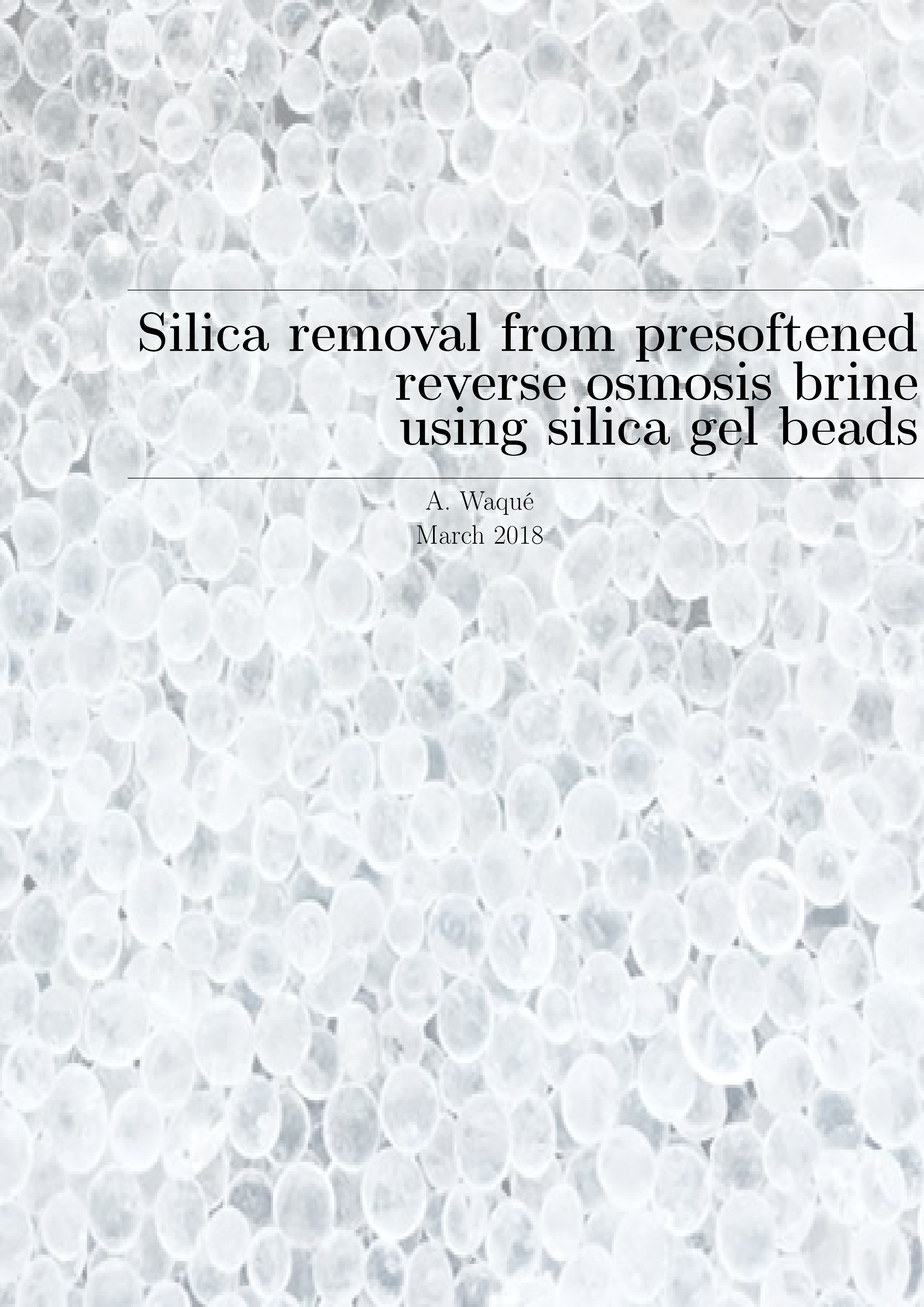

Silica removal from presoftened reverse osmosis brine using silica gel beads

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March 2018

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Silica removal from presoftened reverse osmosis brine using silica gel beads

MASTER OF SCIENCE THESIS

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Preface

This master thesis is the final element of my MSc program Water Management, with specialization in Water Treatment, at Delft University of Technology. I started this master, because I wanted to learn about sustainable ways to deal with our liquid waste streams. For this thesis, I could research a technology to treat such a stream. In order to research this technology, I had to dive deep into the world of silica chemistry. It was quite a challenge to understand and work with silica gel, but setting up my own research and working in the lab has been a valuable learning process of which the product now lies before you.

