

Preheating of silicic acid in silica sol production

Master's Thesis in Innovative and Sustainable Chemical Engineering

YLVA GRAMPP

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Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2018

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Master's thesis KBTX12
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Cover:
A reactor for silica sol production with preheating of the feed.

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Abstract

Silica sols dispersed in water are produced by AkzoNobel Specialty Chemicals. A recipe for the manufacturing of the specific sol studied in this thesis is provided by AkzoNobel. The production of the studied sol includes ion exchange of sodium silicate to silicic acid. Silicic acid then polymerizes and grows to spherical particles by a condensation reaction. To reach a specific size of the sol particles, a sol of smaller particles - a heel - is further grown in a semi-batch reactor by addition of silicic acid, and sodium silicate to keep the pH at a desired level.

The reactor is kept at an elevated temperature to increase the rate of reaction. The heating is currently done with steam in the reactor jacket. Both steam and cooling water consumption would decrease if the silicic acid were to be preheated before addition with an existing hot stream of the process. If the silicic acid can be preheated to 70°C for the studied sol, the savings of steam is calculated as 154 SEK/tonne product.

Due to the reactivity of silicic acid, preheating may cause nucleation and polymerization of silica particles before the feed has reached the reactor and thus affect the particle size distribution. The particle size distribution of a silica sol can be measured with an electrospray differential mobility analyser.

Experiments were performed in lab-scale with a reactor and a water bath as heat exchanger. It was shown that a high preheating temperature results in a new particle formation in addition to condensation on existing particles in the heel, causing a bimodal particle size distribution as opposed to the more often desired monodisperse particle size distribution. The preheating temperature had a greater effect on silicic acid that had been stored and close to no effect on silicic acid fresh from the ion exchanger.

Keywords: colloidal silica, silica sol, preheating, silicic acid, buildup method, column method

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1 Introduction

Made of essentially sand and water, aqueous silica sol is regarded as an environmentally friendly product and has a wide range of applications [1–4]. Since it is stable and has a high specific surface area it is commonly used as a base for catalysts and adsorbers. Silica sols can be used in high-temperature insulating materials and for precision casting as a binding agent. Other applications include beverage clarification, water treatment, and surface polishing, especially for silicon wafers in the electronics industry. They can be added to cement to increase the strength and stability, and into coatings to improve hardness and achieve anti-soiling properties. Silica sols are also used in the pulp and paper industry as a retention aid in papermaking.

The process to produce silica sol has a history that stretches back to the early 1900s [5]. The first patent for commercial production of silica sol was announced in 1915, where Schwering used electro dialysis to manufacture a pure and stable sol of 2.4% silica [6]. A stable silica sol to reach a concentration of 10% silica was first marketed in 1933. In 1941, Bird patented a novel way to manufacture silica sol, starting from water glass and using an ion exchange process [7]. This is still the foundation of the commercial processes used today. It was further improved by Bechtold and Snyder in 1951 and since then it has been possible to manufacture highly concentrated colloidal silica of a uniform and controlled size [5].

This thesis is performed in collaboration with AkzoNobel Specialty Chemicals, which produces silica sols dispersed in water. The production currently within AkzoNobel dates back to 1956 when a colloidal silica plant was started in Leverkusen, Germany. The product range today includes silica sol with a particle diameter of 2-100 nm, a surface area of 30-1100 m²/g, a concentration up to 50% SiO₂ and both alkaline and acidic pH. The particles can be sodium- or ammonium-stabilized and products can have aluminum- or silane-modified surfaces. The products can also be deionized and the structure is tuneable to achieve discrete particles or chains. Although the general process scheme has stayed the same for decades, smaller details of the manufacturing process can still be improved. Furthermore, new products for specific applications are continuously developed. In the last twenty years there has been a trend in colloidal silica buyers where more specific products to be used for additional and complex applications are demanded [5].

1.1 Background

The process to produce silica sol has continuously been improved since the first plant, currently within AkzoNobel, was built in the 1950's. This master thesis will study in further detail a way to improve the energy efficiency of the manufacturing process of one type of sol.

The synthesis of the studied silica sol is performed in a semi-batch reactor where material is fed

to the reactor but not withdrawn until completion of the reaction. Most of the feed consists of silicic acid which is produced on the site in a separate ion exchange unit, and either fed to the reactor directly or via a storage tank.

The reactor is kept at an elevated temperature during the sol synthesis. The reaction is endothermic [8], but the heat of reaction is negligible in comparison to the heat required to raise the temperature to the elevated temperature [3]. Preheating of the silicic acid inlet feed had not been performed at any of AkzoNobels plants until recently. When preheating in full scale it was found that it affected the synthesis of the sol and in particular the particle size distribution. This result has also been confirmed in lab scale at the Process Development Colloidal Silica RD&I department at AkzoNobel, Bohus. A change in particle size distribution is undesired for the customers who expect a certain particle size distribution and the inherent properties of such particles.

The upside to preheating would be that the reactor is not cooled by the inlet feed. This could potentially make the reaction step faster since commercial semi-batch reactors in general are heat transfer rate limited [9]. In addition, by defining the silicic acid feed stream to the reactor as a cold process stream (a stream with a heating demand), the stream can be used in an internal heat exchanger provided that there exists a hot stream that requires cooling. If internal process streams can be used for heating and cooling rather than steam and cooling water, the process becomes more energy efficient. This is especially good from a sustainability point of view since the available energy for many chemical process plants comes from combustion of fossil fuels, such as natural gas or oil, which releases greenhouse gases. With increased integration of the process it also follows that less cold utility is required.

1.2 Objective

The objective of the thesis is to examine in lab scale at which process conditions it is possible to preheat the silicic acid in the silica sol synthesis without experiencing adverse effects on the product. The temperature of the preheating step and the storage time of the silicic acid can be varied. The residence time in the preheating step is also a parameter.

The potential energy saved increases as the preheating temperature increases. An economic and environmental evaluation of the value of the energy saved by applying the best preheating condition is also made.

1.3 Delimitations

AkzoNobel has several recipes for different silica sols out of which one has been chosen for this study, referred to as the studied sol. It will have to be evaluated whether the result of the preheating for the chosen sol is valid for other types of silica sols as well.

The storage time of silicic acid in a full scale plant is often assumed to be four hours. The project investigates storage times between 0 and ≥ 20 hours, where the higher storage times can

be considered as worst case scenarios. The variations of the temperature and residence time in the preheating step are limited to approximately 90°C and five minutes, since this corresponds to existing equipment in the full scale plant.

2 Theory

The term silica is used for any crystalline, amorphous, hydrated, or hydroxylated form of silicon dioxide, SiO_2 . Silica is an abundant material, with crystalline silica in the form of quartz as the main component of the crust of the earth [10]. In most silica compounds the silicon atom is surrounded by four oxygen atoms, creating a SiO_4 tetrahedron as in figure 2.1a. The tetrahedron becomes a building block for sheets, chains and three-dimensional networks by sharing of the oxygen atoms, see figure 2.1b [10]. The SiO_4 units are randomly packed in amorphous silica. Much of the fundamental knowledge about silica chemistry is reported in Ralph K. Iler's 'The Chemistry of Silica' from 1979 [3], called "the definitive book on silica chemistry" [11].

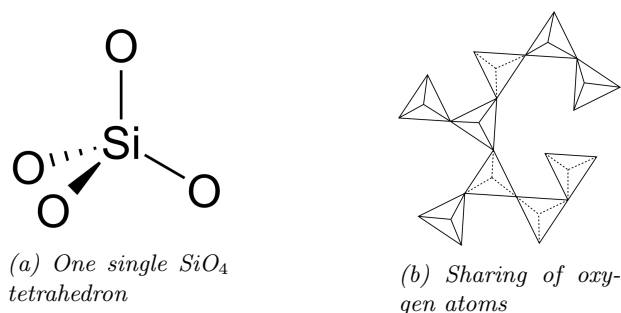


Figure 2.1: The structure of silica and linking of tetrahedrons in an amorphous fashion.

Colloidal silica are particles of amorphous silica with a size in least one dimension between 1 nm and 1 μm [12]. Due to the small particle diameters, colloidal silica has an extremely large specific surface area. Many different groups can be formed on the surface of the particles, among them hydroxyl groups ($\equiv\text{Si-OH}$), called silanol groups, and silanediol groups. Silanol groups on the surface can be silanized, esterified, or stabilized by alkaline ions [10]. The surface can also be modified to incorporate elements such as Na, K or Al.

Silica sol is the stable dispersion of solid colloidal silica particles in a liquid - stable in the sense that the solid particles do not settle or agglomerate at a significant rate [13]. Commercial sols can often be stored for years without settling or gelling [4]. A sol has discrete or separate particles whereas a gel consists of coherent three-dimensional aggregates with siloxane bonding (Si-O-Si) at the contact points [3]. When a sol gels the whole medium becomes viscous. A sol must also be stable against flocculation and coagulation, where the particles are lumped together to form clusters. These clusters may settle or float, depending on the density of the flocs. The difference between sol, gel and flocculation is depicted in figure 2.2.

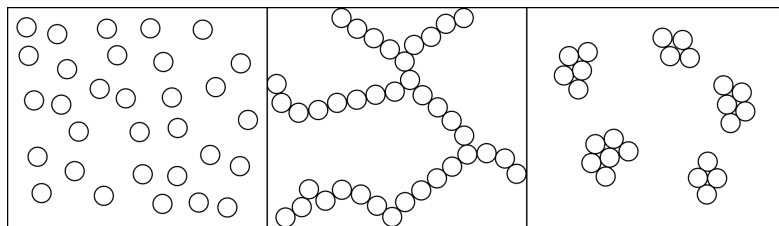


Figure 2.2: From left to right: sol, gel and flocculation.

2.1 Production of silica sol

There are several different ways to produce silica sols. Otterstedt and Brandreth names the most important types of production processes as: the column method, the consol method, the autoclave method and the Stöber method [4].

The autoclave method refers to the process of growing a small particle sol to larger particles in an autoclave. Stöber sols consists of porous particles, made with tetraethyl orthosilicates ($\text{Si}(\text{OEt})_4$) as starting material. The hydrolysis of tetraethyl orthosilicate to form SiO_2 particles takes place in an alcohol. The column method and consol method are methods for producing silica sol dispersed in water. The raw material is sodium silicate, also called water glass [1].

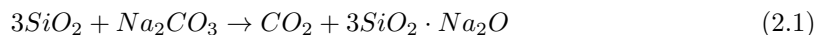
The studied sol is prepared commercially by the column method. More detail regarding the process will follow in the next sections. The process can be divided into three major steps: ion exchange of sodium silicate to produce silicic acid, nucleation and growth of the silica particles in a reactor and finally concentration of the reactor product [14]. The process scheme of a typical column method process is shown in figure 2.3.

The consol process is also based on the ion exchange technique, but ion exchange and polymerization of silica takes place simultaneously as the ion exchange resin and sodium silicate is fed to the reactor. The consol process has simpler equipment and the pH will be kept higher where microgel is less likely to form. However, more sodium will be incorporated in the sol [4].

Another variation to the ion exchange process is called the slurry process, patented in 1963 [15]. Similarly to the consol process, sodium silicate is dosed directly to the reactor. Ion exchange resin is placed in the reactor where ion exchange and growth of particles take place simultaneously.

