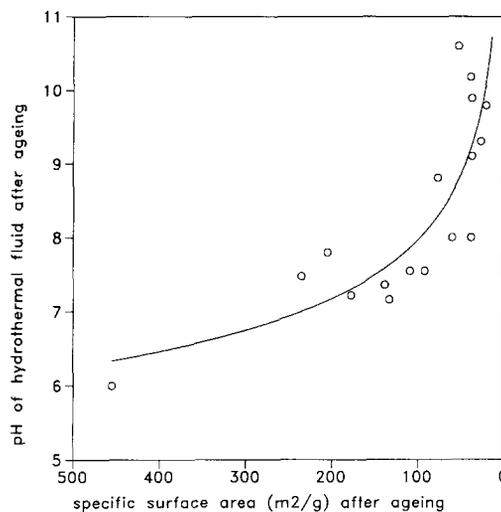


Fig. 1. Increase of the pH of the hydrothermal fluid accompanied with the decrease of surface area with hydrothermal aging of the xerogel spheres. The silica surface areas are measured by Hg penetration from the pore radius and pore volume with assumption of a cylindrical pore shape. The pore volume of the xerogel spheres remained on constant on 0.8 ml/g with aging.

continued until the surface area decreased to about 50 m<sup>2</sup>/g, and the pH of the fluid was between 10 and 11.

### 3.2. Increased silica solubility at high pH levels

Silica solubility at high final pH levels of the hydrothermal fluid after aging is shown in Fig. 2. The pattern of Fig. 2 is common for amorphous silica [8,9]. Both the ‘true’ and MSA solubility rapidly increase when the pH reaches the first ionization constant of MSA, which is 9.35 in 1M NaCl at 298 K reported by Busey and Mesmer [10]. The solid line is the pure theoretical solubility,  $S(T, \text{NaCl}, \text{pH})$ , of MSA both in neutral and ionized form,  $[\text{MSA}] + [\text{MSA}^-]$ , based on the relation

$$S(298 \text{ K}, 1\text{M NaCl}, \text{pH}) = 106 \times (1 + 10^{\text{pH}-9.35}) \text{ (mg SiO}_2\text{/l)}. \quad (1)$$

The neutral pH solubility of 106 ppm is slightly lower than the usual reported value of 115 ppm due to the salting out effect of the 1M NaCl

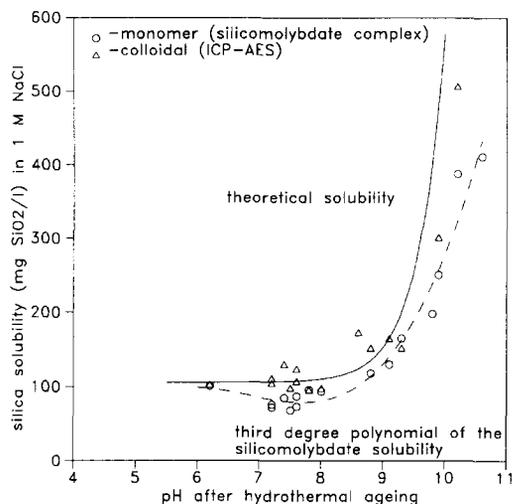


Fig. 2. The solubility of silica in the hydrothermal fluid both in colloidal and monomer form as a function of the pH after hydrothermal ageing of the porous silica gel spheres.

solution [11,12]. The solubility of silica as measured from the yellow silicomolybdate complex is slightly below the 'true' solubility of silica, because a small quantity of silica is present as polymers. The amount of silica present as polymers is about 36 and 120 ppm (= mg SiO<sub>2</sub>/l) at a pH of 7 and 10, respectively (Fig. 2). The solubility calculated from the silicomolybdate concentration suggests a faint minimum between pH 7 and 8, which is not due to the scatter of the silicomolybdate solubility. On page 454 in a publication of Alexander et al. [8] and on page 366 in a publication of Volosov et al. [9], a similar minimum in silica solubility at pH 7–8 is shown. The dashed curve through the silicomolybdate solubility represents a third degree polynome.