I would like to take the opportunity to thank some people for the support they have given me during my thesis work. First, I would like to thank the members of my committee; professor Luuk Rietveld, professor Geert-Jan Witkamp, Henri Spanjers, Bas Heijman and Amir Haidari for supporting me and giving me the freedom to set up and carry out my own research. This project was first planned to be part of the ZeroBrine project. I would like to thank Henri Spanjers for giving me the opportunity to join the first meetings of the ZeroBrine project and some workshops in the field of industry water. These experiences were very valuable to me. Yasmina Bennani-Doekhi, thank you for your enthusiasm and invaluable advice when I was starting my research. I would also like to thank David de Ridder, who has worked together with me on my quest to measure total silica. Your endless effort to improve the measurements with the ICP-MS was most helpful. My appreciation also goes out to Armand Middeldorp, for helping out in the lab whenever possible. Thank you to Vincent Toussaint from Evides Industry Water for providing RO brine and lots of information about the scale found in the membrane units. And to my colleagues from room 4.93 for providing a great work environment.

Finally, I would like to thank my friends and family for their support and much needed distraction. Although I can not name all, I have to mention a few. I would like to thank the members of the Ladysmith project group for their friendship ever since we left for our adventure in South Africa. Martine, for just always saying the right things. Karin, for living three doors away. Terry, we became friends before we could even speak in complete sentences. We started our school careers at the Hummeldonk, went our separate ways, but are now finishing at the same time. Who could have expected that? I cannot wait to celebrate this together surrounded by the beautiful peaks in Nepal.

Anna Waqué
Delft, March 2018

Abstract

Brine that is produced during reverse osmosis (RO) could be further concentrated by another RO step. In the absence of bivalent cations, silica is a limiting factor because a high concentration of silica can cause irreversible fouling of the membranes. To prevent silica scale formation during the further concentration of brine with RO, silica should be removed in a separate process. Silica gel beads have a large specific surface area and can be used to precipitate silica. Previous research on the removal of silica using silica gel beads for solutions with a relatively high silica concentration showed that a removal of $30-60\%$ is possible. In this research the effect of the dosage of silica gel beads, pH, temperature and the presence of 1 or 10 mg/L of ferric and aluminum on the removal of silica using silica gel beads from a solution with a low silica concentration was investigated. Starting with a silica concentration of 180 $mgSiO_2/L$ a removal up to 30% was obtained after 8 hours (pH 8.5, 21°C). The removal of silica using silica gel beads was limited, because silica gel dissolved when the solution is unsaturated with regard to silica. The equilibrium concentration was approximately 102 $mgSiO_2/L$. The difference between the concentration of silica in solution and the equilibrium concentration appeared to be a driver of the removal. The increase in removal efficiency as a result of using a higher dose of silica gel seemed to be limited. Operating at pH 10 instead of 8.5 resulted in a lower removal efficiency. Lowering the pH to 7 or 5 did not result in a decrease of the removal efficiency. Changing the temperature to 10 or 35°C or adding 1 or 10mg/L of ferric or aluminum did not increase the removal efficiency either, but even decreased the efficiency. The obtained removal efficiency might be too low for direct application of fixed bed column filtration with silica gel beads as interstage silica removal technique in a RO system that is used to concentrate brine. A combination of filtration with silica gel and a technology that can concentrate the brine without scaling to concentrations up to 500 $mgSiO_2/L$ could be an interesting solution to make brine treatment more energy-efficient, because the need for an evaporation step is minimized. Preliminary calculations showed that a relatively small column ($\sim 26L$) could be implemented to decrease the silica concentration from 170 to 140 $mgSiO_2/L$.

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Acronyms

ICP-MS Ion Couple Plasma Mass Spectrometry.

MIP Mercury Intrusion Porosimeter.

RO Reverse Osmosis.

SEM Scanning Electron Microscope.

TOC Total Organic Carbon.