2.1.1 Production of sodium silicate

Sodium silicate is made in a process where sand and soda ash is melted in an oven. Carbon dioxide is released and sodium silicate is the product according to the following reaction [3]:



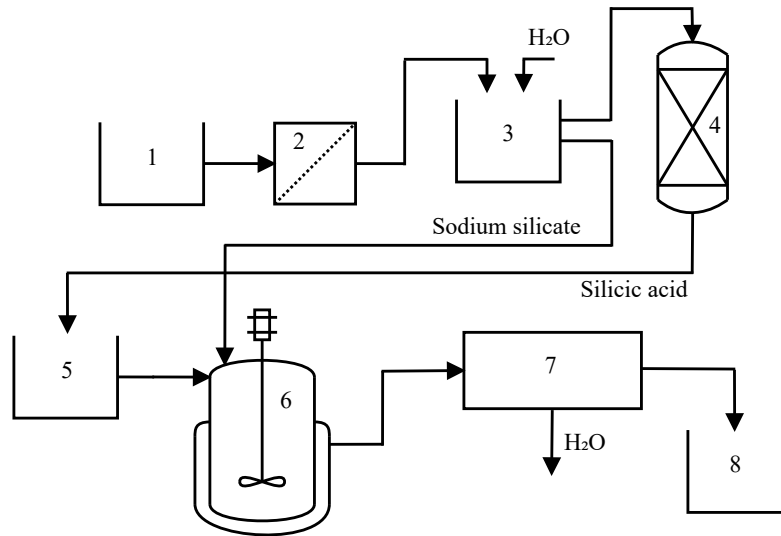


Figure 2.3: Dissolved sodium silicate is stored in (1). The solution is filtered (2) and diluted with water in (3). The ion exchanger (4) converts the sodium silicate to silicic acid which can be stored in (5) before it enters the reactor (6). Sodium silicate is also dosed to the reactor. Concentration of the reactor product is done in a separation step (7) before storage in the quality assurance tank (8).

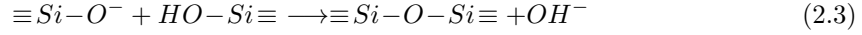
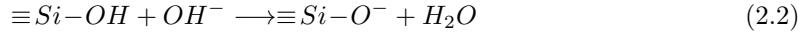
The solid sodium silicate is dissolved and diluted with water to reach 5-6% silica content. It is also filtrated to remove impurities and larger silica particles before it enters the ion exchanger.

2.1.2 Ion exchange of sodium silicate

The ion exchange process that is used to produce silicic acid is based on the 1941 patent by Bird [16], where a solution of sodium silicate is passed through a cation ion-exchange resin column. Sodium ions are removed and replaced by hydrogen ions. The hydrogen ions are eventually exhausted and a breakthrough of sodium ions will occur [17]. The ion exchange beds must be regenerated after exhaustion. A common arrangement is to have ion exchange columns ordered in parallel and working in cycles [18]. The regeneration is done with a strong acid and washing is performed with water between regeneration and exhaustion. Dilution with water, breakthrough of sodium ions and current operating conditions will cause the quality of the silicic acid to vary both from batch to batch and within a batch.

The resulting solution after sodium silicate is passed through the column is called silicic acid and contains oligomeric and monomeric silica in the form of $\text{Si}(\text{OH})_4$. It is a metastable solution which will polymerize quickly when heated [3] and gel upon standing for a longer period [14]. The step between the ion exchange and the reactor is thus time sensitive. A sign that the silicic acid is close to gelling is that the viscosity rapidly increases, from a viscosity of 1 cP to a viscosity of 20 cP or even above 100 cP [19].

The polymerization of silicic acid is a condensation reaction starting with the ionization of a silanol group, see reaction 2.2-2.3.



Due to the reactivity of monomeric silica, the silicic acid soon contains larger units of silica, around 2 nm in size [4]. Monomeric silica is acidic and is more likely to become ionized with an increasing pH. The point of zero charge is found between pH 2 and 3. As can be seen from reaction 2.2 and 2.3, hydroxyl ions are catalyzing the condensation reaction. The metastable behaviour of silicic acid around pH 2-3 is explained by some to be due to the scarcity of ionized surface groups. Others explain the metastability as the result of the hydration of the surface of particles, forming a layer of water molecules hydrogen-bonded to the silanol groups, and consequently dehydration at a higher pH [3, 20].

The concentration also effects the stability of silicic acid. When comparing silicic acid of different concentration, prepared the same way, Bergna found that silicic acid of 5% silica took 24 hours to gel at room temperature, while silicic acid of 4% took 48 hours [19]. The temperature and the salt concentration are also important for the stability of silicic acid [3].

Depending on how the production line is built, the silicic acid can either go straight to the reactor or to a storage tank. In a storage tank the silicic acid from batches and within batches will mix, but the silicic acid is also aged during storage and will slowly continue polymerization. The residence time in the storage tank is important to prevent gel formation.

2.1.3 Reactor

Iler describes three stages for the polymerization of silica: polymerization of monomer to form particles, growth of particles, and linking together of particles to form three-dimensional networks throughout the liquid medium, thickening it to a gel [3]. The findings of Iler has been confirmed in later studies [4]. Polymerization includes nucleation and growth of particles but also aggregation of particles. The types occur predominantly under different conditions as seen in figure 2.4. Both forms of polymerizations will be described in the following sections.

Particle growth

Iler makes a distinction between polymerization at pH 2-7 and pH above 7 [3]. One way to create a silica sol is to allow the monomeric silica from the ion exchanger react with itself according to reaction 2.2-2.3. This would correspond to a reaction at pH 2 to 3. At pH 2 to 3, the reaction is significantly slower than at a higher pH and has therefore been studied in great detail. Between pH 2 and 7, the rate of reaction 2.2-2.3 is proportional to the OH^- concentration. The condensation occurs so that the siloxane (Si-O-Si) bonds are maximised and the Si-OH groups are minimised, thus leading to ring structures [3]. This is followed by addition of monomer and condensing of internal hydroxyl groups, forming very small, compact, spherical units [3]. These small units are the precursors of colloidal particles. Particles of 1-2 nm that consists of 10-100

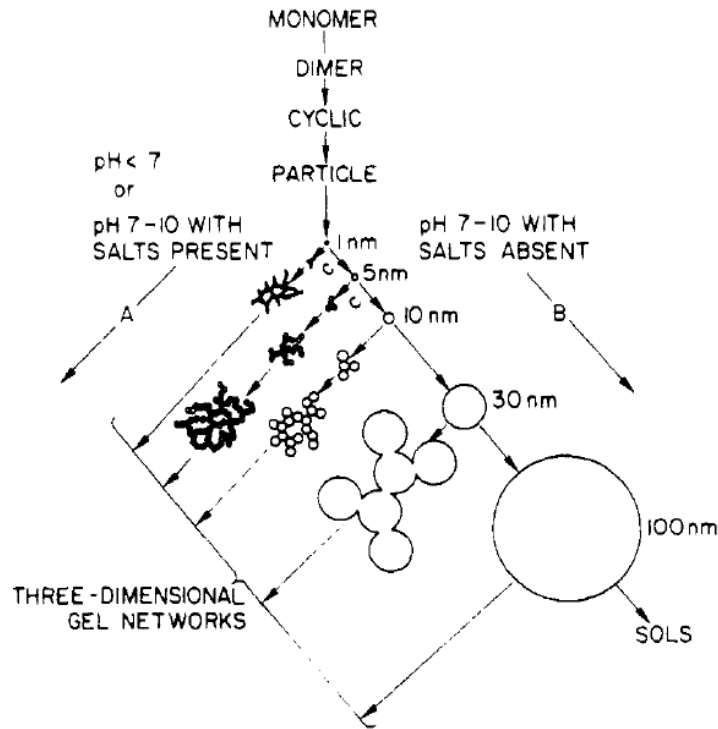


Figure 2.4: Polymerization behaviour of silica, starting from silicic acid, under different conditions. Figure reprinted from reference [3] with permission from John Wiley & Sons.

SiO_2 units serves as nuclei where dissolved monomeric units condense on the surface of the larger spheres.

Continued growth of the spherical units takes place by Ostwald ripening, where more soluble particles dissolve and deposit on less soluble particles [3]. The solubility depends on the size of the particles, the temperature and the pH. The growth stops when the difference in solubility between the particles is only a few ppm, and thus the final size of the particles depend both on the temperature and the pH. A high temperature, often close to 100°C , and a pH above 9 is often used to promote particle growth.

Aggregation

Growth also occurs by aggregation of particles. Attachment between silica particles is thought to occur by the formation of siloxane bonds. With the presence of OH^- as a catalyst, a Si-OH group on the surface of one particle and a Si-O $^-$ group on the surface of another particle can condense and form a Si-O-Si bond [3]. The linking together of particles creates branched chains and three-dimensional network regions much like a microgel. If the microgel region grows to occupy about half of the total volume, the viscosity become infinite and the sol has gelled [3].

With a higher pH, the particles are more negatively charged and will thus repel each other, which reduces the risk of aggregation. The most stable point that resists aggregation occurs between pH 8 and 10.5 for a Na-stabilized sol [3]. A high salt concentration may cause the sol to coagulate. The mechanisms of sol stability with regard to pH, salts and temperature are described in detail in Iler's 'The Chemistry of Silica' [3].

Commercial production

Whether discrete or aggregated particles are desired depends on the application for which the sol will be used. For example, when the sol is used as retention aid in papermaking, the retention capability increases with an increasing degree of microaggregation [21]. In coating applications a non-aggregated sol is often preferred [22]. As seen in figure 2.4, changing parameters such as pH and salt concentration is required to promote one mechanism over the other.

Most commercial silica sols consists of discrete, dense spherical particles [21]. The studied sol in this project belongs to this group. For commercial production of silica sols with discrete particles, the reaction takes place at a pH between 8-10 and at elevated temperatures to speed up the polymerization [4, 14]. A commercial reactor is equipped with a steam heated jacket. In the pH interval 8-10, the rate of growth is several orders of magnitudes faster than at pH 2 [4]. The pH is often adjusted by the use of alkali silicate solutions with different $\text{SiO}_2:\text{Na}_2\text{O}$ ratios.

Buildup process

The studied sol is produced by a variation to the reactor step called the buildup process. The objective is to control the silica polymerization to give the desired particle size distribution.

In a 1951 patent by Bechtold and Snyder, the process by Bird was further refined as to allow control of particle size and other modifications [23]. Their process introduced the use of a heel. A heel is a smaller sized silica sol. Bechtold and Snyder created the heel by the same ion-exchange process as was patented by Bird and thereafter by heating a part of the silicic acid to at least 60°C in which particles of less than 10 nm were formed. The heel is then used as a nuclei for further particle growth. The particle size of the original sol is increased by deposition of silica [4]. The process can be carried out in a semi-batch fashion as in figure 2.5, where a diluted heel is placed in the reactor and silica in the form of silicic acid and sodium silicate is added.

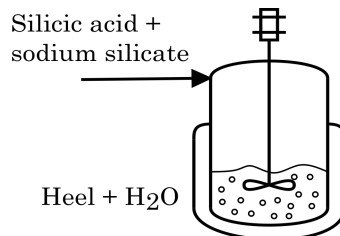


Figure 2.5: Semi-batch reactor for the buildup process of silica sol.

Iler defines the buildup ratio B_r as

$$B_r = \frac{W_a}{W_n} \quad (2.4)$$

where W_a is the amount of silica added to the particles and W_n is the amount of silica already present as heel [3]. The final particle diameter d_f can be related to the initial particle diameter d_i as follows [3]:

$$\left(\frac{d_f}{d_i}\right)^3 = \frac{W_n + W_a}{W_n} = 1 + B_r \quad (2.5)$$

The formula is based on the assumption of ideal particle growth, i.e. all silicic acid will deposit on the available silica particles, no new particles are formed and the particles do not agglomerate. The particles are also assumed to be spherical and uniformly coated by the depositing silica.

In a patent from 1972, Albrecht specifically treats the optimum rate of silicic acid addition to the reactor [24]. A sol with particles of 48 nm was grown by addition of silicic acid to a heel with particles of 21.3 nm. The flask was heated to boiling temperature and the pH was kept above 8 with addition of sodium silicate.

