Silicic Acid Polymerization and SiO$_2$ Nanoparticle Growth in Hydrothermal Solution

Vadim V. Potapov $^{1,*}$, Angel A. Cerdan $^2$ and Denis S. Gorev $^1$

$^1$ Research Geotechnological Center, Far Eastern Branch of Russian Academy of Sciences, 30, Severo-Vostochny Highway, 683002 Petropavlovsk-Kamchatsky, Russia
$^2$ Chemical Department of Moscow State University, Leader Scientist, Russian Federation, Leninskie Gory, 1, 119991 Moscow, Russia
* Correspondence: vadim_p@inbox.ru

Abstract: The approach of numerical simulation of orthosilicic acid OSA polymerization and SiO$_2$ nanoparticle formation in hydrothermal solution have been developed based on the model of the homogeneous stage of nucleation and the subsequent growth of particles. The influence of surface tension on the interface of SiO$_2$–water, the rate of molecular deposition, and Zeldovich factor $Z$ were evaluated. Temperature dependence on time, pH, initial OSA concentration, and ionic strength are the main parameters that determine the kinetics of colloid phase formation, the final average size of SiO$_2$ nanoparticles, and the particle size distribution and its polydispersity index. The results of the numerical simulation were verified with experimental data on OSA polymerization and measurement of nanoparticles sizes using the method of dynamic light scattering in a wide range of temperatures of 20–180 $^\circ$C, pH = 3–9, SiO$_2$ content $C_t$ of 300–1400 mg/kg, and ionic strength $I_s$ of 0.0001–0.42 mol/kg. The results obtained can be used in the technology of hydrothermal synthesis of sols, gels, and nanopowders to regulate the kinetics of OSA polymerization and SiO$_2$ nanoparticle growth, particle size distribution, morphology, and structure of products.

Keywords: hydrothermal synthesis of SiO$_2$ nanoparticles; kinetics of orthosilicic acid polymerization; nanoparticle size distribution

1. Introduction

Hydrothermal synthesis of SiO$_2$ nanoparticles is the new technological method with a low production cost, high density of silanol groups, low toxicity, excluding the use of chemical reagents and other green chemistry methods of nanoparticle synthesis [1–3], and allows to obtain different forms of nanosilica—sols, gels, powders, products of the sol-gel process applied in concrete, agricultural plants, medicines, and other materials [4–7]. The technology of hydrothermal synthesis includes the stages of OSA polymerization, ultrafiltration membrane concentration of nanoparticles, the sol-gel process, vacuum sublimation, and others [4–6]. The temperature regime, the stage of polymerization, pH, initial OSA concentration $C_s$, and ionic strength influenced the rate of SiO$_2$ nanoparticle formation, the average nanoparticle size, and the index of polydispersity of nanoparticles in hydrothermal sols. Therefore, the density, morphology, agglomerate dimensions and fractal structures, volume, surface, diameters, and structure of pores of nanopowders produced from hydrothermal sols are also affected [4,5]. There is a need to regulate the parameters at the stage of OSA polymerization of silicic acid by means of numerical simulation to achieve the necessary characteristics of sols, gels, and nanopowders.

The kinetics of OSA polymerization with different mechanisms has been studied by many researchers under various conditions: pH, initial concentration of dissolved silica $C_s$, solution temperature, ionic strength, and sizes and molecular weight of SiO$_2$ particles formed.
At sufficiently high concentrations of silica in 2–6 wt.% sodium silicate salt solutions with the ratio SiO$_2$:Na$_2$O = 3.25 and with acidification at pH = 1.7, when the increase in molecular weight was accompanied mainly by the aggregation of small particles the degree of polymerization increased proportionally to the square root of the polymerization time [8].

At the monomer concentration of 0.24 % in the absence of salts [9,10], the average molecular weight at pH = 2.0 increased linearly depending on the square root of time; at pH = 3.2, 3.8, it increased proportionally with time; at pH = 4.36—linearly from the square of time. At pH = 2.2, temperature 90 °C, the average particle diameter was 1.3 nm. At a higher silica concentration of 8 g/L after about 150 h at pH = 3.0 or 75 h at pH = 2.0 the average molecular weight reached 300 SiO$_2$ with a smaller resulting particle size of 0.9 nm [11]. The average molecular weight of the newly formed polymerized acid prepared by removing Na from a solution of sodium silicate at pH= 2–3 was about 660 SiO$_2$ atoms [12]. At pH = 2.1, temperature 25 °C, in 0.24 wt.% SiO$_2$ solution after 60 days after the start of polymerization, the proportion of monomeric silica was 14% and the particle diameter was 1.4 nm [13]. At pH = 8.8, growth of particles occurred during 1 min, that is 3·10$^4$ times faster than at pH = 2.0. In studies performed at 25 °C, pH = 2.0, in the solution of monosilicic acid 2.4% SiO$_2$ for 24 days the particle diameter was 1.65 nm; after 8 days it was about 3.4 nm [14–16]. In a wide range of SiO$_2$ contents at pH =3.0 and pH = 6.1, the initial average diameter of the nuclei was 1.5 nm and the final particle size was about 3 nm [17]. In [18], after 30 days of polymerization at pH = 7.0 and 25 °C with a total concentration of SiO$_2$ in a solution of 0.4 g/L the diameter of nanoparticles corresponding to the solubility was 3.7 nm.

In the pH = 7.0–10.0 region, when colloid particles are formed, but the aggregation process cannot proceed, the reaction order was 3 [13,19]. However, in [20], at different initial concentrations of OSA the apparent “order” of the polymerization reaction was determined as equal to 2 at a pH above 2 and was equal to 3 at a pH below 2 [20], whereas the second-order reaction rate constant decreased. It was found that the rate of polymerization was the greatest at pH = 8.3 and close to the maximum in the pH = 7.0–9.0 region, and at pH < 7.0 and pH > 9.0 it noticeably decreased [21].

The detailed study of polymerization in the wide area of concentrations of 0.2–1.8 g/L of silica and pH = 4.0–10.0 at 25 °C confirmed that there is an induction period during which the polymerization of the monomer is only slight or nonexistent. A decrease in the monomer content as it polymerizes at pH = 7.0 and 25 °C at an initial content of 0.05 wt. % occurred according to the law 0.37·(t − 0.35)$^{-0.333}$ [22]. The induction period was 0.35 h. After 1 h after the decrease in the monomer content, silica particles began to grow rapidly without the formation of any intermediate product. The presence of a long induction period at pH = 4.5–5.5 and a temperature of 95 °C is shown in [23]. The induction period characterizes the metastability of the system and for aqueous silicic acid at pH = 7.75, t = 20 °C, C$_s$ = 1450 mg/kg under mixing conditions it decreased from 3.25 to 2.75 h [20,21]. In the strongly acidic region, the rate of the process is proportional to [H$^+$]$^{1.2}$ at pH < 1.8, and in the weakly acidic region at pH > 3.4 –[OH$^-$]$^{0.9}$ [24,25]. The rate increases initially with an increase in temperature from 20 to 90 °C and decreases with a decrease in the initial OSA concentration [24,25]. The results obtained in [26] for OSA solutions with a SiO$_2$ content of 300–1200 mg/kg and low salinity in the temperature range from 5 to 180 °C confirmed that the temperature changes at a constant silica concentration do not significantly affect the increase in induction time at temperatures from 90 to 180 °C.

In a dimer–monomer mixture at pH = 2.0 [27] the polymerization mechanism and particle sizes differed from the results of monosilicic acid polymerization obtained for polycyclic polymer formation in [14–16]: at the beginning the discrete particles of less than 4 nm in size formed, then such particles aggregated [27].

Thus, the experimental data obtained by the authors showed significant differences in the values of the polymerization reaction order, the rate constant, the induction period, the sizes of the formed nanoparticles, and the different effects of temperature, pH, and ionic...
strength on these parameters. Taking this into account, it is justified to use the method of numerical simulation of polymerization based on a certain mathematical model.