Glossary

amorphous silica non-crystalline silica (Society for Mining, Metallurgy and Exploration, Inc., 1998).

batch RO a process in which a set quantity of feed solution is concentrated over time up to the required final brine salinity by RO. The contained volume of fluid is recirculated, resulting in a time-varying salinity in the batch RO system (Warsinger et al., 2018).

brine concentrate stream of reverse osmosis.

colloidal silica small silica particles with a minimal diameter of 5 nm (Milne et al., 2014).

crystalline silica a silica substance with a crystalline structure, thus the atoms and molecules form a three-dimensional repeating pattern. The most common type is quartz (sand). The structure of quartz consists of silocon-oxygen tetrahedrons (SiO_4) that are joined in the oxygen corners (Society for Mining, Metallurgy and Exploration, Inc., 1998). Quartz has a very low solubility of $5-6$ $mgSiO_2/L$ (pH 7, 20-25 ℃) (Bremere et al., 2000) .

equilibrium concentration the observed amorphous silica solubility concentration.

ferric iron(III).

gel a system that consists of a continuous solid skeleton made of colloidal particles or polymers that enclose a continuous liquid phase. (Bergna and Roberts, 2005).

monomeric silica also called orthosilicic acid, silicic acid or monosilicic acid (Ning, 2002). The formula H_4SiO_4 is used to describe this type of silica ($Si(IV)$) by convention, however it is not the only thermodynamically stable uncharged form. The forms SiO_2 and H_2SiO_3 are also stable, but have a lower equilibrium concentration (Nikolaychuk, 2014).

particular silica silica particles that can be separated with a 0.45 μm filter (Milne et al., 2014).

polymeric silica dimers, trimers and higher order oligomers that are the result of the condensation reaction of monomeric silica that bond through silicon oxygen bonds. The condensation polymers ultimately have the form $(SiO_2)_n$ (Milne et al., 2014; Iler, 1979).

pre-equilibrium concentration Concentration at which equilibrium seems to be reached, when viewed on a short time-scale. The removal rate seems to approach zero at this point (Sugita et al., 2000; Fleming, 1986).

pseudo-equilibrium point Concentration at which the reaction rate of silica polymerization in supersaturated solutions approaches zero. After this point is reached, the reaction proceeds at a much slower rate towards the equilibrium concentration (Fleming, 1986).

reactive silica silica that reacts with molybdic acid within 10 minutes. Monomeric silica reacts within 2 minutes under assay conditions, while dimeric silica reacts completely within 10 minutes. Reactive silica therefore comprises monomeric and dimeric silica (Ning, 2002).

reverse osmosis high pressure membrane process that produces high quality water. Pathogens, organic micropollutants, colloids, natural organic matter and salts end up in the brine stream (Salvador Cob et al., 2012) .

silanol silicon and the attached OH group (Si-OH) (Milne et al., 2014).

silica generic name that is used to denote silicon dioxide related components (that are a result of dehydration-polymerization of silicic acid) (Ning, 2002).

silicate combinations of silicon-oxygen tetrahedra (SiO_4) and other elements, such as sodium, potassium, calcium, magnesium, iron and aluminum (Society for Mining, Metallurgy and Exploration, Inc., 1998).

silicon chemical element with symbol Si. Silicon is a metalloid (Society for Mining, Metallurgy and Exploration, Inc., 1998).

soluble silica reactive silica and dissolved polymers (Ben Sik Ali et al., 2004).

List of Symbols

β	Formation constant	-
τ	Empty bed contact time	min
A_s	Surface area per unit liquid volume: $A_s = C_s * S_w$	m^2/m^3
C	Concentration of reactive silica	$mgSiO_2/L$
C_e	Equilibrium concentration	$mgSiO_2/L$
C_s	Concentration of silica gel beads	kg/m^3
C_T	Concentration of total silica	$mgSiO_2/L$
C_x	Pre-equilibrium concentration, $C_x > C_e$	$mgSiO_2/L$
I	Ionic strength	mol/L
K	Equilibrium constant	-
k	Kinetic constant	m^3/sm^2
L_{bed}	Height of the filter bed	cm
Q	Flow	L/min
R	Silica removal rate	kg/m^3s
S_w	Surface area per unit mass of beads	m^2/kg
V_{bed}	Volume of the filter bed	m^3
d	Diameter	$\text{Å} = 10^{-10}m$