### 3.3. Adsorption of OH<sup>-</sup> or H<sup>+</sup> as a function of the pH

In Fig. 3, adsorption of OH<sup>-</sup> at pH > 7.7 and adsorption of H<sup>+</sup> at pH < 7.7 is obvious if hydrothermally treated porous silica gel spheres are added to sodium-free solutions of different pH. At pH < 5, the amount exchanged Na<sup>+</sup> in solution with the silica surface is measured by AES

(◊). The amount of desorbed Na<sup>+</sup> from the silica surface is equal to the amount of adsorbed H<sup>+</sup>. Below pH 5, a linear plot can be constructed of the log(H<sup>+</sup><sub>ads</sub> m<sup>2</sup>/mol) versus the pH of the solution. The slope of this plot, 0.85, indicates that Na<sup>+</sup> and H<sup>+</sup> are exchanged in a 1:1 ratio.

When the porous hydrothermally treated silica spheres are added to solutions of 1 and 3M NaCl of different pH, OH<sup>-</sup> is adsorbed at pH > 6.2 and H<sup>+</sup> is adsorbed at pH < 6.2. The results of addition of porous silica spheres to solutions of 1 and 3M NaCl of different pH are equal.

### 3.4. Acid treatment of the spheres

Before the addition to solutions of different pH, one batch of the hydrothermally treated silica spheres was treated with 50 wt% sulphuric acid, subsequently washed with distilled water until a neutral pH was measured and dried at 393 K. These silica spheres were added to solutions of a different pH. At pH > 3, only adsorption of

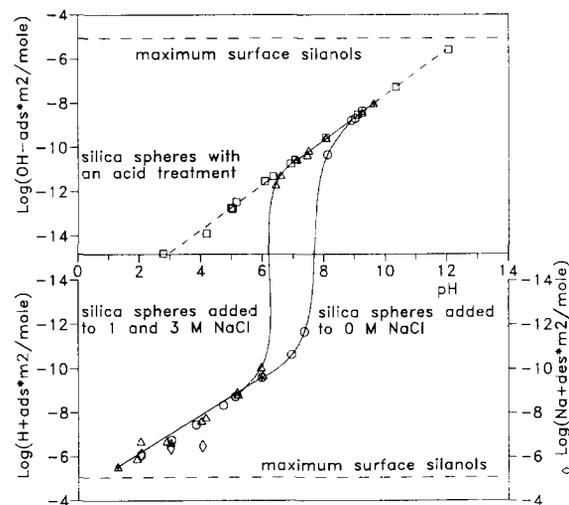


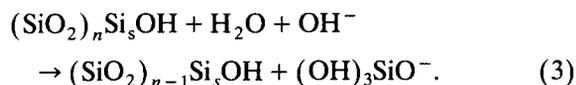
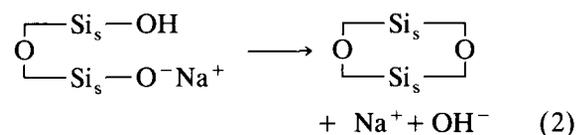
Fig. 3. Exchange of Na<sup>+</sup> at the surface of 1 g of an aged silica xerogel sample of a specific surface area of 156 m<sup>2</sup>/g as a function of the pH. The porous silica gel spheres are added to 50 ml distilled water (○) and 1 and 3M NaCl (△). The exchanged Na<sup>+</sup> in solution is measured with atomic emission spectroscopy (◊). The squares and dashed line represents the same sample, which had an acid treatment before the Na exchange experiments.

$\text{OH}^-$  took place, as shown by the linear curve  $\log(\text{OH}_{\text{ads}}^- \text{ m}^2/\text{mol})$  versus the pH. The slope of the curve was exactly unity. For comparative reasons, sodium-free fumed silica (Aerosil 380, Degussa, BRD) was also added to the solutions of differing pH. The results of the experiment are not represented in Fig. 3, but again at  $\text{pH} > 3$  only  $\text{OH}^-$  was adsorbed. The pattern resembled the experiments with the acid-treated spheres.

## 4. Discussion

### 4.1. Solubility of silica in the hydrothermal fluid of different pH levels

Changes in the pH affect the silica solubility and, thereby, affect the ripening process and the porous structure of a silica gel [13,14]. The ripening process involves condensation of (surface) silanol groups. One technique, providing evidence of the condensation of silanol groups and release of  $\text{Na}^+$  (Eq. (2)), is surface titration. The depolymerization of silica is catalyzed by hydroxyl ions and by the increased negative charge of the silica surface at high pH levels [15] (Eq. (3)):