One of the mathematical models of orthosilicic acid polymerization is Fleming’s model [28]. Fleming suggested that the process under study is characterized by two main areas of flow. In the first region, the initial concentration of silicic acid exceeds the pseudo-equilibrium concentration of Cₓ, and the polycondensation reaction is a first-order reaction both with respect to the difference \((C_{s} - C_{x})\) and with respect to the surface concentration of \(C_{SiO}^{-}\) ionized groups of SiO\(^-\), that is, the surface charge of colloid particles. The second area is defined by the condition \(C_{s} < C_{x}\).

The decrease in the rate of transition of monomeric silica to colloid is explained using the Weres-Yi-Tsao model [29]. The authors studied two processes: the formation of colloid particles at the homogeneous stage of nucleation and the subsequent growth of particles due to OSA molecular deposition. From this model, developed on the basis of classical concepts of nucleation by Lose-Pound, it follows that the supersaturation of \(S_{N}(T)\), equal to \(C_{s} / C_{e}\), \(C_{e}\) (solubility of amorphous silica in water at temperature T), and pH are the main factors determining the rate of nucleation \(I_{N}\) of silicic acid in an aqueous solution.

The authors of [30] used two methods to study the OSA polymerization, transfer in nanocolloids, and nanosilica precipitation in synthetic solutions based on the \(Na_{2}SiO_{3}\) precursor: (1) the concentration model, when the rate of monomeric silica concentration \(C_{s}\) decrease is proportional to the 4-th order of \(k_{1} C_{s}^{4}\) and the rate of nanosilica transfer to precipitated silica is proportional to the 1-st order of \(k_{2} C_{nano}\); and (2) the supersaturated model, when the rate of monomeric silica concentration \(C_{s}\) decrease is proportional to the 4-th order of the difference \(k_{1} (C_{s} - C_{e})^{4}\), \(C_{e}\) — solubility of amorphous silica in the water at 25 °C. In the wide range of initial \(C_{s}\) 240–1200 mg/kg, ionic strength 0.01–0.24 mol/kg, and pH = 3–7 it was obtained that constants \(k_{1}\) and \(k_{2}\) did not differ for concentration and supersaturation models. The models cannot predict the sizes and distribution of \(SiO_{2}\) particles.

The method of molecular dynamic simulation for OSA polymerization was developed in [31,32] at the temperature up 2700 K and can provide the structure of polymerized clusters which was in accordance with the \(^{29}\)Si NMR method.

The models with different orders of polymerization reaction [8], taking into account the concentration of OH\(^-\) groups [33] and ionic strength [28] have been used for analysis of experimental results of orthosilicic acid polymerization in hydrothermal solutions [34].

In [35], the model of Weres-Yi-Tsao [29] has been applied to experimental results in hydrothermal solutions because it can predict not only time dependence of the OSA concentration but also evaluate how the average size of \(SiO_{2}\) nanoparticles depends on time. The main purpose of this work was to investigate nanoparticle size distribution dependence on the temperature, ionic strength, and other parameters of the polymerization process needed to regulate the characteristics of nanosilica sol, gel, and powders produced using the technology of hydrothermal synthesis [4–7]. For this purpose, it is necessary: (1) to study the dependence of surface tension \(\sigma_{sw}\), rate of molecular deposition \(R_{md}\), and Zeldovich factor \(Z\) on the temperature and pH to explain the mechanisms of their influence on the results of the polymerization process; (2) to examine the dependence of the average nanoparticle size and induction period on temperature, pH, and ionic strength; (3) to study the nanoparticle size distribution under conditions of time variable temperatures; (4) to verify the results of the numerical simulation with the experimental data in wide range of T, pH, and \(I_{s}\); and (5) to compare the results of the numerical simulation under time-variable temperature conditions at different technological stages of the hydrothermal sol production with the results of determining the average size of \(SiO_{2}\) nanoparticles and their size distribution using the DLS method.
2. Method of Numerical Simulation of OSA Polymerization

The initial concentration of molecules of orthosilicic acid formed due to dissolution of minerals of rocks [4–7] is determined using quartz solubility \( C_{cr} \) (mol/kg) of \( \alpha \)-quartz in water at the temperature \( T(K) \) [36]:

\[
\lg C_{cr} = -1.468 + \frac{252.9}{T} - \frac{3.217 \cdot 10^5}{T^2}.
\] (1)

After the hydrothermal solution reaches the surface pressure and the temperature decreases, the supersaturation of the solution depends on solubility \( C_e \) of amorphous silica [37]:

\[
\lg C_e = -0.1185 - \frac{1.126 \cdot 10^3}{T} + \frac{2.3035 \cdot 10^5}{T^2} - \frac{3.6784 \cdot 10^7}{T^3}.
\] (2)

Polymerization of orthosilicic molecules in oversaturated solution is provided by the formation of siloxane bonds and dehydration:

\[
H_4SiO_4 + H_4SiO_4 \rightarrow Si_2O_7H_6 + H_2O
\] (3)

The total silica concentration \( C_t \) in the solution is equal to the sum of the concentrations of colloid silica \( C_{col} \), soluble silicic acid \( C_s \), and ions of silicic acids \( C_{in} \):

\[
C_t = C_{col} + C_s + C_{in}.
\] (4)

The fraction of dimers does not exceed 1.0% from \( C_e \), the fraction of trimers is no more than 0.1% [26], the fraction of tetramers and low-molecular cyclic polymers is less than 0.1%, and the fraction of \( C_{in} \) does not exceed 14.0%.

The physical and chemical characteristics of the hydrothermal solution from the Mutnovsky geothermal electric plant are presented in the Table 1.

Table 1. Characteristics of the hydrothermal solution from the Mutnovsky field, ionic strength \( I_s = 14.218 \text{ mmol/kg} \), \( I_s = \sum c_j \cdot z_j^2 / 2 \), \( c_j \), \( z_j \) (concentration (mol/kg) and charge of the j-th ion in solution), \( (z_{Na} = 1, z_K = 1, z_{Ca} = 2, z_{Mg} = 2, z_{Al} = 3) \), pH = 9.35, electric conductivity \( \sigma_{el} = 1.1–1.3 \text{ mS/cm} \), \( n/c \)—not calculated.

| Component      | Concentration |
|----------------|---------------|
|                | mg/L          | mg equ/L     |
| Na\(^+\)       | 239.4         | 10.413       |
| K\(^+\)        | 42.0          | 1.074        |
| Ca\(^{2+}\)    | 1.6           | 0.0798       |
| Mg\(^{2+}\)    | 0.72          | 0.0592       |
| Fe\(^{2,3+}\)  | <0.1          | <0.0053     |
| Al\(^{3+}\)    | 0.27          | 0.033        |
| NH\(_4^+\)     | 1.1           | 0.0609       |
| Li\(^+\)       | 0.71          | 0.102        |
| Total cation concentration | 285.9 | 11.827 |
| Cl\(^-\)       | 198.5         | 5.591        |
| HCO\(_3^-\)    | 81.0          | 1.327        |
| CO\(_3^{2-}\)  | 19.9          | 0.663        |
| SO\(_4^{2-}\)  | 192.1         | 3.9995       |
| HS\(^-\)       | 4.95          | 0.15         |
| H\(_2\)S\(_0^0\)| 5.92          | -            |
| F\(^-\)        | n/d           | n/d          |
| Total anion concentration | 496.5 | 11.73 |
| H\(_3\)BO\(_3^\)  | 106.9         | nc           |
| (H\(_4\)SiO\(_4\))\(_h\) | 1190  | nc           |
| (H\(_4\)SiO\(_4\))\(_s\)  | 222           | nc           |
| Mineralization \( M_h \) | 1638.9   | nc           |
We developed the mathematical model \cite{29} which is based on the calculation of the rate of nucleation \( I_N \) (nuc\(l/\text{kg s} \)) dependent on oversaturation \( S_N \) (T) = \( C_e/C_c \):

\[
I_N = \frac{Q_{LP} \cdot Z \left( R_{md} \cdot A_{cr} \cdot N_A \cdot \rho \cdot M_{S_i}^{-1} \right)}{e^{-\Delta F_{cr}}}.
\]  
(5)