The concentration of growing particles must not be too small compared to the rate of addition, or new nuclei will form [1]. The rate of silica addition to the reactor in g/h per ml of sol in the reactor at time t can be described as:

$$F_t = kS_0C_t^{2/3}C_0^{1/3} \quad (2.6)$$

where S_0 is the surface area of the heel in $\text{m}^2/\text{g SiO}_2$, C_t the concentration in the reactor at time t in $\text{g SiO}_2/\text{ml}$ and C_0 the initial concentration. The constant k is a value relating the rate of addition of silica to the maximum available area in m^2/ml to deposit on:

$$k = \frac{F_t}{S_0C_t^{2/3}C_0^{1/3}} \quad (2.7)$$

Albrecht, Iler and Otterstedt et al. have all made observations of the maximum rate of silica addition compared to the available silica surface while still achieving ideal particle growth without any new particle formation [3, 4, 24]. Iler cites a k -value of 0.005 at 90°C [3], same as Albrecht at 100°C [24]. Otterstedt et al. observed new particle formation at a k -value higher than 0.007 [4]. The method of addition and specifically the rate of addition, is important to the resulting particle growth. New particle formation in addition to the buildup of the heel particles creates a bimodal particle distribution.

Modifications of the sol

When a sol has been made from ion-exchanging a sodium silicate solution, the surface groups are stabilised with Na^+ ions. Another alkali can be added to make the surface stabilised with another cation, such as NH_4^+ acting as counter ion instead [4]. Sodium aluminate can be added to the sol to create a surface of aluminosilicate ions which will make the sol more stable towards gelling at a low pH [4]. Silane modified sols have been shown to improve the stability, water resistance and dirt pick-up resistance for silicate paint [22].

There are also modifications to reverse the charge of the silica particles to keep them stable in a lower pH region. Some modifications are performed on a electrolyte free sol, i.e. a synthesised sol which is passed through another ion exchange unit [14].

2.1.4 Dewatering

Dewatering of the reactor product is performed to ease the transportation of the sol [14]. A high concentration is also desired in many applications.

According to Iler, the most common method to concentrate silica sols in the industry in 1979 was by evaporation [3]. Evaporation is a practical approach since the high temperature not only evaporates the water and concentrates the solution, but also promotes further condensation on the particles and hence is a part of the growth step. The evaporation must be carefully controlled as to not let the silica get too concentrated locally and build up on walls or form a gel. However, due to rising costs of heating, it was predicted that other methods would increase in use in the future. Other methods mentioned by Iler includes ultrafiltration and centrifugation.

2.2 Particle size measurement

Bechtold and Snyders buildup process results in quite monodisperse particles with a size distribution around an average value, similar to a normal distribution [23]. There are several ways to express the average diameter or size distribution of particles [4]. One common way is by the mass weighted mean diameter:

$$\bar{d}_m = \frac{\sum_{i=1} m_i d_i}{M} \quad (2.8)$$

where m is the mass of the particles of a specific diameter and M is the total mass of all particles. Another way is to present the average size of the particles by the number weighted mean diameter:

$$\bar{d}_n = \frac{\sum_{i=1} n_i d_i}{N} \quad (2.9)$$

where n is the number of particles of a specific diameter and N is the total number of particles. The mean diameter takes a different value depending on the chosen method. Larger particles with a higher mass will contribute more to the mean diameter in equation 2.8 than small particles with lower mass, while all particles independent of size contributes equally for the number weighted mean diameter.

Owing to the nature of the reaction, the grown silica particles can be assumed to be spherical. The surface area of silica sols has historically been used to find an average size of silica particles [25], relating the specific surface area S to the average diameter as follows:

$$S = \frac{6}{\rho \bar{d}} \quad (2.10)$$

where ρ is the density of the particles, often assumed to be 2.2 g/cm^3 [4]. A common method to measure the specific surface area is by titration with NaOH as proposed by Sears in 1956 [26]. The method is based on an empiric relationship between the amount of adsorbed hydroxyl ions and the surface area of silica particles.

While undesired for some applications, it is probable that the particles are aggregated to some extent. The aggregated particles are either included in the average size or not, depending on the method of analysis. Ways to study the particle size distribution includes electron microscopy, dynamic light scattering, centrifugal liquid sedimentation and electrospray differential mobility analysis (ES-DMA).

An example graph with the result of a ES-DMA analysis is pictured in figure 2.6. A desired size distribution of a monodisperse particle follows line 2 in figure 2.6. Non-ideal particle growth during the buildup process may cause a bimodal particle size distribution instead. The first peak, line 1 in figure 2.6, can overlap more or less with the original peak, making the populations harder to distinguish. In the case of bimodality, a quantification of the bimodality is proposed by estimating the number of particles with smaller size in the first peak and compare it to the total number of particles in both peaks. Estimating the number of particles can be done by estimating the area of the first and second peak. The bimodality quantification is written as:

$$B = \frac{A_1}{A_1 + A_2} \quad (2.11)$$

where B is a percentage of the particles that exist due to new particle nucleation and growth, instead of secondary nucleation on the existing heel.

2.2.1 Principles of ES - DMA

The combination of electrospray, an ion mobility drift cell and a macroion detector has been used previously to determine the particle size distribution of colloidal silica [27, 28].

The unit used to transfer the sol to gas phase, by creating fine droplets of the sol containing one

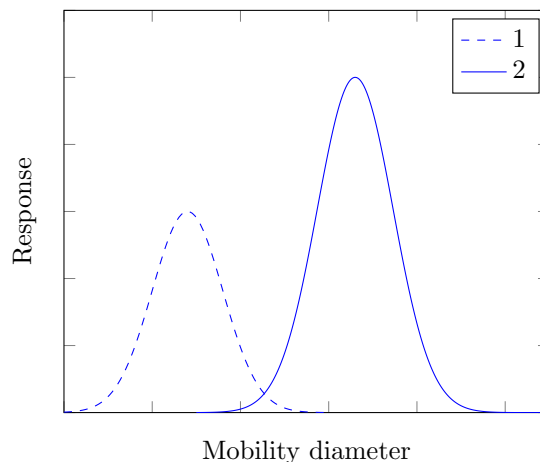


Figure 2.6: An example graph showing the particle size distribution as measured by ES-DMA of two populations in the same sample.

particle in each droplet, is called an electrospray [28]. It is also the name of the phenomenon behind the formation of a jet. The colloidal liquid is transported to a tip of a capillary which acts as an electrode. The liquid is surrounded by an insulating environment of CO_2 and clean air. A plate counter electrode is placed opposing the capillary and when a voltage in a specific range is applied the liquid takes the form of a cone extended by a jet [27]. The breakup of the jet is the source of a fine aerosol. The solvent evaporates from the particles and particles with a high surface charge are created. The electrospray unit also includes a neutralizer that uses a soft X-ray ionizer to remove excess charge on the particles and create singly-charged ions [29].

The resulting ions and carrier gas then enter an ion mobility drift cell called a differential mobility analyser [29, 30]. In the middle of the cell, parallel to the trajectory of the carrier gas, is an electrode with a narrow gap at the bottom. An electric field causes the positively charged ions to migrate through the cell, towards the electrode. The migration speed of the particles depend on the charge and the drag force and only those ions of the same electrical mobility will go through the narrow gap on the electrode [31]. The drag force depends on the diameter and shape of the particles. The ions can be separated by varying the force of the electric field and thus the particles are separated by their mobility diameter.

The separated particles are counted by a condensation particle counter [29]. To make the particles distinguishable by a photodetector they must grow in size. This is done by saturating the environment around the particles with vapour and thereafter cooling, causing the vapour to condense on the particles until the size is sufficiently large. The number of particles that correspond to a specific mobility diameter are counted. Since colloidal silica particles often are spherical, the mobility diameter is approximated to be the physical diameter [32]. The number of particles of each size can be related to the mass by the density.

2.3 Heat integration

The current way to view the buildup process, with all the heating occurring in the reactor jacket, implicates a case of non-adiabatic mixing when cold silicic acid enters the hot reactor. Viewing the feed stream as a separate stream with a heating demand allows for heat integration with the rest of the process [33]. The silica sol of this study is made in a semi-batch fashion, but there are several products in AkzoNobels portfolio that are made continuously. For these products, the outlet stream from the reactor or from subsequent concentration steps operated at a high temperature can be used to preheat the feed. For this project it is assumed that there exists a hot stream, currently cooled by cold utility, to be used for internal heat exchange.

Preheating the feed of silicic acid to the reactor with an existing process stream would lead to a lower steam demand. In Sweden 2016, 13% of the total energy consumed in the chemical industry originated from a fossil source [34]. Decreasing the hot utility demand thus leads to reduction in CO₂ emissions. The cooling water consumption also decreases when the streams of a process plant are fully integrated. A common way to cool in a process plant is by water once-through cooling systems, where the water comes from a river, lake, canal or the sea. If the released water is much warmer than the original source it may have an impact on the ecosystem and there might be strict environmental regulations regarding the maximum allowed temperature on the released water [18]. The temperature of the cooling water may also be classified as a hard energy target due to restrictions enforced by a wastewater treatment plant with biological treatment.

With the assumption that the silicic acid stream can be integrated, the saving of steam can be calculated as:

$$Q = mC_p\Delta T \quad (2.12)$$

where the mass of steam is calculated as:

$$m_{steam} = \frac{Q}{\Delta H_{cond}} \quad (2.13)$$

The economical savings due to decreasing the steam demand can be calculated per tonne of product as:

$$\text{Saving [SEK/tonne]} = \frac{\text{Steam saving [kg/tonne]}}{\text{Steam price [SEK/kg]}} \quad (2.14)$$

When assuming full integration, the heat savings correspond to an equally large cold utility saving. The cost of cooling water is normally much lower than the cost of steam and can therefore be neglected.

The usage of steam in the process industry is often associated with burning of fossil fuels. The CO₂ emissions from combustion of various fossil fuels can be estimated for a choice of steam generator, e.g. a oil boiler.

$$m_{CO_2} \text{ [kg/tonne]} = \frac{Q \text{ [GJ/tonne]}}{\text{Oil boiler efficiency}} \cdot \text{Oil CO}_2 \text{ emissions [kg/GJ]} \quad (2.15)$$

3 Materials and method

The project consists of two parts with emphasis on the first: i) synthesis of a sol in lab scale to find a viable preheating condition and ii) an economic evaluation of preheating in full scale.

A synthesis recipe for the studied sol is given by AkzoNobel. The laboratory equipment and procedure is described in section 3.2. The chemicals used as start material and the product for each synthesis is analysed with the methods described in section 3.3.

3.1 Chemicals

Sodium silicate of 5.67% SiO_2 and a $\text{SiO}_2:\text{Na}_2\text{O}$ -ratio of 3.3 is provided by AkzoNobel. An alkaline sol of 40.12% SiO_2 to be used as heel is also provided. More information on the sodium silicate and the heel sol can be found in appendix A.

All syntheses except two, were performed with silicic acid taken directly from the outlet of an ion exchanger in the full scale plant. Storage of silicic acid is done in a sealed plastic container.

One batch of silicic acid was obtained from a storage tank collecting silicic acid after the ion exchange in the full scale plant, much like tank number 6 in figure 2.3. The residence time in the storage tank is not known precisely but four hours can usually be assumed. Silicic acid for one synthesis was produced in lab scale using a 24% SiO_2 sodium silicate solution provided by AkzoNobel. The sodium silicate was diluted to 4.9% SiO_2 with deionized water and passed through a lab scale ion exchange column.

3.2 Sol syntheses

18 syntheses were performed in lab scale. The varied parameters are indicated in table 3.1. The temperature is referring to the temperature in the preheating step and the number of hours refers to the age of the silicic acid after the ion exchange. Synthesis 2 was performed with shorter duration between the preheating and the reactor, 3.5 min instead of approximately 5 min for all other experiments. After the first six syntheses had been performed it was suspected that the storage time of the silicic acid was an important parameter. The subsequent syntheses were therefore focused on varying the temperature of the preheating step and the storage time of the silicic acid. The temperature interval was chosen based on the result from the previous syntheses. The residence time of 5 min was chosen based on the existing equipment in the full scale plant.