1 Introduction

Silica scale causes major problems in various industries that use natural water as a source. Silica is present in natural water at 1-100 mg/L as SiO_2. When the concentration of silica exceeds the saturation concentration, scaling can occur. Scaling results in a decrease of the productivity level of the affected systems. Silica scaling is especially a challenge in membrane units, cooling systems and low-pressure boiler systems found in, for example, the production of drinking water or high grade water, (geothermal) energy production, the microelectronics industry or in the mining industry (Nalco Chemical Company, 2009; Milne et al., 2014; Ning, 2002).

Silica scaling-related problems have become more pressing as a result of the increasing use of high pressure membrane system reverse osmosis (RO). RO is increasingly used as a treatment step in the production of drinking water or high grade water from saline, brackish or polluted water sources in areas with a rapid industrial growth and forthcoming environmental regulations. A main environmental challenge of RO is the production of a concentrate (brine) stream (Greenlee et al., 2009; Haidari et al., 2018).

Especially in inland areas, it is often not allowed and it is furthermore undesirable to discharge brine due to environmental constraints. It is therefore advantageous to use minimal resources, produce minimal or no waste and recover valuable resources from the waste stream (Milne et al., 2014). Thus, following these requirements for sustainable operation, the brine stream needs to be treated. This treatment becomes more cost-effective when the brine is concentrated first, because it can decrease the total energy demand of brine treatment. RO can be used to further concentrate brine effectively, but the high concentrations of certain ions in the brine can cause scale formation on the membrane.

In RO systems with natural feed water, calcium and magnesium have a high scaling potential. However, these components can be effectively removed using ion exchange or calcium can be removed using other softening techniques, as a pretreatment step or interstage technique. After removal of these components, silica is the main limiting factor in the reaching of high recoveries (Salvador Cob et al., 2012).

In RO systems, silica scale can already form at a concentration of 180 $mgSiO_2/L$, depending on the conditions. By taking additional RO steps to concentrate brine, silica is concentrated. Thus, preventing silica scale formation is important in RO systems that are used to concentrate brine (Ben Sik Ali et al., 2004). Therefore, scale mitigation methods are sought that require few resources, including energy, and that produce only a minimum amount of waste from which valuable products can later be recovered (Salvador Cob, 2014).

A review of some possible mitigation methods is given in chapter 2. One of the methods that could be used to remove silica is column filtration with silica gel beads. Research into the removal of silica with silica gel in geothermal energy applications shows that silica can be removed from a solution with a high silica concentration ($> 200\ mgSiO_2/L$) (Sugita et al., 1998a,b, 1999, 2000, 2003). The removal of silica from brine with a relatively low concentration of silica (180 $mgSiO_2/L$) using silica gel has only been researched briefly by Bremere et al. (2000); Salvador Cob et al. (2014). Column filtration with silica gel might be used to remove silica in between RO steps. In that way, RO could be used to concentrate brine without the formation of silica scale. To investigate whether column filtration with silica gel is suitable for application, the effect of factors that influence the removal, such as pH, temperature, ferric and aluminum, needs to be researched. The pH and temperature have a large influence on the solubility of silica (Milne et al., 2014). Traces of ferric and aluminum are known to enhance scale formation and might therefore also be able to enhance the removal of silica using silica gel beads.

The purpose of this study is to investigate the removal of silica using silica gel beads and the applicability of fixed bed column filtration with silica gel beads in brine treatment. Different experiments were performed to test the effects of silica concentration, pH, temperature, small doses of ferric and aluminum on the removal efficiency. Both the removal equilibrium and kinetics were investigated by means of batch and column experiments. The experimental conditions were based on the conditions of RO brine from the demiwater plant Botlek of Evides Industry water. The model solution had a start concentration of 180 $mgSiO_2/L$, pH 8.5 and a temperature of 21℃.

Research questions

In this research, the following main research question is answered based on experimental research.

What is the influence of pH, temperature, a small dose of iron and a small dose of aluminum on the removal of silica from a low concentration silica solution using silica gel beads?

To answer the main question, the following sub-questions were formulated.