where \( \Delta F_{cr} \) is the change in free energy due to the formation of a nucleus of critical radius \( R_{cr} \), with a specific surface area \( A_{cr} \) = 4 \( \pi \) \( R_{cr}^2 \), and the number of Si\(O_2\) molecules \( n_{cr} \), \( \sigma_{sw} \) is the surface tension at the silica–water interface, \( R_{md} \) is the rate of molecular deposition of Si\(O_2\) on a solid surface, kg/(m\(^2\)-s), \( k_B = 1.38 \times 10^{-23} \) J/K, \( M_{S_i} = 0.060 \) kg/mol, \( N_A = 6.02 \times 10^{23} \) mol\(^{-1}\), \( Q_{LP} \) is the Lothe–Pound factor, \( Q_{LP} \) = 2200 kg/m\(^2\), and \( Z \) is the Zeldovich factor, calculated as follows:

\[
R_{cr} = 2 \cdot \frac{\sigma_{SW} \cdot M_{S_i}}{3 \cdot \rho \cdot N_A \cdot k_B \cdot T \cdot \ln S_N}.
\]  
(6)

\[
n_{cr} = \left( \frac{4 \pi}{3} \right) \cdot \left( \frac{\rho \cdot N_A \cdot M_{S_i}}{3 \cdot \sigma_{sw}^3} \right) \cdot \frac{M_{S_i}}{R_{cr}^3}.
\]  
(7)

\[
\Delta F_{cr} = \frac{\sigma_{SW} \cdot A_{cr}}{3} = \left( \frac{16 \cdot \pi}{3} \cdot \sigma_{sw}^3 \cdot \frac{M_{S_i}}{\rho \cdot N_A \cdot k_B \cdot T \cdot \ln S_N} \right)^2.
\]  
(8)

\[
Z = \left[ (\frac{\partial^2 \Delta F_{cr}}{\partial n_{cr}^2})/(2 \cdot \pi \cdot k_B \cdot T) \right]^{0.5} = \left( \frac{2}{3} \right) \cdot \left( \frac{3 \cdot M_{S_i}}{4 \cdot \pi \cdot \rho \cdot N_A \cdot M_{S_i}^2} \right)^{\frac{1}{2}} \cdot \left( \frac{\sigma_{sw}}{\rho \cdot k_B \cdot T} \right)^{0.5}.
\]  
(9)

with \( \rho = 2200 \) kg/m\(^3\)—the density of amorphous silica.

The function \( R_{md} \), which is the rate of molecular deposition of Si\(O_2\) as a function of temperature and pH of the solution, is expressed as follows in the model \cite{29}:

\[
R_{md} = F(pH, pH_{nom}) \cdot k_{OH}(T) \cdot f_t(S_a) \cdot \left( 1 - S_N^{-1} \right).
\]  
(10)

\[
\lg k_{OH} = 3.11 - \frac{4296.6}{T}.
\]  
(11)

\[
f_t = S_S^5, S_a < S_t.
\]  
(12)

\[
f_t = S_S^5 + 5 \cdot S_t^4 (S_a - S_t), S_a > S_t.
\]  
(13)

\[
\lg S_t = 0.0977 + \frac{75.84}{T}.
\]  
(14)

\[
F(pH, pH_{nom}) = h_1 \cdot f'(pH) + (1 - h_1) \cdot f'(pH_{nom}).
\]  
(15)

\[
f'(pH_{nom}) = \frac{f(pH_{nom})}{f(7.0)}.
\]  
(16)

\[
\lg f = pH - pK_i + \lg [Na^+].
\]  
(17)

The coefficient of surface tension \( \sigma_{sw} \) depends on temperature and pH via the function \( I(pH, pH_{nom}) \):

\[
\sigma_{sw} = H_\sigma - T \cdot S_\sigma - 2.302 \times 10^{-3} \cdot n_0 \cdot k_B \cdot T \cdot I(pH, pH_{nom}).
\]  
(18)

\[
I(pH, pH_{nom}) = 0.119 \int_{-\alpha}^{PH} F(pH', pH_{nom}(pH')) dP'H'.
\]  
(19)

where \( S_\sigma = (1 - \alpha_i) \cdot S_N \), \( \alpha_i \) is a fraction of silicic acid in ionic form, \( pH_{nom} = pH + \lg([Na^+] /0.069) \), [\(Na^+\)] is an ion activity [\(Na^+\)], mol/kg, \( pK_i = 6.4 \), \( f(7.0) = 0.119, h_1 = 0.45, H_\sigma \), and \( S_\sigma \) are specific enthalpy and entropy of silica surface in water, \( H_\sigma = 63.68 \times 10^{-3} \) J/m\(^2\), \( S_\sigma = 0.049 \times 10^{-3} \) J/m\(^2\)-K, and \( n_0 = 6.84 \times 10^{18} \) m\(^{-2}\) \cite{29}. 

---

*References to equations and constants are included where applicable.*
Time dependence $I_N(t)$ was calculated considering the induction time $\tau_{in}$ that is necessary to grow and form a stable population of the particles with sizes close to critical [29]:

$$I_N(t) = I_N \cdot \left(1 - e^{-\frac{t_p}{\tau_{in}}}\right).$$ (20)

$$\tau_{in} = 1.08 \cdot 10^{-6} \cdot (R_{md})^{-1} \cdot (Q_{LP} \cdot Z \cdot R_{cr}^2 \cdot \exp\left(\frac{-\Delta F_{cr}}{k_B T}\right))^{-0.25}.$$ (21)

Initial values were entered: the temperature $T$, pH, concentration of ions and ionic strength of the solution, total silica $C_t$ content, time step $DT_p$, initial radii $R(I)$, and particle quantity $MP(I)$ of every class “I”. The Runge–Cutt method was used for the numerical simulation.

The total content of colloid, monomeric silica, and the current value of supersaturation were estimated:

$$M_{col} = \sum_{I=1}^{I=N} 4 \cdot \pi \cdot R^3(I) \cdot MP(I) \cdot \frac{1}{3}. \quad (22)$$

$$C_s = C_t - M_{col}. \quad (23)$$

Solution degree of supersaturation $S_N$ was:

$$S_N = \frac{C_s}{C_e(T)}. \quad (24)$$

Then, the calculation of values of $\sigma_{sw}$, $R_{md}$, $R_{cr}$, $Z$, $\tau_{in}$, and $I_N(t)$ corresponding to the current values of $S_N$, pH, and T using the equations was undertaken.

The quantity of new particles appearing during the time $DT_p$ in accordance with the current value of nucleation rate $I_N$ on a given program step (N+1) was calculated and it was equal to the quantity of particles in the new class N+1:

$$MP(N+1) = I_N \cdot DT_p \quad (25)$$

The summary of the concentration of particles $CONP$ was calculated in a program cycle:

$$CONP = \sum_{I=1}^{I=N+1} MP(I). \quad (26a)$$

The increment in mass $DPM$ of every class “I” during the time $DT_p$ was calculated:

$$DPM(I) = 4 \cdot \pi \cdot R^2(I) \cdot R_{md} \cdot DT_p \quad (26b)$$

The calculation of particle radius $R(I)$ corresponding to a new value of particle mass in every class I was:

$$R(I) = \left(R^3(I) + \frac{3 \cdot DPM(I)}{4 \cdot \pi \cdot \rho}\right)^{\frac{1}{3}}. \quad (27)$$

The mean values of $R_a$, $R^2_a$, and $R^3_a$ in all classes of particles were estimated using the program cycle:

$$R_a = \sum_{I=N+1}^{I=N+1} \frac{R(I) \cdot MP(I)}{CONP}. \quad (28)$$

$$R^2_a = \sum_{I=N+1}^{I=N+1} \frac{R^2(I) \cdot MP(I)}{CONP}. \quad (29)$$

$$R^3_a = \sum_{I=N+1}^{I=N+1} \frac{R^3(I) \cdot MP(I)}{CONP}. \quad (30)$$
3. Results

3.1. Dependence of the Surface Tension $\sigma_{sw}$, Rate of Molecular Deposition $R_{md}$, and Zeldovich Factor $Z$ on the Temperature and pH

The main factors influencing the rate of the nucleation process $I_N$ and the final average particle size $R_a$ are the degree of temperature $T$, the degree of supersaturation $S_N(t)$, and pH. In addition, the final result of the numerical simulation is influenced by the functions $f(pH, pH_{nom})$ and $i(pH, pH_{nom})$, specified in the Equations (10)–(19). The results of the calculation of the function $f(pH)$ at different pH in the range from 4.0 to 8.7 are presented in Table 1.