Table 3.1: The experimental design where the varied parameters are the storage time of the silicic acid and the temperature in the preheating step. The numbers indicate the order of the syntheses. The residence time between the preheating step and the reactor was set to around 5 min, for all syntheses except synthesis 2, where it was set to 3.5 min. *synthesis performed with silicic acid produced in lab.

	0 h	5 h	10 h	15 h	19 h	20 h + tank
20°C	1			10	12*, 18	
50°C		9	13	16		
70°C		8	11	15		
80°C, 3.5 min	2					
80°C	3					
90°C	4	7	14	17	6	5

The sol syntheses are performed in a glass reactor of five litres with an outer shell containing oil. The reactor is equipped with an impeller. The oil is connected to a bath for which a temperature can be set. The oil bath can be cooled with water. The temperature inside the reactor is recorded and logged. Evaporating liquid is cooled by air and condensed back into the reactor.

Two Watson Marlow displacements pumps of model 520U are used to dose silicic acid and sodium silicate for experiment 1-6. As from experiment 7, a NE1000 ProSense syringe pump is used to dose sodium silicate. The sodium silicate is dosed directly to the reactor. The silicic acid is first passed through a metal coil inside a water bath, heated to a set temperature, before it is dosed to the reactor. The coil inside the water bath was found to retain a volume corresponding to approximately 2.7 min of heating. The additional 2.3 min (0.8 min for synthesis 2) is the time required to transport the heated silicic acid to the reactor.

Procedure

The heel sol is diluted with deionized water and added to the reactor. The reactor is thereafter heated to 98°C. The dosing of sodium silicate and silicic acid is started when the temperature is reached inside the reactor. The dosage rate is constant throughout the reaction period. The amount of silica added compared to the maximum available area at the beginning of the synthesis gives a k value of 0.0075 according to equation 2.7.

The dosing time is set for three hours, after which the reactor is cooled down. When the temperature in the reactor has declined to 70°C, the product is poured to a plastic container and stored in room-temperature for later analysis.

3.3 Characterisation

The characterisation of the reagents and the products are analysed by the following methods.

3.3.1 Chemical and physical characterisation

Density

The density of the liquids used are measured with a Anton Paar DMA series density meter. The temperature is adjusted to 20°C by the instrument.

A relation between the SiO₂ content of a certain sol and its density has been found empirically, and is reported by AkzoNobel in available tables.

Vaccum filtration

Filtration is done through a membrane filter. A negative pressure is maintained by a vacuum pump. The volume of the filtrate is measured after an appropriate time and can be compared to other samples.

Turbidity

A Hach 2100P ISO turbidimeter is used to measure the turbidity in NTU of the samples.

The analysis of experiment 11 and onward was performed with a different turbidimeter of the same brand.

Viscosity

The viscosity of the liquids are measured with a Brookfield model DV-II+ viscometer with a UL adapter. The temperature of the sample is adjusted to 20°C with the help of a water bath.

pH

A Metrohm 913 digital pH meter with a glass electrode is used to measure the pH of the solutions.

Conductivity

The conductivity of the sample is measured with a WTW Cond 330i/3110 portable conductivity meter.

3.3.2 Particle characterisation

Specific surface area

The specific surface area (SSA) is measured by the Sears method as described in section 2.2 using Tiamo titration devices from Mehtrohm, including software. A sample size containing 1.5 g of SiO₂ is diluted with 100 g of deionized water. The pH is adjusted to 2-3. 30 g NaCl is added and dissolved while stirring. Titration is done with 0.1 M NaOH and the surface area is calculated from the volume of NaOH added to the sample.

The Sears method is not an appropriate method to measure the specific surface area of particles in silicic acid since silicic acid does not only contain small silica particles, but also monomeric silica [4].

ES-DMA

An electrospray differential mobility analyser with software, model 3982 MacroIMS System from TSI, is used to measure the particle size distribution. For most samples a 20mM (pH 8) ammonium acetate buffer is mixed with 4 µl of the sample, resulting in a solution of approximately 400 ppm SiO₂. The dilution is important to avoid that two or more particles occur in the same droplet [27].

The resulting number weighted particle size distributions are used to estimate the bimodality according to equation 2.11. The mass weighted particle size distributions are calculated by using a density of 2.21 g/cm³.

TEM

Three samples (synthesis 9,11 and 17) were selected to be analysed by transmission electron microscopy (TEM). The analysis was performed by and at Glantreo, Cork.

3.3.3 Correlation and ANOVA

The correlation coefficient of two parameters as measured by one of the above methods can be calculated as:

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}} \quad (3.1)$$

The experiments in table 3.1 are mostly done by changing two parameters: the storage time and the temperature of the preheating step. A smaller, complete design is found in table 3.2 and can

be used to determine if there exists interaction effects between the parameters. A test developed by Turkey for two factors and one degree of freedom can be used for this purpose, described in [35]. The hypothesis is that effect of interaction is not significant. This can be tested with the help of a analysis of variance (ANOVA) table and F-test.

Table 3.2: A smaller part of the experimental design in table 3.1 without missing experiments. The numbers indicate the order of the synthesis.

	5 h	10 h	15 h
50°C	9	13	16
70°C	8	11	15
90°C	7	14	17

3.4 Economic and environmental evaluation

The numbers needed for a economic and environmental evaluation can be found in table 3.3. The mass of silicic acid to produce 1 tonne of concentrated sol is calculated based on the lab recipe. The C_p value is assumed to be the same as water since the stream only contains around 5% silicic acid. The heat of condensation of the steam is taken at atmospheric pressure. The steam price is based on a rough estimate from AkzoNobel.

The steam is assumed to be generated with an oil boiler. The efficiency of the oil boiler is an estimation. The CO₂ emissions associated with the production, distribution and combustion of heavy fuel oil is taken from the literature.

Table 3.3: Variables used in the steam saving calculations.

C_p	4 kJ/kg [36]
ΔH_{cond}	2257 kJ/kg [36]
Mass of silicic acid	6700 kg/tonne product
Steam price	0.26 SEK/kg steam
Oil boiler efficiency	0.85
Oil CO ₂ emissions	76 kg/GJ [37]

4 Results

The result from the analysis of the silicic acid and the syntheses products are displayed in the following sections. The result of the steam saving calculations is found in section 4.3.

4.1 Analysis of silicic acid

A new batch of silicic acid was used for each synthesis. The result from chemical and physical characterisation can be found in table 4.1. The density, SiO₂ content, pH and conductivity of each sample all fall in a relatively narrow window. The only exception is the lab made silicic acid of synthesis 12, aged 19 h, which has a different conductivity compared to the other batches. The filter value is varying but no clear trend has been found. The turbidity and viscosity are the characteristics most closely related to the particle size in the silicic acid. The trend of the turbidity and viscosity related to the age of the silicic acid is shown in the next section.

Table 4.1: The result of the chemical and physical characterisation of the silicic acid. The maximum and minimum show the range of the value the parameters have taken, excluding synthesis 12, which was performed on lab made silicic acid. The result table for all batches can be found in appendix A.

	Max.	Min.	Median	Synth. 12
Density (g/cm ³)	1.0333	1.0262	1.0319	1.0261
SiO ₂ content (%)	5.80	4.66	5.57	4.64
pH	2.77	2.56	2.70	2.84
Conductivity (μS/cm)	891	752	811	422
Turbidity (NTU)	1.46	0.57	1.00	0.86
Viscosity (cP)	1.80	1.35	1.45	1.45
Filter value (ml)	615	204	433	600

4.1.1 Effect of ageing on silicic acid

The analysis of the silicic acid was always performed shortly before or after the synthesis was started and thus the age of silicic acid during analysis can be approximated to the same age as the synthesis.

As can be seen in figure 4.1 there is a slight trend of higher turbidity and viscosity as the silicic acid is aged. The correlation coefficient is 0.69 and 0.63 for the aged time versus turbidity and viscosity respectively. Other properties of the silicic acid varying from batch to batch, such as the SiO₂ content and the conductivity, may cause variations in the ageing behaviour. Figure 4.2 compares the silicic acid from the same batch, when fresh and after ageing.

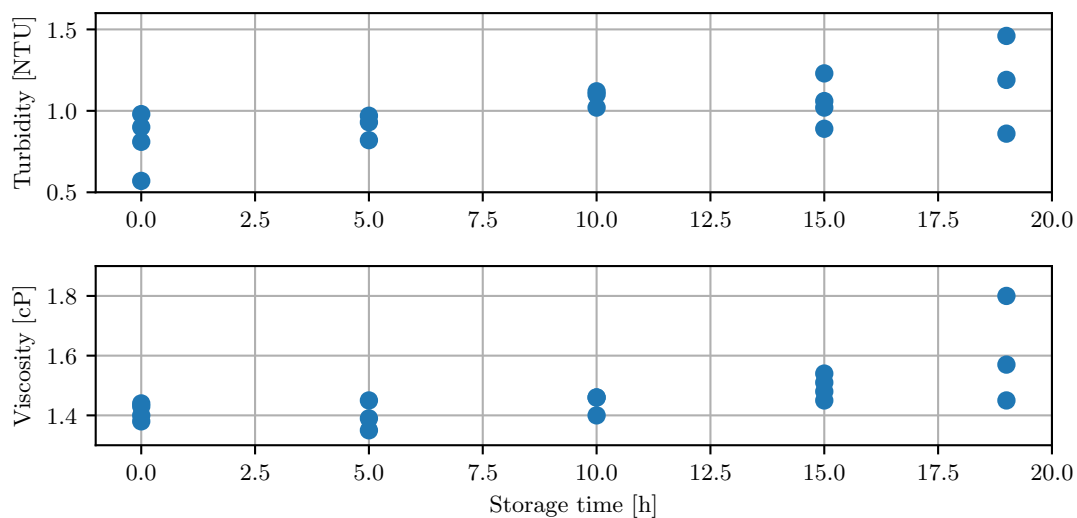


Figure 4.1: Turbidity and viscosity measured at the start of the synthesis for all the batches of silicic acid, except the batch taken from the storage tank and then stored for 20 h.

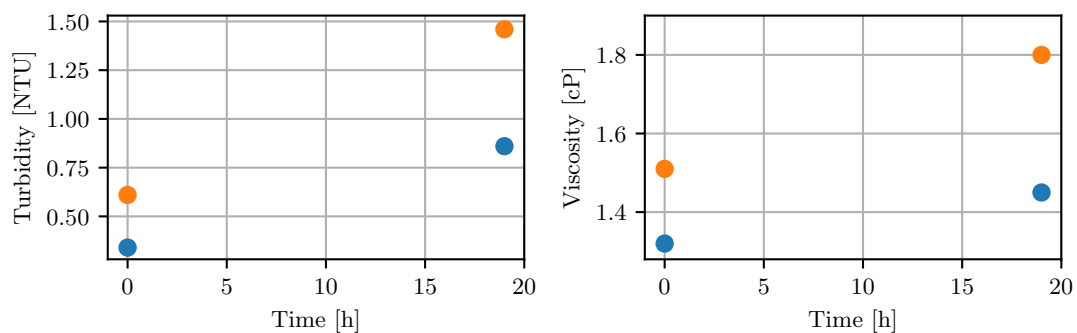


Figure 4.2: Two different samples of silicic acid, both stored 19 hours, and the resulting change in turbidity and viscosity. Orange dots represent sample 18 and blue dots represent sample 12, silicic acid made in lab.

4.1.2 Effect of heating on silicic acid

An experiment was performed to study the effect of heating the silicic acid. A sample of fresh silicic acid was heated to 70°C in the water bath used for preheating and thereafter cooled to room temperature in a cold water bath. The viscosity and turbidity of the sample was measured before and after heating. The result can be seen in table 4.2.

Table 4.2: Comparison of the turbidity and viscosity of silicic acid before and after being heated to 70°C.

	Before	After
Turbidity (NTU)	0.61	0.64
Viscosity (cP)	1.51	1.50

4.2 Sol synthesis product

Once cooled, the product was analysed by the methods described in section 3.3. The main result is presented in table 4.3. The sol produced with lab made silicic acid does not seem to vary substantially from the other sols, but the conductivity is at the minimum value.