- What is the effect of the initial concentration of silica on the removal efficiency, varying from 100 to 200 $mgSiO_2/L$?
- What dosage of silica gel is most efficient to reach the equilibrium concentration after 48h and to what extent can the use of a higher dose of silica gel improve the kinetics?
- What is the effect of changing the pH to 5, 7 or 10 on the removal efficiency?
- What is the effect of changing the temperature to 10 or 35 ℃ on the removal efficiency?
- To what extent can the removal be enhanced by adding 1 or 10 mg/L of ferric?
- To what extent can the removal be enhanced by adding 1 or 10 mg/L of aluminum?

Additionally, the following question will be answered based on literature review and the findings of the experimental research.

To what extent is fixed bed column filtration with silica gel suitable for application as interstage silica removal technique in a RO system that is used to concentrate brine?

How to read this report

The research was broken down into various steps. The structure of this report reflects the steps of the conducted research.

Chapter 1: Introduction

Chapter 2: Background In this chapter, information on the formation of silica scale in RO systems is given in order to assess the relevance of a silica scale mitigation method in brine treatment with RO. A basic knowledge of silica chemistry is needed in order to understand the processes and mechanisms that take place during column filtration with silica gel beads and is therefore provided in this chapter. The factors that influence the solubility and the presence of certain forms of silica are affecting the formation of silica scale. These factors could therefore also have an effect on the removal. A literature review on scale mitigation methods will provide a justification for the choice for silica gel. Lastly, the special characteristics of silica gel are described and an overview of previous research on silica removal using a type of silica gel is given. The factors pH, temperature, ferric and aluminum, that have been tested in the experimental research were chosen based on this literature research.

Chapter 3: Method The experimental research approach, the measurement procedure and setup of both the batch and column experiments are described in this chapter. Additional information can be found in appendix A.

Chapter 4: Results The most important results of the experimental research are presented in this chapter. This chapter also includes the calculations of the kinetic constants. For a complete overview of all results, see appendix B.

Chapter 5: Discussion The most important findings based on the results are discussed and assessed in this chapter. Explanations for the obtained results are given and the limitations and implications of the findings are discussed. Finally, the suitability for application is discussed.

Chapter 6: Conclusion The main conclusions are summarized in this chapter and an answer to the research questions is formulated.

Chapter 7: Recommendations Based on the results, recommendations for future research are given. Research topics are proposed that focus on understanding the mechanisms involved, enhancing the removal and assessing the suitability for application in brine treatment or the treatment of other streams.

2 Silica scale formation and the removal of silica

To determine whether column filtration with silica gel beads is an appropriate method to remove silica from RO brine, a basic knowledge of silica chemistry and the factors influencing silica scaling is required.

2.1 Silica scale in RO systems

RO technology is a pressure-driven membrane technology that can be used to remove ions in order to produce high quality water. During filtration the ions are concentrated on the membrane retentate side (i.e. the feed side). When the concentration of sparingly soluble mineral salts, such as $CaCO_3$, $CaSO_4$ and $BaSO_4$, or the concentration of metal hydroxides and silica, exceeds the solubility limit, scaling can occur (Gabelich et al., 2007). The scale leads to a decline in the permeate flux and could damage the membrane. The formation of scale should, therefore, be prevented. The bivalent ions can be removed effectively before or during RO stages (Salvador Cob et al., 2012; Milne et al., 2014). After the removal of these precipitants based on carbonate or sulfate, the minerals that limit the recovery of an RO unit are silica and aluminosilicates (Rahardianto et al., 2007; Bond and Veerapaneni, 2008; Gabelich et al., 2007).

The reported solubility concentrations of amorphous silica lie in the range of $100 - 140$ $mgSiO_2/L$ at temperature $20 - 25$ °C (Ben Sik Ali et al., 2004). In RO applications, low silica supersaturations of 180 $mgSiO_2/L$ often do not cause problems. However, at higher silica concentrations there is the potential for silica scale formation (Bremere et al., 2000). Silica scale is difficult to remove, especially if the use of aggressive and hazardous chemicals, such as hydrofluoric acid, needs to be avoided. Therefore, silica scaling decreases the cost-effectiveness of RO.