With an increase in pH, the value of the $f(pH)$ function increases (Table 2). Consequently, with an increase in pH, the rate of molecular deposition of $R_{md}$ increases, and the $R_{md}$ parameter will strengthen the tendency to decrease the final average particle size. With an increase in the initial concentration of $C_s$, the rate of molecular deposition also increases (Figures 1 and 2). An increase in temperature has an inhomogeneous effect on the rate of molecular deposition (Figures 1 and 2): first, due to the increase in the kinetics of the process with increasing temperature, the rate of molecular deposition increases, then $R_{md}$ decreases, since with increasing temperature, the solubility of $C_e$ increases, the supersaturation of $S_N$ decreases, and the value of the rate of molecular deposition decreases. At a fixed pH, $R_{md}$ reaches a maximum at a certain temperature and the value of this maximum increases with an increase in the initial concentration (Figure 2).

Table 2. Values of function $f$ at different pH.

| pH  | $f(pH)$ | pH  | $f(pH)$ | pH  | $f(pH)$ |
|-----|---------|-----|---------|-----|---------|
| 4.0 | 0.00025 | 5.9 | 0.017   | 7.5 | 0.21    |
| 4.5 | 0.00079 | 6.0 | 0.022   | 8.0 | 0.32    |
| 5.0 | 0.0024  | 6.5 | 0.055   | 8.5 | 0.44    |
| 5.5 | 0.0075  | 7.0 | 0.119   | 8.7 | 0.49    |

An increase in the rate of molecular deposition with an increase in $C_s$ and temperature will contribute to an increase in the rate of nucleation $I_N$ of OSA and a decrease in the final average particle size.

![Figure 1. Cont.](image-url)
Figure 1. Cont.
Figure 1. Dependence of the rate of molecular deposition $R_{md}$ (g/(cm²·min)) on the temperature $t$ (°C) and concentration $C_s$ (mg/kg). (a) pH = 2.0; (b) pH = 4.0; (c) pH = 6.0; (d) pH = 8.0. $C_s = 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200$ mg/kg.

Figure 2. The temperature $t$ (°C) corresponded to the maximum rate of molecular deposition $R_{md}$ at different concentrations $C_s$, pH = 8.0.

An increase in the rate of molecular deposition with an increase in $C_s$ and temperature will contribute to an increase in the rate of nucleation $I_N$ of OSA and a decrease in the final average particle size.

The values of the function $i$ (pH) in the range from 6.0 to 8.7 are presented in Table 3. With an increase in pH, the value of the function $i$ (pH) increases. Consequently, the surface tension coefficient and the critical radius $R_{cr}$ reduced. The surface tension coefficient $\sigma_{sw}$ decreases with increasing temperature and with increasing pH in accordance with
Equations (18) and (19) (Figure 3a,b). Consequently, $\sigma_{sw}$ will be a factor that, with an increase in temperature and pH, will contribute to a decrease in the critical radius $R_{cr}$, an increase in the nucleation rate $I_N$, and a decrease in the final average particle size $R_a$, competing with the factor of reducing supersaturation $S_N$.

Table 3. Values of function $i$ at different pH.

| pH  | $i$ (pH) |
|-----|----------|
| 6.0 | 0.01     |
| 6.5 | 0.03     |
| 7.0 | 0.07     |
| 7.5 | 0.15     |
| 8.0 | 0.29     |
| 8.5 | 0.48     |
| 8.7 | 0.56     |

Figure 3. Dependence of the surface tension $\sigma_{sw}$ (mJ/m$^2$) on (a) temperature $t$ (°C) and (b) on pH. Initial concentration $C_s = 700$ mg/kg.
The physical meaning of the Zeldovich factor \( Z \), calculated using Equation (9), is that only a certain proportion of particles whose sizes have reached a critical radius continue to grow further. The remaining particles decrease in size. At the same time, the concentration of particles whose sizes are higher than the critical radius is less than the equilibrium concentration. With an increase in temperature at a constant pH, the value of the Zeldovich factor decreases, and at the same time its effect on the rate of nucleation \( I_N \) competes with the opposite effect associated with a decrease in the supersaturation of \( S_N \). An increase in pH leads to an increase in the values of the Zeldovich factor (Table 4).

### Table 4. Dependence of Zeldovich factor \( Z \) on the temperature and pH (-).

| \( t, ^\circ \text{C} \) | \( 4.0 \) | \( 4.5 \) | \( 5.0 \) | \( 5.5 \) | \( 6.0 \) | \( 6.5 \) |
|-----------------|-------|-------|-------|-------|-------|-------|
| 20              | \( 3.8 \times 10^{-2} \) | \( 3.8 \times 10^{-2} \) | \( 3.8 \times 10^{-2} \) | \( 3.8 \times 10^{-2} \) | \( 3.8 \times 10^{-2} \) | \( 3.9 \times 10^{-2} \) |
| 50              | \( 2.1 \times 10^{-2} \) | \( 2.1 \times 10^{-2} \) | \( 2.1 \times 10^{-2} \) | \( 2.1 \times 10^{-2} \) | \( 2.2 \times 10^{-2} \) | \( 2.2 \times 10^{-2} \) |
| 100             | \( 5.8 \times 10^{-3} \) | -     | \( 5.8 \times 10^{-3} \) | \( 5.8 \times 10^{-3} \) | \( 6.0 \times 10^{-3} \) | \( 6.1 \times 10^{-3} \) |
| 130             | \( 1.4 \times 10^{-3} \) | \( 1.3 \times 10^{-3} \) | \( 1.3 \times 10^{-3} \) | \( 1.4 \times 10^{-3} \) | \( 1.4 \times 10^{-3} \) | -     |

3.2. Results of the Numerical Simulation at Different Temperatures and pH: Average Particle Size, Induction Period, and the Particle Size Distribution

The results of numerical simulation showed (Table 5) that when the temperature increases at a constant pH the final average size of SiO\(_2\) nanoparticles increases because the degree of oversaturation and \( I_N \) become higher. When the pH decreases at a constant temperature the final average size increases (Table 5) due to the increase in the surface tension and the increase in the critical size of the nucleus \( R_{cr} \) and the decrease in \( I_N \). If the initial concentration of orthosilicic acid increases the final average size decreases because the degree of oversaturation increases, \( I_N \) increases, and \( R_{cr} \) decreases (Table 6).