The density of the synthesis product closely follows the density of the silicic acid. There are no other clear trends relating the properties of the silicic acid to the final properties of the product.

Table 4.3: The result of the characterisation of the synthesis product. The result table for all batches can be found in appendix A.

	Max.	Min.	Median
Density (g/cm ³)	1.0318	1.0258	1.0307
SiO ₂ content (%)	5.83	4.82	5.65
pH	9.96	9.45	9.77
Conductivity (µS/cm)	546	365	507
Turbidity (NTU)	107	63.5	71
Viscosity (cP)	1.47	1.26	1.29
Filter value (ml)	128	<15	69
SSA (m ² /g)	152.3	122.2	133.0

4.2.1 Particle size measurements

The particle size distribution without preheating or ageing (synthesis 1) and subsequent experiments with mild enough conditions result in a uniform particle size distribution as in figure 4.3. The scale of the x-axis is the same as for all following electrospray graphs. The largest amount of new particle formation is found when heating silicic acid, aged ≥ 19 hours, to 90°C. The particle size distribution of such a sol can be seen in figure 4.4. To be noted is that the distributions in figure 4.3-4.4 are based on the number weighted diameter. The first peak in figure 4.4 is much smaller when looking at the mass weighted diameter in figure 4.5.

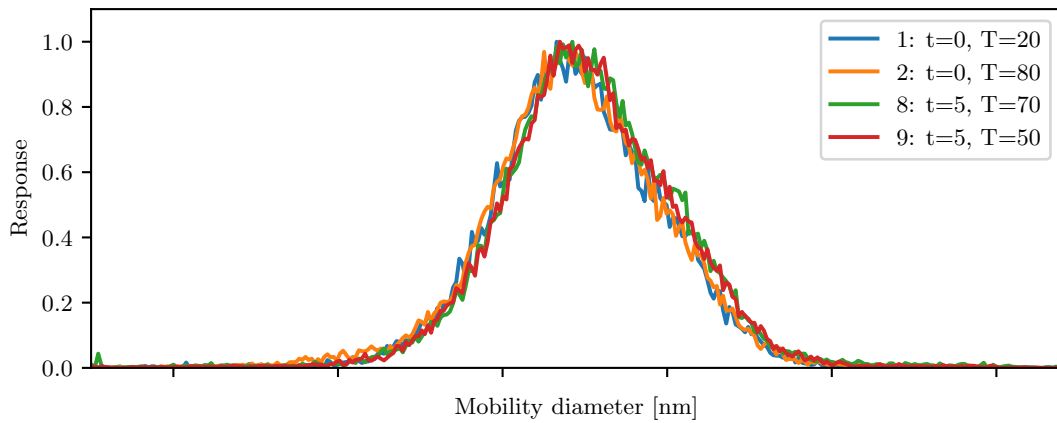


Figure 4.3: The number weighted particle size distribution as measured with ES-DMA. The samples of synthesised sol from experiment 1, 2, 8 and 9 do not show any sign of bimodality. The silicic acid for the experiment had been stored 0 or 5 hours, and heated to temperatures between 20 and 80°C.

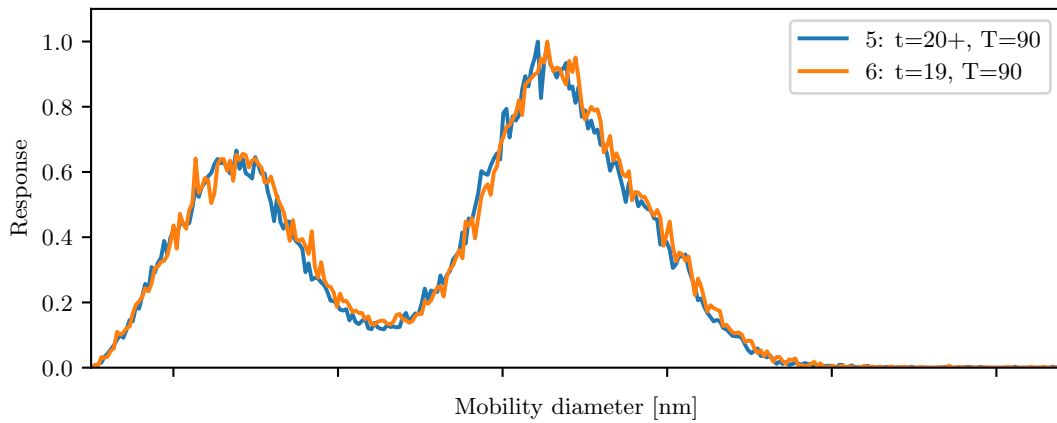


Figure 4.4: The number weighted particle size distribution as measured with ES-DMA for syntheses product 5 and 6. The silicic acid for experiment 5 was taken from a storage tank and thereafter stored for 20 hours. The silicic acid for experiment 6 was taken directly from an ion exchanger and stored for 19 hours. Both samples were preheated to 90°C.

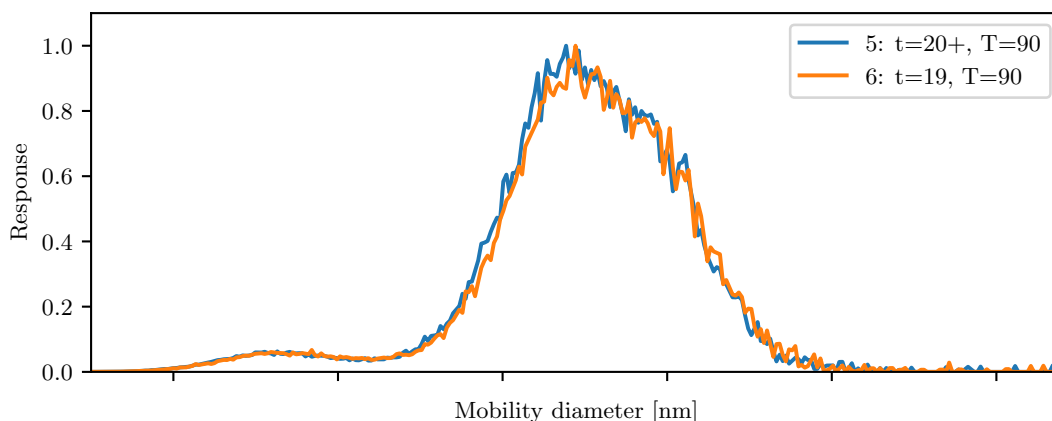


Figure 4.5: The mass weighted particle size distribution as measured with ES-DMA for syntheses product 5 and 6. The number weighted particle size distribution for the same samples is shown in figure 4.4.

The bimodality of the product is calculated from ES-DMA measurements according to equation 2.11. More electrospray graphs can be found in A. In table 4.4 it can be seen that the bimodality seems to increase both with storage time and the temperature of the preheating step. The correlation coefficient between bimodality and storage time is 0.80, while the coefficient between bimodality and temperature is 0.2.

Table 4.4: The resulting bimodality in % for each synthesis of the experimental design. *synthesis performed with silicic acid produced in lab.

	0 h	5 h	10 h	15 h	19 h	20 h + tank
20°C	0			2	18*, 30	
50°C		0	7	9		
70°C		0	5	11		
80°C, 3.5 min	0					
80°C	2					
90°C	4	6	20	29	36	36

Figure 4.6 is the graphic version of table 4.4, excluding the experiments with 3.5 min of heating at 80°C and the experiment with silicic acid taken from the tank and stored 20 h. By looking at figure 4.6 it can be suspected that the effect of temperature and storage time is not additive. The increase between 70°C and 90°C, especially at a higher storage time, may implicate an interaction effect between the temperature and the storage time.

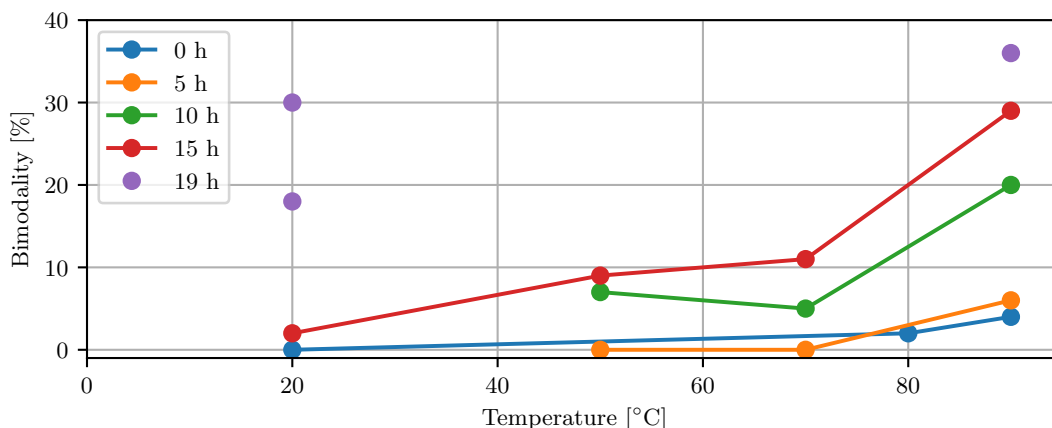


Figure 4.6: 16 of the experiments and the resulting bimodality in %. The experiment with a different heating duration and the experiment with silicic acid taken from the tank are excluded.

The result in table 4.5 are used to follow the procedure of Turkeys test of interaction effects between the factors. To investigate the hypothesis that the interaction effect is not significant, the test statistic for interaction $F_0=42.8$ is compared with $F_{\alpha,1,3}$. Using $\alpha=0.05$, $F_{0.05,1,3}=10.13$. $42.8 > 10.1$ and thus the hypothesis must be rejected. The complete ANOVA table for the calculation of the interaction effect can be found in appendix A.

Table 4.5: The resulting bimodality in % for nine samples with varying values of temperature and storage time.

	5 h	10 h	15 h
50°C	0	7	9
70°C	0	5	11
90°C	6	20	29

The specific surface area of the product seems to be correlated to the bimodality as can be seen in figure 4.7. The correlation coefficient between the parameters is 0.94. No other property of the product seems to follow the change in particle size distribution.

During synthesis 2, for which fresh silicic acid was heated to 80°C for 3.5 min, a sample was taken once an hour to follow the particle growth of the particles. The result from the electro spray is shown in figure 4.8 together with the particle size distribution of the heel sol.

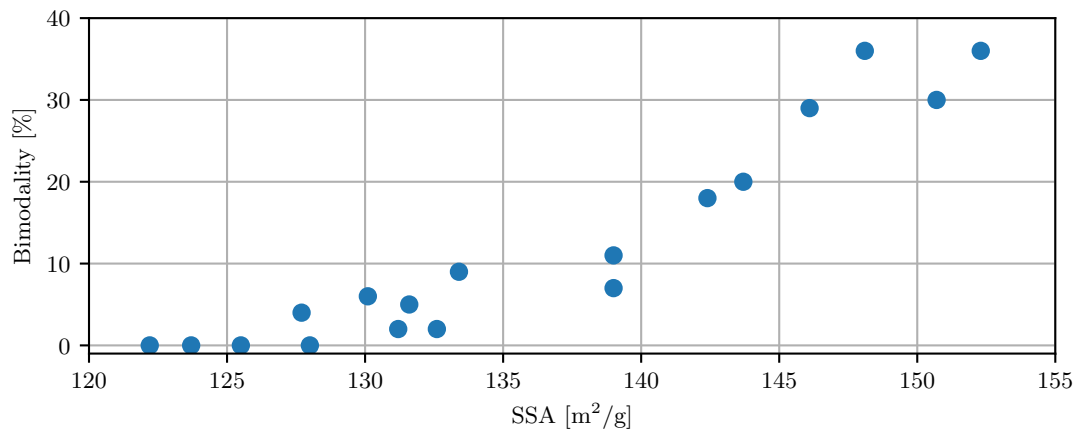


Figure 4.7: The specific surface area related to the bimodality for all syntheses products.