The subscript,  $s$ , means surface. More ionized MSA in solution increases the pH, because MSA is a weak acid ( $\text{pK}_a = 9.8$ ) with respect to that of the ionized surface silanol groups ( $\text{pK}_a = 7.2$ ). The acid constant,  $\text{pK}_a$ , of the MSA is 9.35 in 1M NaCl [15]. According to Eq. (3), the solubility of silica is increased after the hydrothermal treatment. With a  $\text{pK}_a$  of 9.35 and Eq. (3), the solubility,  $S$ , at any pH can be estimated from the relation  $S = S_0^* (1 + 10^{\text{pH} - 9.35})$  [13] with the neutral pH solubility,  $S_0$ , of about 106 ppm in 1M NaCl. The theoretical solubility with the relation based on Eq. (3) is shown by the solid line in Fig. 2. The release of NaOH during aging requires a

layer of adsorbed sodium at the silica surface or in the silica gel structure.

### 4.2. The existence of a layer of adsorbed $\text{Na}^+$

The existence of a layer adsorbed sodium can be proved by surface titration by hydroxyl ions. Two approaches are followed in the literature to explain the adsorption of hydroxyl ions on glasses and porous gels [16]. The first approach assumes the silica surface to be a porous gel [17]. Various cations can penetrate into the surface of the silica gel. The second approach, the 'site-binding' model, involves a combination of electrostatic effects and complexation of counter ions on localized sites of the surface. The difference between the two approaches is the affinity of alkali metal adsorption. According to the first approach, the extent of adsorption decreases with larger ionic radii of the adsorbing ions. Since the ionic radii increase in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ , the extent of adsorption should drop in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ . The second approach, the site binding model, predicts the affinity to increase in the reverse order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  [18,19]. The appropriate explanation therefore depends on the nature of the silica. The 'site-binding' model is the most suitable for our gels.

The maximum silanol group coverage expected on the surface of the hydrothermal treated silica spheres is about  $5.8 \text{ nm}^{-2}$  after calcination at 383 K, which can also be written as  $92.6 \mu\text{C cm}^{-2}$  or  $9.60 \mu\text{mol m}^{-2}$  [20]. The iso-electric point (IEP) and the point of zero charge (PZC) of the silica gel are both located between pH 2 and 3 [21], while the first ionization constant  $\text{pK}_a$  of the surface silanol is 7.2. Normally, the difference between the IEP and the  $\text{pK}_a$  of other oxides is less than 2 [16]. The surface ionization is expected to increase at a high sodium chloride concentration [21,22].

The intrinsic acid constant,  $\text{pK}_i$ , for complexation with  $\text{Na}^+$  is 6.2. No adsorption of  $\text{H}^+$  or  $\text{OH}^-$  should proceed, when the Na complexed spheres are added to a 1 and a 3M NaCl solution of this pH, as is illustrated in Fig. 3. Addition of the  $\text{Na}^+$ -containing spheres to Na-free solutions results in more  $\text{H}^+$  being exchanged against  $\text{Na}^+$

in order to establish the corresponding  $\text{Na}^+$  concentration in the solution. Consequently, the curve intersects the pH-axis at a  $\text{pH} > 6.2$  approaching the  $\text{pK}_a$  of silanols, namely, 7.7 in a sodium-free experiment. The existence of a layer adsorbed sodium on the silica surface is thus clearly demonstrated by the surface silanol titration experiments in Fig. 3. The layer of adsorbed  $\text{Na}^+$  can completely be removed by treating the spheres with 50 wt% sulphuric acid. After all the  $\text{Na}^+$  has been removed from the silica surface, the IEP is 3 (Fig. 3).

The existence of adsorbed Na at the silica surface and within the silica gel structure might also be the reason for the destruction of the spherical shape with hydrothermal treatment with not previously dried hydrogel spheres. If the hydrogel spheres are aged in demineralized water, the spherical shape is lost and a powder is obtained. Aging in 1M NaCl leads to no destruction of the hydrogel bodies. We attribute the loss of the spherical shape with aging in demineralized water to the large osmotic forces of sodium in the silica gel structure.

## 5. Conclusions

(1) The condensation of sodium complexed silanols during hydrothermal aging increases the pH in the hydrothermal fluid, and increases the corresponding silica solubility.

(2) Silica gels free of sodium can be distinguished from silica gels containing sodium by surface titration experiments. If the sample contains sodium, a pseudo PZC of 6.2–7.7, is found.

(3) The existence of Na in the silica gel structure is probably the reason for the destruction silica hydrogel bodies with hydrothermal aging. The sodium in the gel structure causes a high osmotic pressure with aging.

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