### Table 5. Dependence of Zeldovich factor \( Z \) on the temperature and pH (-).

| \( t, ^\circ \text{C} \) | \( 4.0 \) | \( 4.5 \) | \( 5.0 \) | \( 5.5 \) | \( 6.0 \) | \( 6.5 \) |
|-----------------|-------|-------|-------|-------|-------|-------|
| 20              | \( 4.2 \times 10^{-2} \) | \( 4.8 \times 10^{-2} \) | \( 6.4 \times 10^{-2} \) | \( 1.1 \times 10^{-1} \) | \( 1.5 \times 10^{-1} \) | \( 3.3 \times 10^{-1} \) |
| 50              | \( 2.4 \times 10^{-2} \) | \( 2.8 \times 10^{-2} \) | \( 4.1 \times 10^{-2} \) | \( 7.6 \times 10^{-2} \) | \( 1.2 \times 10^{-1} \) | \( 3.5 \times 10^{-1} \) |
| 100             | \( 6.7 \times 10^{-3} \) | \( 8.2 \times 10^{-3} \) | \( 1.2 \times 10^{-2} \) | \( 3.1 \times 10^{-2} \) | \( 6.2 \times 10^{-2} \) | \( 8.6 \times 10^{-3} \) |
| 130             | \( 1.6 \times 10^{-3} \) | \( 2.1 \times 10^{-3} \) | \( 3.3 \times 10^{-3} \) | \( 1.0 \times 10^{-2} \) | -     | -     |

### Table 6. Values of the final mean size of silica particles (nm) under different temperatures \( t \) and initial concentrations of solution \( C_s \), pH = 8; (-) means that it was not estimated.

| \( C_s, \text{ mg/kg} \) | \( 20 \) | \( 40 \) | \( 50 \) | \( 60 \) |
|-----------------|-------|-------|-------|-------|
| 300             | 93.5  | -     | -     | -     |
| 350             | 12.4  | 1019.9| -     | -     |
Table 6. Cont.

| $C_S$, mg/kg | $t$, °C |
|--------------|---------|
|               | 20      | 40     | 50     | 60     |
| 400          | 4.35    | 49.1   | 586.3  | -      |
| 500          | 1.79    | 4.08   | 8.96   | 32.7   |
| 600          | 1.246   | 1.84   | -      | 3.80   |
| 700          | 0.87    | 1.05   | -      | 1.31   |
| 800          | 0.73    | 0.83   | -      | 0.95   |
| 1000         |         |        |        |        |

| $C_S$, mg/kg | $t$, °C |
|--------------|---------|
|               | 70      | 80     | 85     | 90     |
| 300          | -       | -      | -      | -      |
| 350          | -       | -      | -      | -      |
| 400          | -       | -      | -      | -      |
| 500          | -       | -      | -      | -      |
| 600          | 7.56    | 24.14  | 56.14  | 169.8  |
| 700          | -       | 3.48   | -      | 6.49   |
| 800          | -       | 1.81   | -      | 2.30   |
| 1000         | -       | 1.10   | -      | 1.21   |

After nucleation and polymerization completion the fraction of dimers is not more than 1.0 % of solubility $C_e(T)$, the concentration of trimers is about 0.1 %, and the concentration of tetramers and polymers with circular structures of less than 6 units of SiO$_2$ is lower than 0.1 % [26].

The concentration of ions H$_3$SiO$_4^-$ and H$_2$SiO$_4^{2-}$ is not more than 14.0 % calculated from the dependences of constants of orthosilicic acid ionization of the first $K_1$ and second $K_2$ stages:

$$
\lg K_1 = -\frac{2549}{T} - 15.36 \cdot 10^{-6} \cdot T^2
$$

$$
\lg K_2 = 5.37 - \frac{3320}{T} - 20 \cdot 10^{-3} \cdot T
$$

The function of oversaturation $S_N$ vs. time $T_p$ showed the long period of induction $\tau_{in}$ and homogeneous nucleation which becomes much longer at low values of pH when $S_N$ changes slightly and the period of rapid growth of SiO$_2$ nanoparticles when $S_N$ decreases sharply (Figures 4 and 5, Table 7). The number of new particles $PNS$ depending on the duration of nucleation $T_p$ reached a constant value when the rate of nucleation $R_{nuc}$ rapidly decreased (Figures 4 and 5). The period of homogeneous nucleation increases when pH decreases and the initial degree of oversaturation $S_N$ decreases at higher temperatures and low initial $C_s$ concentrations (Table 7). The relation $(t_{hom}/t_{hetg})$ increases when the temperature increases and pH decreases (Table 7).

![Figure 4](image-url)  
*Figure 4. The number of new particles PNS (nucl/kg) versus time $T_p$; $T = 50 °C$, the initial concentration is $C_s = 700$ mg/kg, pH $= 8$.**
Figure 5. The rate of nucleation \( R_{\text{nuc}} (\text{nucl}/(\text{kg} \cdot \text{s})) \) versus time \( T_p \); \( T = 50 \, ^\circ\text{C} \), the initial concentration is \( C_a = 700 \, \text{mg/kg} \), pH = 8.

Table 7. Durations of homogeneous \( t_{\text{hom}} \) and heterogeneous \( t_{\text{hetg}} \) nucleation at different temperatures, pH, \( C_s \).

| Temperature, °C | pH | Initial OSA Concentration \( C_a \), mg/kg | \( t_{\text{hom}} \), min | \( t_{\text{hetg}} \), min | \( t_{\text{hom}}/t_{\text{hetg}} \) |
|-----------------|----|---------------------------------|-----------------|-----------------|-----------------|
| 20              | 5  | 700                             | 80.385.3        | 4.369.195       | 0.018398        |
| 20              | 6  | 700                             | 825.45          | 454.617.5       | 0.013199        |
| 20              | 7  | 700                             | 749.63          | 81.199.24       | 0.009241        |
| 20              | 8  | 700                             | 50.20           | 513.377         | 0.009779        |
| 50              | 5  | 700                             | 118.281.1       | 3.027.379       | 0.039968        |
| 50              | 6  | 700                             | 11.123.75       | 250.812.4       | 0.044351        |
| 50              | 7  | 700                             | 715.82          | 20.328.97       | 0.035215        |
| 50              | 8  | 700                             | 13.47           | 776.68          | 0.007375        |
| 80              | 5  | 700                             | 4.352.938       | 7.15.10^2       | 0.0608          |
| 80              | 6  | 700                             | 373.867.6       | 5.374.710       | 0.067065        |
| 80              | 7  | 700                             | 10.519.41       | 143.413.7       | 0.07335         |
| 80              | 8  | 700                             | 19.635          | 328.12          | 0.05984         |
| 100             | 5  | 700                             | 7.07.10^6       | 5.32.10^10      | 0.133           |
| 100             | 6  | 700                             | 4.89.10^6       | 3.53.10^6       | 0.139           |
| 100             | 7  | 700                             | 32.828.60       | 2.19.10^7       | 0.15            |
| 100             | 8  | 700                             | 116.61          | 638.40          | 0.182           |
| 120             | 5  | 700                             | 1.08.10^19      | 4.94.10^19      | 0.219           |
| 120             | 6  | 700                             | 3.95.10^17      | 1.78.10^18      | 0.22            |
| 120             | 7  | 700                             | 4.71.10^13      | 1.87.10^14      | 0.252           |
| 120             | 8  | 700                             | 26.324.92       | 7.435.34        | 0.3584          |

In Figure 6, the distributions of the number of particles vs. radius formed at constant \( T = 50–60 \, ^\circ\text{C} \), pH = 4 and 8, and initial OSA concentrations \( C_a = 700 \) and 800 mg/kg are shown. The form of the function of SiO\(_2\) particle number distribution by radius has a maximum corresponding to the average radius \( R_a \). Figure 6 shows an asymmetrical distribution, that is the right branch of the silica particle size distribution formed at constant temperature is convex and the left branch is concave.

Figure 6. Cont.
The average radius of SiO$_2$ nanoparticles and the distribution by radius were determined using the method of dynamic light scattering (DLS). Values $R_a$ were in the range from 5.0 up to 20.0 nm and values of particles radii were in the range from 1.0 up to 50.0 nm [4–7].

3.3. Simulation of OSA Polymerization at Different Ionic Strengths

The dependence of $C_s(T_p)$ is also affected by the ionic strength of the $I_s$ solution. The simulation results were obtained at $t = 20$ °C, pH = 8.0, and $C_s = 700$ mg/kg and various values of $I_s$: 0.014, 0.07, 0.14, 0.28, 0.4, 0.8, 1.0, 1.2, 1.4, 7.1, 10.6, and 14.2 mol/kg. With an increase in $I_s$ from 0.014 to 0.8 mol/kg, the $C_s(T_p)$ dependence shifts to the left and acquires a concave shape (Figure 7a,b). In the range of ionic strength values from 0.8 to 1.4 mol/kg, with an increase in $I_s$, the rate of decrease of $C_s(T_p)$ was lower and the curves shift to the right. The shape of the curves becomes convex. At values of $I_s > 1.4$ mol/kg, the curves $C_s(T_p)$ are shifted to the left again.