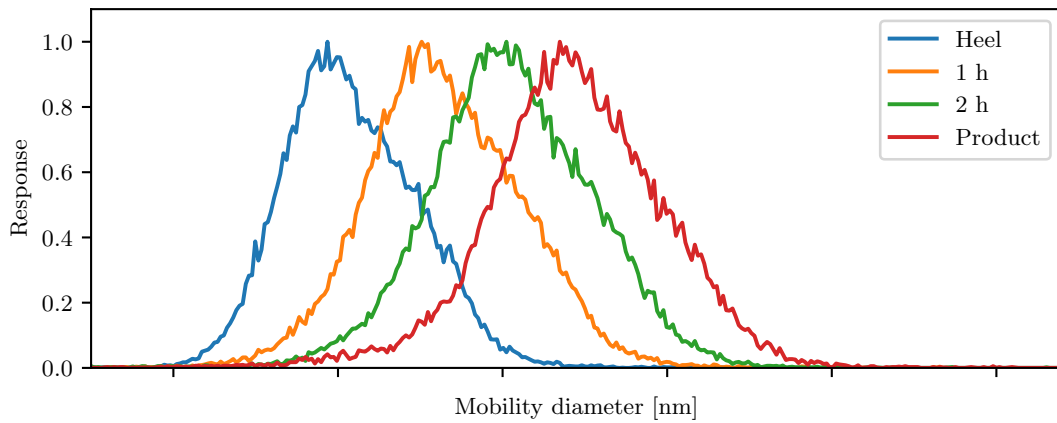


Figure 4.8: The growth of particles during the reaction, from heel to finished synthesis product. Based on the number weighted particle diameter as measured by ES-DMA. The synthesis was made with fresh silicic acid, heated to 80°C with a residence time of 3.5 min between the preheating step and the reactor.

A similar graph for a synthesis with new particle formation is seen in figure 4.9. The new particles are present even after one hour and they continue to grow both in size and number.

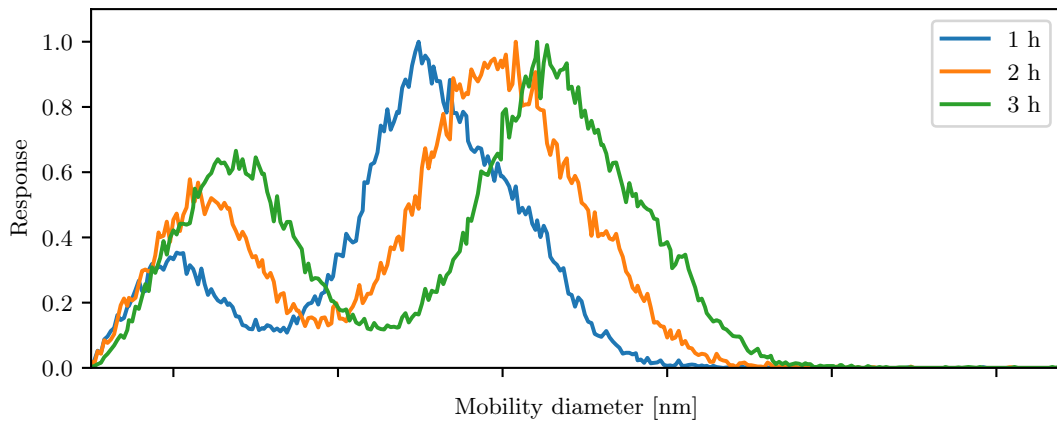


Figure 4.9: The growth of particles during synthesis 5. The silicic acid had been taken from the storage tank and stored 20 hours. The preheating temperature was set at 90°C. Based on the number weighted particle diameter.

TEM

Three samples of synthesis product of different bimodality were chosen for TEM analysis. For synthesis 9, in figure 4.10, the calculated bimodality is 0%. The silica sol particles seem to be spherical and non-aggregated.

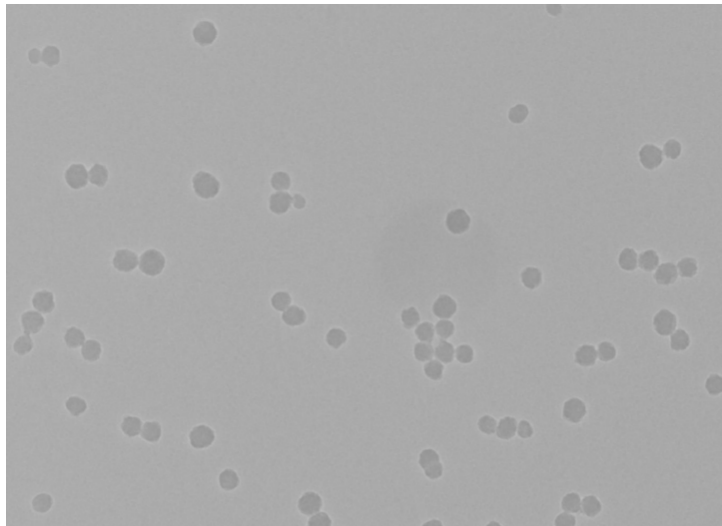


Figure 4.10: TEM of sample 9: $t=5$ h, $T=50^\circ\text{C}$.

For synthesis 11, in figure 4.11, the calculated bimodality is 5%. There seem to be some smaller particles present.

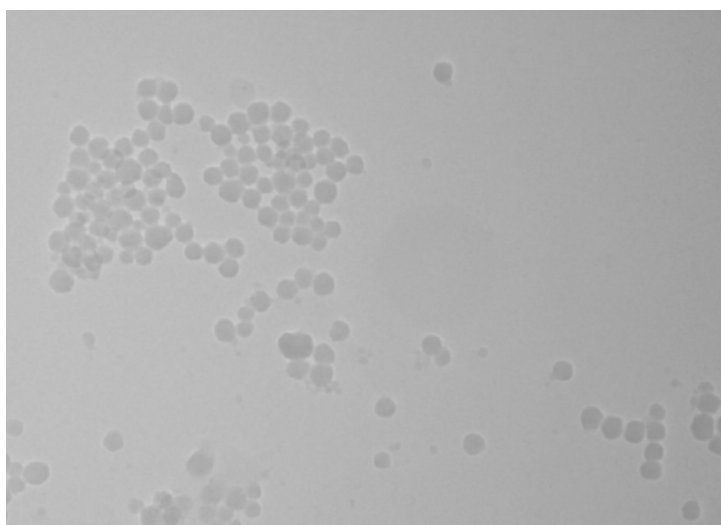


Figure 4.11: TEM of sample 11: $t=10$ h, $T=70^{\circ}\text{C}$.

For synthesis 17, in figure 4.12, the calculated bimodality is 29%. Again there seem to be some smaller particles present both in the solution and between the larger particles in the aggregates.

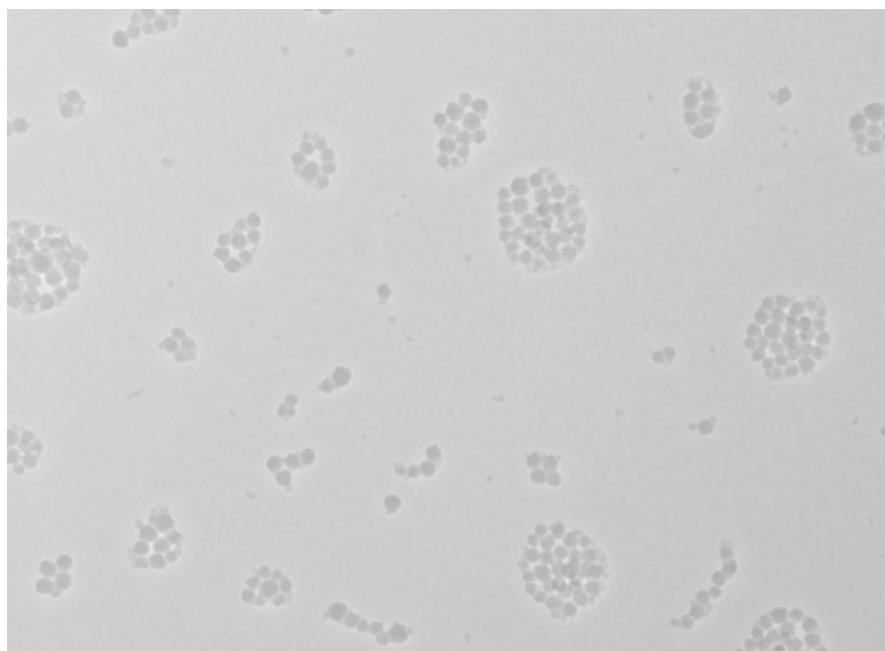


Figure 4.12: TEM of sample 17: $t=15$ h, $T=90^{\circ}\text{C}$.

4.3 Saving of steam

Using the values in table 3.3, the heat demand to preheat silicic acid from 20°C to three different temperatures for one tonne of product is calculated according to equation 2.12. The heat corresponds to the saved steam demand according to equation 2.13. The result is shown in table 4.6.

Table 4.6: The economic benefit of preheating silicic acid and decreasing the steam demand for three different preheating temperatures.

	50°C	70°C	90°C
Q [kJ/tonne]	804 000	1340 000	1876 000
m_{steam} [kg/tonne]	356	594	831
Saving [SEK/tonne]	93	154	216

The steam is assumed to be produced in an oil boiler. The decrease in CO₂ emissions associated with the decrease in steam demand for one tonne of product is presented in table 4.7.

Table 4.7: The reduction in CO₂ emissions when preheating silicic acid and decreasing the steam demand for three different preheating temperatures.

	50°C	70°C	90°C
Q [GJ/tonne]	0.80	1.34	1.88
Q_{oil} [GJ/tonne]	0.95	1.58	2.20
m_{CO_2} [kg/tonne]	72	120	168

5 Discussion

The effects of the variation within the silicic acid, the procedure and the syntheses products will be discussed in the following sections.

5.1 Silicic acid

The silicic acid is from a new batch for each synthesis run and it is the main reactant by mass. It is probable that some variations in the product can be explained by variations in the silicic acid. The factory-made silicic acid is taken both on different days and from different ion exchange units which is causing the variations in density, SiO_2 content, pH and conductivity. The variations in turbidity and viscosity can also be somewhat explained by variations in the batches, but as shown in figure 4.1, there seems to be a slight correlation between a higher viscosity/turbidity and the storage time. It is known that the silicic acid will start to polymerize at room temperature when stored. Larger and larger particles are formed as a result. The scattering of light by particles in the solution depends greatly on the particle size, and as such it is expected that the turbidity increases when the particle size increases. When the particles have begun to aggregate it is also expected that the viscosity increases. However, the measured changes in viscosity and turbidity are still small compared to a batch of silicic acid close to gelling, as described in section 2.1.2. The viscosity and turbidity measurement is probably not accurate enough to predict the behaviour of the silicic acid in the synthesis.

When the particle size increases, or when the particles in the silicic acid has had time to aggregate, the filter value should decrease due to clogging of the filter. This does not seem to be the case. Even aged silicic acid reaches filter values of 600 ml, and the minimum value of 204 ml in table 4.1 is found for a fresh batch of silicic acid. One explanation for this could be that the particle size still is very small in the silicic acid, so that the filter value measurement is not accurate enough in this regard. When the filter value is as low as around 200 ml, it is probably due to some changes in the plant.

5.1.1 Silicic acid prepared in lab

The silicic acid made in lab scale has several differences with the one made in plant scale. The most obvious one is the conductivity. Dilution of the sodium silicate in the lab was done with deionized water. Deionized water was also used to flush the ion exchange column. In plant scale, process water is often used for both applications. The process water probably contains more ions. The silica content is also lower than usual. Water was used both before and after sodium silicate was added to the column and the resulting silicic acid was diluted with said water due to lack of exact measurement equipment. However, the sol produced with the silicic acid from the lab is

not significantly different from the other sols in table 4.3. This may indicate that the properties of the silicic acid are not completely related to the properties of the synthesis product. The lab scale sample of silicic acid is one of the samples in figure 4.2. Both samples have increased in viscosity and turbidity, indicating the same behaviour regardless of preparation method.