The dependence of the final average particle size on the ionic strength of the $I_s$ solution is non-monotonic also (Table 8, Figure 8). With an increase in $I_s$ from 0.014 to 0.8 mol/kg, $R_a$ increases. Starting from the value $I_s = 0.8$ mol/kg, the final average particle size decreases. This non-monotonic dependence is explained by the fact that with an increase in $I_s$, the rate of molecular deposition of $R_{md}$ increases due to an increase in the degree of ionization of orthosilicic acid $\alpha_{SIIL}$. Therefore, the rate of nucleation of OSA $I_N$ increases (Equation (5)). At the same time, the growth rate of the formed particles increases (Equation (10)). Thus, the final average size of silica particles is influenced by...
two competing factors—growth of $I_N$ and $R_{md}$ which determines the non-monotonic behavior of the $R_a (I_s)$ dependence.

![Graph](image-url)

**Figure 7.** The dependence of the concentration of dissolved silicic acid (a) and supersaturation (b) on time. $t = 20 \, ^\circ C$, pH = 8.0, initial concentration $C_s = 700 \, mg/kg$, and various values of ionic strength (mol/kg).
Table 8. The final average size of silica particles in solutions with different ionic strength values. 
\( t = 20 \, ^{\circ}C, \text{pH} = 8.0, \) and \( C_s = 700 \, \text{mg/kg}. \)

| \( I_s, \, \text{mol/kg} \) | \( R_{av}, \, \text{nm} \) | \( I_s, \, \text{mol/kg} \) | \( R_{av}, \, \text{nm} \) | \( I_s, \, \text{mol/kg} \) | \( R_{av}, \, \text{nm} \) |
|------------------------|---------------|------------------------|---------------|------------------------|---------------|
| 0.014                  | 0.99          | 0.4                    | 1.048         | 1.4                    | 1.042         |
| 0.07                   | 1.029         | 0.8                    | 1.049         | 7.1                    | 0.9           |
| 0.14                   | 1.036         | 1.0                    | 1.047         | 10.6                   | 0.79          |
| 0.28                   | 1.044         | 102                    | 1.045         | 14.2                   | 0.7           |

Figure 8. Particle size distribution with different ionic strength values. \( t = 20 \, ^{\circ}C, \text{pH} = 8.0, \) and initial concentration \( C_s = 700 \, \text{mg/kg}, I_s \, (\text{mol/kg}). \)

3.4. Simulation of OSA Polymerization under Time-Variable Temperatures

A significant influence of the variable temperature regime on the rate of the OSA nucleation process and the final average size of silica particles was revealed.

To simulate the process of nucleation of OSA under variable temperature conditions, the following law of temperature \( t \) reduction with polymerization time \( T_p \) was chosen:

\[
t = t_2 + (t_1 - t_2) \cdot e^{-\frac{T_p}{\tau_0}}
\]  

(33)

Dependence (1.34) corresponds to the rate of heat \( q, \, \text{W}/(\text{m}^2\cdot\text{s}) \) exchange with an environment with a constant temperature \( t_0 \) according to Newton’s law \( q = \alpha \cdot F \cdot (t - t_0) \), \( t_1, t_2 \) are the initial and final temperatures of the solution; \( \alpha \)—coefficient of heat exchange \( W/(\text{m}^2\cdot\text{s} \cdot ^{\circ}\text{C}) \); \( F \)—area of heat exchange, \( \text{m}^2 \); \( \tau_0 \)—the characteristic cooling time of the solution. Calculations were performed at \( t_1 = 100 \, ^{\circ}C \) and \( t_2 = 20 \, ^{\circ}C \) for solutions of the Mutnovsky hydrothermal field at \( C_s = 700 \, \text{mg/kg} \) and \( \text{pH} = 8.0 \); \( \tau_0 \) was taken to be 120, 240, 360, and 480 min.

Figure 9 shows that the smaller the \( t_{1n0} \), the higher the level of supersaturation of \( S_N \). Consequently, the rate of OSA nucleation increases. This leads to a decrease in the final average particle size.

The effect of the initial concentration on the rate of the nucleation process and the final average size of silica particles in the variable temperature regime turned out to be ambiguous. The temperature was lowered from 100 to 20 \( ^{\circ}C \), \( \text{pH} = 8.0 \), and \( \tau_{1n0} = 360 \) min. The
initial concentration assumed various constant values—500, 600, 700, 800, and 1000 mg/kg. Figure 10 shows a comparison of the dependencies obtained.

At variable temperatures, the supersaturation functions of time have a non-uniform behavior. The supersaturation of the solution $S_N = C_s / C_e$ depends on the solubility of $C_e$, which decreases, and faster than the value of the concentration of $C_s$.

Figures 9c and 10c show a more symmetrical distribution, that is both branches of the silica particle size distribution are convex in contrast to the case of constant temperatures when the right was convex and the left was concave. Thus, the temperature regime at the stage of polymerization strongly influenced the index of polydispersity of hydrothermal sols and the density, morphology, agglomerate dimensions, volume, surface, diameters, and structures of pores of nanopowders produced from hydrothermal sols [5].

Figure 9. Cont.
Figure 9. The time dependences of the concentration of dissolved silicic acid $C_s$ (a), supersaturation (b), and particle size distribution (c). The temperature decreases from $100$ to $20 \, ^\circ C$, $pH = 8.0$, and $C_s = 700 \, mg/kg$. 

Figure 10. Cont.
Figure 10. Dependence of $C_s$ on $T_p$ (a), $S_N$ on $T_p$ (b), and particle size distribution (c). The temperature decreases from 100 to 20 °C and $\tau_{un0} = 360$ min.

3.5. Comparison of the Experimental Data with Results of the Numerical Simulation

Experimental data $C_s(T_p)$ obtained in sodium silicate solutions with Na$^+$ cations removed by ion exchange and low ionic strength [26] were in agreement with the results of numerical simulation in the wide range of temperatures and initial OSA concentration $C_s$ (Figure 11) [35]:

- $t = 30, 90, 120, 150, 180$ °C,
- $C_s = 383, 620, 110, 1200$ mg/kg,
- $\text{pH} = 7.0, 7.4, 7.85$;
- $I_s = 0.000132–0.00134$ mol/kg.

Figure 11. Comparing the experimental data [19] with the results of the numerical simulation. (a) $t = 30$ °C, $C_s = 383$ mg/kg, pH 7.0; (b) $t = 150$ °C, $C_s = 1008$ mg/kg, pH 7.85. $I_s = 0.000132–0.00134$ mol/kg. ▪—results of the simulation; ▲—experimental data.
The comparison of the experimental data on OSA polymerization and the results of the numerical simulation for the solution of the Pauzhetsky hydrothermal field showed that the discrepancy of about 12–14.2% was within the uncertainty of the yellow molybdate method for determining the concentration of dissolved silicic acid for the following conditions [35]:

\[ t = 20 \, ^\circ\text{C}; \ C_s = 315.6–338 \, \text{mg/kg}; \ \text{pH} = 8.2–8.35; \ \text{and} \ I_s = 0.04284 \, \text{mol/kg}. \]

The results of the simulation of OSA polymerization at the temperatures of 84–95 °C and high ionic strength for solutions with different chemical compositions showed an agreement with the experimental data obtained at Wairakei and Broadlands hydrothermal fields [35]:

\[ t = 84 \, ^\circ\text{C}, \ \text{pH} = 8.1, \ \text{and} \ C_s = 570 \, \text{mg/kg} \ (\text{Wairakei}); \ t = 95 \, ^\circ\text{C}, \ \text{pH} = 8.0, \ \text{and} \ C_s = 620 \, \text{mg/kg} \ (\text{well 11 at Broadlands}); \ t = 95 \, ^\circ\text{C}, \ \text{pH} = 7.7, \ \text{and} \ C_s = 900 \, \text{mg/kg} \ (\text{well 22 at Broadlands}); \ I_s = 0.05–0.06 \, \text{mol/kg}. \]

The results of the simulation of the distribution of the number of SiO$_2$ nanoparticles vs. radius for solutions in which OSA polymerized at the temperatures 33–43 °C, pH = 6.7–8.1, $C_s = 366–546 \, \text{mg/kg}$, and $I_s = 0.043 \, \text{mol/kg}$ corresponded to the results of particles radii measured using the DLS method [35,38] in the range of 50–225 nm.

The experimental results of [24,25] on the maximum nucleation rate $v_{\text{max}}$ determined as $(C_{s2} - C_{s1})/(T_{p2} - T_{p1})$ were in agreement with the results of the numerical simulation in the region of pH = 4–6, in which the model used [35] was applicable (pH = 4–8).

The comparison of the average diameter measured using helium chromatography in a synthetic solution with an initial $C_s = 880 \, \text{mg/kg}$ at 20 °C and pH = 7.0 [39] were in good agreement with results of the numerical simulation [35].

The values of the $k_1$ constant for concentration and supersaturation models obtained in [30] for synthetic solutions in the wide range of initial $C_s = 240–1200 \, \text{mg/kg}$, ionic strength 0.01–0.24 mol/kg, and pH = 3–7 corresponded to the times $T_p$ of $C_s$ decrease calculated in our numerical simulations for the same conditions.

The experimental results [35] with $C_s(T_p)$ curves characterized by $k_p$ constants of the OSA reaction of the polymerization at different temperatures 20–50 °C, different pH = 4–8.5, and ionic strengths 0.01–1.1 mol/kg corresponded to the models [8,28,33].

4. Simulation the Particle Size Distribution in Hydrothermal Sol Production Technology

The technological flow sheet for the solution of the Mutnovsky geothermal electric power plant GeoPP includes the well, separator, pipe silencer, tank for the solution cooling and aging to develop OSA polymerization, ultrafiltration membrane module, and volumes for concentrated sol, Figure 12a. The temperature decreases with the linear dependence in every element from the well to silencer from 300 to 96 °C at pH = 8.0 and with the dependence (1.33) in the aging tank in which the temperature decreases from 96 to 70 °C.

When the duration of aging was 20 h and taun = 11 h, the average SiO$_2$ nanoparticle radius calculated using the numerical simulation was 12.5 nm (Figure 12b) and it was 12.9 nm measured using the DLS method. When the duration of aging was 100 h and taun = 15 h, the final average diameters were 68.6 and 66 nm using the DLS method. If pH = 5.0, the temperature decrease during aging of 24 h was from 96 to 23 °C, taun = 12 h, and the calculated diameter was 160 nm and the diameter measured using the DLS method was 154 nm.

The temperature and aging duration can be varied to regulate the average particle diameter from 5 to 160 nm.

For the solution from wells at Cerro Prieto GeoPP with the values $C_s = 950 \, \text{mg/kg}$, pH = 7.3, $I_s = 0.4227 \, \text{mol/kg}$, aging duration 65 min, taun = 60 min, and temperature decrease from 100 to 30 °C [23,24], the final average radius calculated in the present work was $R_A = 1.32 \, \text{nm}$ and it was 1.35 nm as a result of the calculation in [29].

For the solutions of the Wairakei GeoPP, New Zealand, at aging temperatures of 70 and 20 °C during 50 h, $C_s = 490 \, \text{mg/kg}$, and $I_s = 0.05 \, \text{mol/kg}$, the calculated average radii were 60.7 and 9.5 nm, and the radii measured using DLS were 60 and 10 nm.
showed the long period of induction for the SiO2 nanoparticles, and the form of the particle size distribution. The main parameters that determine the kinetics of colloid phase formation, the final average size of nanoparticles, and the form of the particle size distribution are the temperature, pH, initial OSA concentration, and ionic strength. The temperature decreases at higher temperatures and low initial concentration of OSA in a hydrothermal solution and on the SiO2 nanoparticle size distribution. The increase in the surface tension and the critical size of the nucleus. The average radius increases when the pH decreases due to the increase in the surface tension and the critical size of the nucleus. The average radius decreases when the initial OSA concentration and degree of oversaturation increases.

The function of oversaturation $S_N$ depending on the time of polymerization $T_p$ showed the long period of induction $\tau_{in}$ and homogeneous nucleation which becomes much longer at low values of pH. The period of homogeneous nucleation increases when pH decreases and the initial degree of oversaturation $S_N$ decreases at higher temperatures and low initial concentration of OSA.

5. Conclusions

The mathematical model we adopted allowed us to investigate the influence of various physical and chemical factors in a wide range of values on the rate of polymerization of OSA in a hydrothermal solution and on the SiO2 nanoparticle size distribution. The results of the numerical simulation were verified using a comparison with experimental data. The temperature, pH, initial OSA concentration, and ionic strength are the main parameters that determine the kinetics of colloid phase formation, the final average size of SiO2 nanoparticles, and the form of the particle size distribution.

The final average radius decreases when the temperature decreases, and the degree of oversaturation becomes higher taking into account the surface tension, rate of molecular deposition, and Z-factor. The average radius increases when the pH decreases due to the increase in the surface tension and the critical size of the nucleus. The average radius decreases when the initial OSA concentration and degree of oversaturation increases.

The particle size distribution based on DLS results. $d$ is the particle diameter, nm. Well 054 at the Mutnovsky field.
Cs concentrations. The relation of homogeneous and heterogenous durations (t_{hom} / t_{hetg}) increases when the temperature increases and pH decreases.

The dependence of the curve Cs vs. Tp and final average particle size Ra on the ionic strength Is is non-monotonic. With an increase in Is from 0.014 to 0.8 mol/kg, the kinetics of OSA polymerization accelerate, but Ra increases. Starting from the value of Is = 0.8 mol/kg, the final average particle size decreases. This non-monotonic dependence is explained by the fact that with an increase in Is, the rate of molecular deposition of R_md increases due to an increase in the degree of ionization of orthosilicic acid αSIL. Therefore, the rate IN of OSA nucleation increases. At the same time, the growth rate of the formed particles increases. Thus, the final average size of silica particles is influenced by two competing factors—the increases in IN and R_md which determine the non-monotonic behavior.

At variable temperatures, the supersaturation functions of time have a non-uniform behavior. The supersaturation of the solution SN = Cs / Ce depends on the solubility of Ce, which decreases, and faster than the value of the concentration of Cs. Both branches of the silica particle size distribution are concave in contrast to the case of constant temperatures. The variation in temperatures during the stage of OSA polymerization can influence the index of polydispersity of particles, its distribution regarding sizes, and the homogeneity and symmetrical form of the distribution. The temperature regime at the stage of polymerization highly influenced the index of polydispersity of hydrothermal sols and, thus, the density, morphology, agglomerate dimensions and fractal structures, volume, surface, diameters, and structures of pores of nanopowders produced from hydrothermal sols.

The results obtained can be used for regulating the kinetics of SiO$_2$ nanoparticle formations, sizes, the polydispersity of the distribution of sizes, and the concentrations of nanoparticles in the technology of the hydrothermal synthesis of sol, gel, and powder. The results can be applied to the technology of the production of synthetic water sols based on Na$_2$SiO$_3$ precursors and the technology of precipitated silica.