5.1.2 Heating of silicic acid

It is expected that heating the silicic acid also promotes the polymerization. The test that was performed on fresh silicic acid at 70°C, with the result in table 4.2, does not show any measurable difference on the silicic acid after heating. This test does not however represent a synthesis performed at 70°C without storage time since the reaction time is set at three hour, thus making the silicic acid in the synthesis older at the end of the synthesis. Based on the analysis of the synthesis product, 70°C is not enough heating to affect a fresh batch of silicic acid.

5.2 Sol syntheses

The sol syntheses were performed according to plan. The temperature of 98°C was held during all syntheses. The recipe was built based on the addition of silica in grams and the rate had to be adjusted to account for the different concentrations of the silicic acid. The different rates corresponds to a different residence time in the preheating step, which was not accounted for since the change was deemed too small.

One confirmation that the produced sol is the same as the desired is that the analysed parameters in table 4.3 are quite consistent throughout all syntheses. The SiO₂ content is at the expected level considering the amount of added silica as both heel and feed.

The filter value is varying significantly between the products, but there is no clear trend relating the filter value to the age of the silicic acid or the preheating temperature. The low filter value is believed to correlate to a high amount of microgel in the sample. The gel could originate from regions in the reactor with poor mixing where the pH has been too low. Changing the dosage pump of the sodium silicate to a syringe pump before synthesis 7 was done to lessen these effects by forcing the dosing points further apart. The filter value was thereafter improved from the lowest values of <15. But the filter value of the synthesis product is still not comparable to the filter value of a commercial product (the heel filter value is 300 ml, see appendix A). Perhaps this is caused by the preheating equipment such as the coil or the hose. These were used for all samples, even at 20°C. Apart from the preheating step, there are also several other differences between the equipment in lab scale and in commercial scale that might be part of the explanation.

5.2.1 Particle size distribution

As seen in figure 4.3 all the sols without noticeable bimodality has reached the same mobility diameter, which indicates that the process conditions have been similar enough to create the same sol. For the sols in 4.3 it can be assumed that they have grown the same way as the synthesis product 2, shown in figure 4.8. With no second peak it can be assumed that the particles have grown ideally, without any new particle nucleation, even though the k -value is slightly higher than proposed by the citations in section 2.1.3, meaning that the addition of silicic acid is too high compared to the available surface area. The cited maximum k -value is reported for different conditions and it is probable that the value of 0.0075 is within the acceptable range for the conditions of the chosen synthesis.

When looking at the values in table 4.4 it is suspected that the temperature of the preheating step and the storage time is affecting the particle size distribution. The linear correlation is much stronger between the storage time and the bimodality than between the temperature and the bimodality. However, these values are limited by the chosen experiments. In figure 4.6 it can be seen that the slope of the line increases as the temperature increases from 70°C to 90°C. Overall, the growth of new particles does not seem to be linear. This suspicion is strengthened by the interaction test performed on the nine values in table 4.5. The preheating temperature seems to have a greater effect to aged silicic acid. Since the factors are interacting and no repeats were made of the experiments in table 4.5 it is difficult to test the effects of the preheating temperature or storage temperature alone.

The same mechanism is thought to occur in the silicic acid both while preheating and storing: polymerization according to reaction 2.2-2.3. It is probable that when the condensation has caused larger particles to form in the silicic acid it will affect the buildup process. The larger particles are not as soluble as the monomer and they can also act as nuclei, competing with the heel particles for the addition of new silica. As shown in figure 4.9, during the synthesis the new particles grow in size due to addition of silica.

The specific surface area and the bimodality are highly positively correlated, see figure 4.7. This is expected since smaller particles have a higher SSA, and a bimodality in this project is caused by a second population of smaller particles.

The interpretation of the electropray measurement can be different depending on which diameter is compared: the number weighted mean diameter or the mass weighted mean diameter. The difference is depicted in figure 4.4 and 4.5. Larger particles will contribute more to the total mass and thus the smaller peak becomes even smaller in figure 4.5. The graphs picturing the number weighted diameters are chosen for this project to study the peak of smaller particles in more detail.

The bimodality estimation is based on an imprecise integration. Furthermore, the electropray measurement is only performed on a small sample. The sample may not represent the total volume. The numbers should therefore be treated with caution. This can explain the seemingly strange result in table 4.4, where the 10 h sample is more bimodal after preheating to 50°C than after 70°C.

A storage time of 15 h is much longer than the expected storage time in a full scale plant. A

maximum of 5 h storage time is more realistic. A high preheating temperature does not seem to have great effect on the synthesis product after it has been stored 5 h.

Definition of adverse effects

When the change in particle size distribution should be considered a problem is not easily answered. It would depend on the application for the silica sol.

Two of the pictures from the TEM analysis, figures 4.11-4.12, reaffirms that there exists smaller particles in the samples. The fact that some smaller particles are visible in the TEM analysis even though the bimodality is only estimated to 5% for synthesis 11 could be used to claim that the conditions of 10 h and 70°C has affected the particle size distribution enough to cause problems for some customers.

5.3 Saving of steam

Based on the calculated steam saving, tables 4.6-4.7, it is difficult to say whether the preheating of silicic acid is worth the investment cost required to install an internal heat exchanger. From the relatively low savings in SEK/tonne it can be suspected that the savings of steam alone are not a sufficiently large economical incentive to give grounds for a redesign of the process.

There might be other advantages to preheating that are not directly related to the cost of steam. A higher degree of heat integration decreases both the steam demand and the cooling demand. For older plants, especially on shared sites, the ability to expand the utility systems may be greatly limited. An extension on another process that increases the utility demand could be compensated by a setup that decreases the utility demand somewhere else, such as preheating of silicic acid in the silica sol production.

The reactor is not the only unit operation with an energy requirement, but most of the energy consumed can be assumed to be related to the reactor step or the concentration step. The calculated decrease in CO₂ emissions is based on the assumption that the steam is generated in an oil boiler, which is probably not true on many sites.

The decrease in CO₂ emissions related to the reactor step is probably substantial, but the effect on the process as a whole is unknown. As shown in reaction 2.1, CO₂ is also released in the production of sodium silicate.

5.4 Future studies

The particle size distribution of the silica sol seems to be affected by the age and preheating temperature. Both the age and preheating temperature can be related to the degree of polymerization in the silicic acid. Perhaps it would be interesting to investigate if the particle size

distribution in the silicic acid can be related to the particle size distribution of the sol synthesis product. With some preparations, including change of buffer, the particle size distribution in silicic acid of different ages and after preheating may be possible to study in the ES-DMA.

In some instances a bimodal particle size distribution may even be advantageous and preheating the silicic acid may be a way to create a silicic sol of controlled particle size distribution. The measurements in this study would have to be repeated to give a value of the reproducibility. The reason behind the low filter values would also have to be explored.

There might be ways to lessen the effect of preheating by changing the recipe of production, perhaps by increasing the salt concentration. It should also be noted that the result may differ in laboratory scale and pilot or plant scale.

6 Conclusion

Preheating of silicic acid at a sufficiently high temperature, or storing of the silicic acid before reaction for an adequate number of hours, will result in a change in the particle size distribution of the synthesised silica sol. The polymerisation will not be ideal and new particles will form instead of silica depositing on the heel particles. A high preheating temperature has a larger effect on the synthesis if the silicic acid has been stored for 10 hours or more.

What is a sufficiently high temperature and an adequate number of hours to induce a substantial effect will have to be evaluated in each case since it depends on the application of the sol.

Out of the tested storage times, 5 hours is probably the most likely storage time in a commercial plant. With the assumption that the silicic acid is stored for 10 hours, a preheating temperature of 70°C will only cause a small new particle formation. The new particles make up 5% of the total number of particles.

The experiments would have to be repeated to acquire knowledge of the sources of variation. The silicic acid is varying from batch to batch which might affect the synthesis product.

If an internal heat exchanger is installed in the full scale plant and the heat is exchanged with an existing hot stream, a preheating temperature of 70°C would result in a steam saving cost of 154 SEK/tonne product. 120 kg less CO₂ per tonne product would be released under the assumptions in the project.

Bibliography

- [1] W. O. Roberts, in *Colloidal silica: fundamentals and applications*, H. E. Bergna and W. O. Roberts, Eds. CRC press, 2005, vol. 131, ch. Manufacturing and Applications of Water-Borne Colloidal Silica.
- [2] AkzoNobel. (2018). Levasil colloidal silica, [Online]. Available: <https://colloidalsilica.akzonobel.com/about/sustainability/>. (accessed: 2018-03-06).
- [3] R. K. Iler, *The Chemistry of Silica - Solubility, Polymerization, Colloid and Surface Properties and Biochemistry*. John Wiley & Sons, 1979, ISBN: 978-0-471-02404-0.
- [4] J.-E. Otterstedt and D. A. Brandreth, *Small particles technology*. Springer Science & Business Media, 1998.
- [5] C. C. Payne, in *Colloidal silica: fundamentals and applications*, H. E. Bergna and W. O. Roberts, Eds. CRC press, 2005, vol. 131, ch. Applications of Colloidal Silica: Past, Present, and Future.
- [6] B. Schwerin, *Manufacture of chemically-pure soluble silicic acid*. US Patent 1,132,394, Mar. 1915.
- [7] O. W. Flörke, H. A. Graetsch, F. Brunk, L. Benda, S. Paschen, H. E. Bergna, W. O. Roberts, W. A. Welsh, D. M. Chapman, M. Ettliger, *et al.*, “Silica,” in *Ullmann’s Encyclopedia of Industrial Chemistry*, Wiley Online Library, 2008. DOI: 10.1002/14356007.a23_583.pub3.
- [8] M. Dubois and B. Cabane, “Polymerization of silicic acid in a collapsed lamellar phase,” *Langmuir*, vol. 10, no. 5, pp. 1615–1617, 1994.
- [9] J. Worstell, *Batch and Semi-batch Reactors: Practical Guides in Chemical Engineering*. Butterworth-Heinemann, 2015, ISBN: 978-0-12-801305-2.
- [10] H. E. Bergna, in *Colloidal silica: fundamentals and applications*, H. E. Bergna and W. O. Roberts, Eds. CRC press, 2005, vol. 131, ch. Colloid Chemistry of Silica: An Overview.
- [11] H. E. Bergna and W. O. Roberts, *Colloidal silica: fundamentals and applications*. CRC Press, 2005, vol. 131.
- [12] D. Everett, “Manual of symbols and terminology for physicochemical quantities and units, appendix ii: Definitions, terminology and symbols in colloid and surface chemistry,” *Pure and Applied Chemistry*, vol. 31, no. 4, pp. 577–638, 1972.
- [13] H. E. Bergna, in *Colloidal silica: fundamentals and applications*, H. E. Bergna and W. O. Roberts, Eds. CRC press, 2005, vol. 131, ch. The Language of Colloid Science and Silica Chemistry.
- [14] A. Yoshida, in *Colloidal silica: fundamentals and applications*, H. E. Bergna and W. O. Roberts, Eds. CRC press, 2005, vol. 131, ch. Silica Nucleation, Polymerization, and Growth Preparation of Monodispersed Sols.
- [15] P. H. McNally and N. W. Rosenberg, *Process for producing a stable silica sol*, US Patent 3,113,112, Dec. 1963.

- [16] P. G. Bird, *Colloidal solutions of inorganic oxides*, US Patent 2,244,325, Jun. 1941.
- [17] K. Dorfner, *Ion exchangers*. Walter de Gruyter, 1991.
- [18] R. Smith, *Chemical process: design and integration*. John Wiley & Sons, 2005.
- [19] H. E. Bergna, in *Colloidal silica: fundamentals and applications*, H. E. Bergna and W. O. Roberts, Eds. CRC press, 2005, vol. 131, ch. Silicic Acids and Colloidal Silica.
- [20] J. Depasse and A. Watillon, "The stability of amorphous colloidal silica," *Journal of Colloid and Interface Science*, vol. 33, no. 3, pp. 430–438, 1970.
- [21] J.-E. Otterstedt and P. Greenwood, in *Colloidal silica: fundamentals and applications*, H. E. Bergna and W. O. Roberts, Eds. CRC press, 2005, vol. 131, ch. Some Important, Fairly New Uses of Colloidal Silica/Silica Sol.
- [22] P. Greenwood, "Surface modifications and applications of aqueous silica sols," PhD thesis, Chalmers University of Technology, 2010.
- [23] M. F. Bechtold and O. E. Snyder, *Chemical processes and composition*, US Patent 2,574,902, Nov. 1951.
- [24] W. L. Albrecht, *Method of preparing silica sols containing large particle size silica*, US Patent 3,673,104, Jun. 1972.
- [25] J. L. Bass, in *Colloidal silica: fundamentals and applications*, H. E. Bergna and W. O. Roberts, Eds. CRC press, 2005, vol. 131, ch. Particle Size and Characterization Techniques.
- [26] G. W. Sears, "Determination of specific surface area of colloidal silica by titration with sodium hydroxide," *Analytical Chemistry*, vol. 28, no. 12, pp. 1981–1983, 1956.
- [27] A.-C. Johnsson, "On the electrolyte induced aggregation of concentrated silica dispersions—an experimental investigation using the electrospray technique," PhD thesis, University of Gothenburg, 2011.
- [28] I. W. Lenggoro, B. Xia, K. Okuyama, and J. F. de la Mora, "Sizing of colloidal nanoparticles by electrospray and differential mobility analyzer methods," *Langmuir*, vol. 18, no. 12, pp. 4584–4591, 2002.
- [29] *Macroions macroion mobility spectrometer model 3982 user guide*, A, TSI Incorporated, Oct. 2014.
- [30] P. Kulkarni, P. A. Baron, and K. Willeke, *Aerosol measurement: principles, techniques, and applications*. John Wiley & Sons, 2011.
- [31] D. K. Song, I. W. Lenggoro, Y. Hayashi, K. Okuyama, and S. S. Kim, "Changes in the shape and mobility of colloidal gold nanorods with electrospray and differential mobility analyzer methods," *Langmuir*, vol. 21, no. 23, pp. 10 375–10 382, 2005.
- [32] P. F. DeCarlo, J. G. Slowik, D. R. Worsnop, P. Davidovits, and J. L. Jimenez, "Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. part 1: Theory," *Aerosol Science and Technology*, vol. 38, no. 12, pp. 1185–1205, 2004.
- [33] I. C. Kemp, *Pinch analysis and process integration: a user guide on process integration for the efficient use of energy*. Elsevier, 2011.
- [34] Energimyndigheten. (2018). Energiläget i siffror 2018 (excel), [Online]. Available: <http://www.energimyndigheten.se/statistik/energilaget/?currentTab=1#mainheading>. (accessed: 2018-05-08).
- [35] D. C. Montgomery, *Design and analysis of experiments*. John Wiley & Sons, 2013.

- [36] S.-E. Mörtstedt and G. Hellsten, *Data och diagram: Energi-och kemitekniska tabeller*. Liber AB, 2012.
- [37] S. Papadokonstantakis, *KVM013 Industrial Energy Systems course compendium*. Division of Energy Technology, Department of Space, Earth and Environment, Chalmers University of Technology, 2017.

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A Figures and tables

A.1 Sodium silicate and heel

Characterisation of the starting material was performed to confirm the quality. The result of the analysis for the sodium silicate and the alkaline sol used as heel can be found in table A.1. The alkaline sol was diluted to 5% SiO₂ before the filter value test to get a comparable value to the produced sol.

Table A.1: The starting material for every sol synthesis: sodium silicate and an alkaline sol used as heel.

	Sodium silicate	Heel sol
Density (g/cm ³)	1.0605	1.2976
SiO ₂ content (%)	5.67	40.12
pH	11.57	9.90
Conductivity (μS/cm)	22300	5370
Turbidity (NTU)	0.72	20.3
Viscosity (cP)	1.57	15.9
SSA (m ² /g)	-	226.1
Filter value, diluted to 5% (ml)	-	300

A.2 Silicic acid

The result of the characterisation for each batch of silicic acid is found in tables A.2-A.3.

Table A.2: Result of the characterisation of the silicic acid.

	Density (g/cm ³)	SiO ₂ conc. (%)	pH	Conductivity (μS/cm)
1	1.0326	5.68	2.56	812
2	1.0303	5.32	2.61	882
3	1.0325	5.67	2.58	863
4	1.0323	5.64	2.67	891
5	1.0303	5.32	2.68	802
6	1.0324	5.65	2.71	814
7	1.0332	5.78	2.69	858
8	1.0310	5.43	2.76	811
9	1.0262	4.66	2.76	752
10	1.0321	5.60	2.66	826
11	1.0326	5.68	2.71	796
12	1.0261	4.64	2.84	422
13	1.0316	5.52	2.77	792
14	1.0304	5.33	2.74	763
15	1.0317	5.54	2.71	809
16	1.0333	5.80	2.72	808
17	1.0323	5.64	2.69	811
18	1.0313	5.48	2.69	831

Table A.3: Characterisation of the silicic acid, continued.

	Turbidity (NTU)	Viscosity (cP)	Filter value (ml)	Age (h)
1	0.81	1.44	545	0
2	0.57	1.40	615	0
3	0.90	1.43	204	0
4	0.98	1.38	575	0
5	1.32	1.53	515	20 + tank
6	1.19	1.57	425	19
7	0.93	1.45	460	5
8	0.97	1.39	490	5
9	0.82	1.35	450	5
10	0.89	1.45	440	15
11	1.10	1.46	380	10
12	0.86	1.45	600	19
13	1.12	1.46	305	10
14	1.02	1.40	310	10
15	1.23	1.48	340	15
16	1.02	1.54	320	15
17	1.06	1.51	280	15
18	1.46	1.80	225	19

A.3 Synthesis product

The result of the characterisation for each syntheses product is found in tables A.4-A.5.

Table A.4: Characterisation of the synthesis product.

	Density (g/cm ³)	SiO ₂ conc. (%)	pH	Conductivity (μS/cm)
1	1.0309	5.68	9.69	443
2	1.0289	5.34	9.54	518
3	1.0308	5.66	9.85	508
4	1.0305	5.61	9.45	514
5	1.0294	5.42	9.57	465
6	1.0312	5.73	9.70	546
7	1.0317	5.81	9.57	507
8	1.0301	5.54	9.85	467
9	1.0258	4.82	9.78	476
10	1.0302	5.56	9.83	524
11	1.0309	5.68	9.75	505
12	1.0259	4.83	9.87	365
13	1.0317	5.81	9.87	516
14	1.0306	5.63	9.87	504
15	1.0311	5.71	9.96	512
16	1.0318	5.83	9.8	506
17	1.0308	5.66	9.74	497
18	1.0299	5.51	9.63	520

Table A.5: Characterisation of the synthesis product, continued.

	Turbidity (NTU)	Viscosity (cP)	Filter value (ml)	SSA (m ² /g)
1	63.5	1.34	100	123.7
2	69.8	1.31	128	128
3	71.2	1.31	<15	132.6
4	70.8	1.29	<15	127.7
5	64	1.27	<15	148.1
6	65.7	1.33	93	152.3
7	70.1	1.29	30	130.1
8	67.8	1.3	110	122.2
9	66.3	1.29	114	125.5
10	70	1.32	82	131.2
11	107	1.29	68	131.6
12	92	1.26	94	142.4
13	103	1.26	44	139
14	98.8	1.27	62	143.7
15	99.6	1.28	62	139
16	102	1.29	70	133.4
17	90.6	1.32	72	146.1
18	98.7	1.47	62	150.7

To conclude if the effects of the temperature and the storage time of silicic acid are interacting an ANOVA test was performed. The result is shown in table A.6.

Table A.6: ANOVA table for the calculation of interaction effect between the parameters in table 4.5.

	Sum of squares	Degrees of freedom	Mean square	F ₀
Temperature	312.7	2	156.4	116.7
Stor. time	338	2	169	126.11
Nonadditivity	57.3	1	57.3	42.8
Error	4.02	3	1.34	
Total	712	8		

Figure A.1 shows the ES-DMA measurements for the syntheses performed with preheating of the silicic acid at 70°C. The result of three syntheses performed with preheating of the silicic acid at 90°C is shown in figure A.2. The silicic acid had been aged 5, 10 and 15 hours respectively.

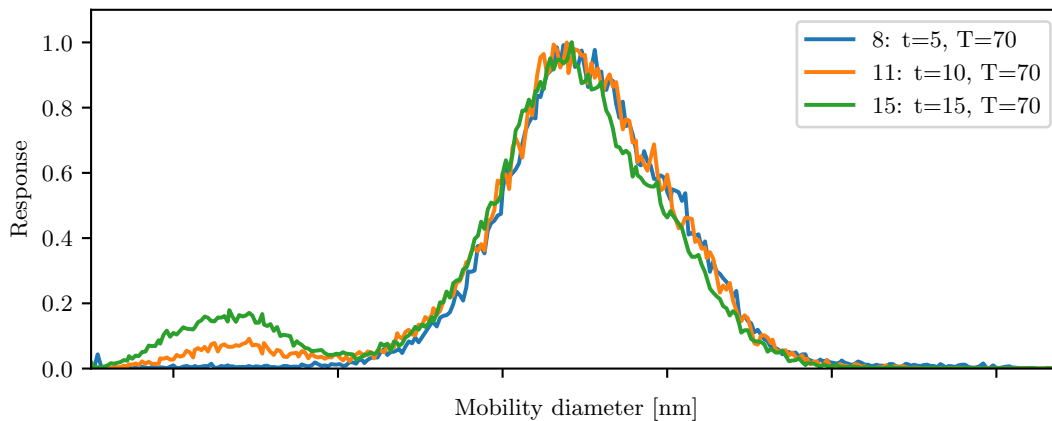


Figure A.1: The number weighted particle size distribution for synthesis product 8, 11 and 15 - all at the same preheating temperature. The calculated bimodalities in % are: 0, 5, 11 respectively.

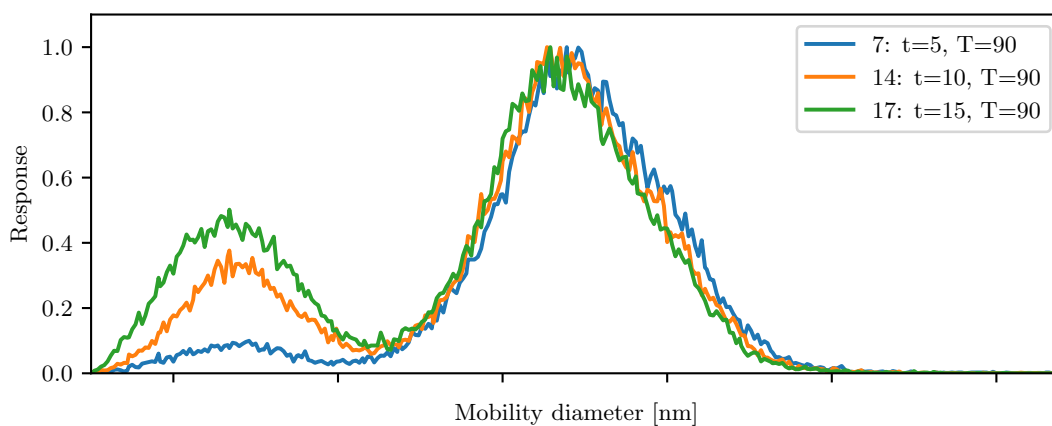


Figure A.2: The number weighted particle size distribution for synthesis product 7, 14 and 17 - all at the same preheating temperature. The calculated bimodalities in % are: 6, 20, 29 respectively.