**Author Contributions:** Conceptualization, V.V. Potapov and A.A. Cherepyanov; methodology, V.V. Potapov and A.A. Cherepyanov; investigation, V.V. Potapov, A.A. Cherepyanov and D.S. Gorev; data curation, V.V. Potapov and A.A. Cherepyanov; writing—original draft preparation, V.V. Potapov, A.A. Cherepyanov and D.S. Gorev; writing—review and editing, V.V. Potapov and D.S. Gorev; supervision, V.V. Potapov. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Meng, L.; Duwal, S.; Lane, J.M.D.; Ao, T.; Stoltzfus, B.; Knudson, M.; Park, C.; Chow, P.; Xiao, Y.; Fan, H.; et al. Pressure Induced Assembly and Coalescence of Lead Chalcogenide Nanocrystals. *J. Am. Chem. Soc.* 2021, 143, 2688–2693. [CrossRef] [PubMed]

2. Dubey, R.; Rajesh, Y.; More, M. Synthesis and Characterization of SiO$_2$ Nanoparticles via Sol-gel Method for Industrial Applications. *Mater. Today Proc.* 2015, 2, 3575–3579. [CrossRef]

3. Duan, H.; Wang, D.; Li, Y. Green chemistry for nanoparticle synthesis. *Chem. Soc. Rev.* 2015, 44, 5778–5792. [CrossRef] [PubMed]

4. Potapov, V.; Fediuk, R.; Gorev, D. Obtaining sols, gels and mesoporous nanopowders of hydrothermal nanosilica. *J. Sol-Gel Sci. Technol.* 2020, 94, 681–694. [CrossRef]

5. Potapov, V.; Fediuk, R.; Gorev, D. Hydrothermal SiO$_2$ Nanopowders: Obtaining Them and Their Characteristics. *Nanomaterials* 2020, 10, 624. [CrossRef]

6. Potapov, V.; Fediuk, R.; Gorev, D. Membrane concentration of hydrothermal SiO$_2$ nanoparticles. *Sep. Purif. Technol.* 2020, 251, 117290. [CrossRef]

7. Potapov, V.; Efimenko, Y.; Fediuk, R.; Gorev, D. Effect of hydrothermal nanosilica on the performances of cement concrete. *Constr. Build. Mater.* 2020, 269, 121307. [CrossRef]

8. Iler, R.K. Polymerization of polycilicic acid derived from 3.3 ratio sodium silicate. *J. Phys. Chem.* 1953, 57, 604–607. [CrossRef]
9. Alexander, G.B. The Reaction of Low Molecular Weight Silicic Acids with Molybdic Acid. J. Am. Chem. Soc. 1953, 75, 5655–5657. [CrossRef]
10. Alexander, G.B. The Polymerization of Monosilicic Acid. J. Am. Chem. Soc. 1954, 76, 2094–2096. [CrossRef]
11. Schwarz, R.; Knaff, K.G. Zur Kenntnis der Kieselsäuren. X. Über Alkoxyssilane und Oligokieselsäuren. Z. Für Anorg. Und Allg. Chem. 1954, 275, 176–192. [CrossRef]
12. Bechtold, M.F. Polymerization and Properties of Dilute Aqueous Silicic Acid from Cation Exchange. J. Phys. Chem. 1955, 59, 532–541. [CrossRef]
13. Goto, K.J. States of silica in aqueous solutions. II. Chem. Soc. Jap. Pure Chem. Sect. 1955, 76, 1364–1366.
14. Marshall, W.L. Amorphous Silica Solubilities: I. Behaviour in Aqueous Sodium Nitrate Solutions: 25–300 °C, 0–6 Molal. Geochim. Cosmochim. Acta 1980, 44, 907–913. [CrossRef]
15. Hoebbel, D.; Wieker, W. Über Kondensationsreaktionen der Monokieselsäure. Z. Für Anorg. Und Allg. Chem. 1973, 400, 148–160. [CrossRef]
16. Hoebbel, D.; Wieker, W. Über die dünnschichtchromatographische Trennung trimethylsilylierter Kieselsäuren. Z. Für Anorg. Allg. Chem. 1974, 405, 163–166. [CrossRef]
17. Baumann, H. Polymerization and depolymerization de kieselsaure unter verschiedenen begingungen. Kolloid-Z. 1959, 162, 28–35. [CrossRef]
18. Ginzburg, F.L.; Sheidina, L.D. Radiochemistry. 1955, 76, 1364–1366.
19. Hoch, B.G. The Polymerization of Monosilicic Acid. J. Am. Chem. Soc. 1954, 76, 2094–2096. [CrossRef]
20. Okkerse, C. Submicroporous and Macroporous Silica. Ph.D. Thesis, Delft, The Netherlands, 1961.
21. Richardson, E.; Waddams, J.A. Use of the silico-molybdate reaction to investigate the polymerization of low molecular weight silicic acids in dilute solutions. Res. Corresp. 1954, 7, 43.
22. Tarutani, T. Chromatographic behavior of silicic acid on sephadex columns. J. Chromatogr. 1970, 50, 523–526. [CrossRef]
23. Makrides, A.K.; Turner, M.; Slaughter, J. Condensation of silica from super-saturated silicic acid solutions. J. Colloid Interface Sci. 1980, 73, 345–367. [CrossRef]
24. Frolov, Y.G.; Shabanova, N.A.; Popov, V.V. Influence of temperature and pH on polycondensation of silicic acid in an aqueous medium. Colloid. J. 1983, 45, 179–182.
25. Frolov, Y.G.; Shabanova, N.A.; Popov, V.V. Polycondensation silicic acid in an aqueous medium. Influence of the concentration of silicic acid. Colloid. J. 1983, 45, 382–386.
26. Rothbaum, H.; Rohde, A. Kinetics of silica polymerization and deposition from dilute solutions between 5 and 180 °C. J. Colloid Interface Sci. 1979, 71, 533–559. [CrossRef]
27. Coudurier, M.; Baudru, R.; Donnet, J.B. Etude de la polycondensation de l’acide disilique. Bull. Soc. Chem. Fr. 1971, 9, 3154–3160.
28. Fleming, B.A. Kinetics of reaction between silicic acid and amorphous silica surfaces in NaCl solutions. J. Colloid Interface Sci. 1986, 110, 40–64. [CrossRef]
29. Weres, O.; Yee, A.; Tsao, L. Kinetics of silica polymerization. J. Colloid Interface Sci. 1981, 84, 379–402. [CrossRef]
30. Conrad, C.F.; Icopini, G.A.; Yasuhara, H.; Bandstra, J.Z.; Brantley, S.L.; Heaney, P.J. Modeling the kinetics of silica nanocolloid formation and precipitation in geologically relevant aqueous solutions. Geochim. Et Cosmochim. Acta 2007, 71, 531–542. [CrossRef]
31. Garofalini, S.H.; Martin, G. Molecular Simulations of the Polymerization of Silicic Acid Molecules and Network Formation. J. Phys. Chem. 1994, 98, 1311–1316. [CrossRef]
32. Rao, N.Z.; Gelb, L.D. Molecular Dynamics Simulations of the Polymerization of Aqueous Silicic Acid and Analysis of the Effects of Concentration on Silica Polymorph Distributions, Growth Mechanisms, and Reaction Kinetics. J. Phys. Chem. B 2004, 108, 12418–12428. [CrossRef]
33. Greenberg, S.A. Polymerization of silicic acid in alkaline solutions a kinetics study. J. Polym. Sci. 1958, 27, 523–527. [CrossRef]
34. Potapov, V.V.; Serdan, A.A.; Kashpura, V.N.; Gorbach, V.A.; Tyurina, N.A.; Zubakha, S.V. Polycondensation of orthosilicic acid in hydrothermal solutions at different temperatures, pH values, and ionic strengths. Glas. Phys. Chem. 2007, 33, 44–49. [CrossRef]
35. Potapov, V.V.; Cerdan, A.A.; Kashutina, I.A. Numerical Simulation of the Polycondensation of Orthosilicic Acid and of the Formation of Silica Particles in Hydrothermal Solutions. J. Volcanol. Seism. 2019, 13, 216–225. [CrossRef]
36. Crerar, D.A.; Anderson, G.M. Solubility and solvation reactions of quartz in dilute hydrothermal solutions. Chem. Geol. 1971, 8, 107–122. [CrossRef]
37. Marshall, W.L. Amorphous Silica Solubilities: I. Behaviour in Aqueous Sodium Nitrate Solutions: 25–300 °C, 0–6 Molal. Geochim. Cosmochim. Acta 1980, 44, 907–913. [CrossRef]
38. Ohsawa, S.; Kawamura, T.; Nakamatsu, N.; Yusa, Y. Geothermal blue water colored by colloidal silica. In Proceedings of the World Geothermal Congress, Kyushu, Tohoku, Japan, 28 May–10 June 2000; pp. 663–668.
39. Crerar, D.A.; Axtmann, E.V.; Axtmann, R.C. Growth and ripening of silica polymers in aqueous solutions. Geochim. Cosmochim. Acta 1981, 45, 1259–1266. [CrossRef]