Silica scaling can be caused by different mechanisms, depending on the silica concentration, the concentration of other components in solution and many physical and chemical variables, the most important of which are pH and temperature (Milne et al., 2014). The results of RO membrane autopsies confirm that the type and composition of the formed scale depends on the solution matrix. Silica scaling is highly complex and, therefore, not yet well understood.

Scale can be caused by the polymerization and accumulation of colloidal silica particles or by direct deposition on the membrane (Milne et al., 2014). Silica monomers can polymerize and form silica colloids. These silica colloids are often considered to be the most common cause of membrane scaling. Most research has therefore focused on controlling silica polymerization. However, it is not yet clear how the formation of silica polymers leads to silica scaling. The polymers formed can also react with traces of polyvalent metal ions to form metalsilicate scale. Analysis of sixty-six fouled membranes showed that a large percentage of the scale contained ferric (88%) or aluminum (75%) (Darton, 1999). Thus, ferric and aluminum seem to enhance scaling of silica. The second main mechanism is the direct deposition of silica monomers on the membrane surface by means of heterogeneous nucleation. For heterogeneous nucleation to take place, non-silica colloids, pre-existing scale or metal corrosion products need to be present (Bremere et al., 2000).

Semiat et al. (2003) showed that the scaling mechanism is dependent on the saturation concentration for synthetic silica solutions (without ferric and aluminum). At concentrations lower than 150 $mgSiO_2/L$ direct deposition is the main scaling mechanism, while at concentrations between 300 and 600 $mgSiO_2/L$ polymerization and accumulation is the main mechanism.

2.2 Silica solubility and forms of silica

In nature, silica can be present in crystalline form, such as quartz, or in the form of amorphous silica (Ning, 2002). Silica in water mainly originates from silicate minerals in the earth. The dissolution reaction is catalyzed by anions, such as OH^- and F^-. The silica hydrolyzes to form H_4SiO_4. This reaction only occurs at pH values below 11 (Milne et al., 2014). A simplified version of the reaction equation is (Milne et al., 2014):

$$x(SiO_2) + 2H_2O \leftrightarrow (x-1)SiO_2 + H_4SiO_4 \tag{2.1}$$

2.2.1 Forms of silica

Silica in solution is often described as H_4SiO_4 (monomeric silica or monosilicic acid), however it can be present in many other forms, such as polymeric, colloidal and particulate silica and as ions. To the further understanding of the scaling mechanisms, knowledge of all types of silica that can be present and their interactions is important. At neutral pH mainly monomeric silica is present. In natural water with a concentration lower than 100 $mgSiO_2/L$ at $25°C$, monomeric silica can be stable for a long time. If the concentrations are higher, silica polymerization can occur, leading to polymers, colloids and suspended particles (Ben Sik Ali et al., 2004; Iler, 1979).

Polymeric silica is formed during a condensation reaction. It can be a dimer, trimer or higher order oligomer. During the condensation reaction a silicon oxygen bond is formed between the silanol groups ($Si-OH$) of two monomeric silica molecules, since the bond energy of the $Si-O$ bond is higher than the bond energy of the $Si-H$ bond and even more than twice as high as that of the $Si-Si$ bond (Ning, 2002). The condensation reaction often involves a non-ionic monomeric silica molecule and an ionic monomeric silica molecule, see Figure 2.1. In acidic conditions two non-ionic monomeric molecules interact, see Figure 2.2.

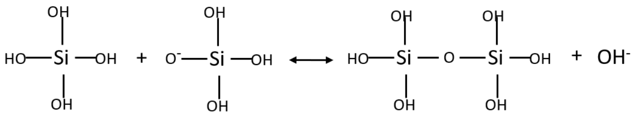

Figure 2.1: Dimerization reaction under alkaline conditions, after Makrides et al. (1980); Milne et al. (2014).

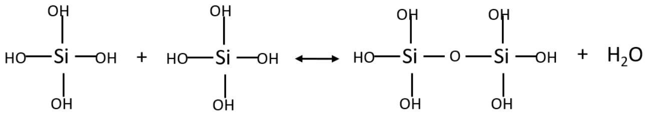

Figure 2.2: Dimerization reaction under acidic conditions, after Bischop and Bear (1972); Milne et al. (2014).

It is considered that the reaction mechanism is dependent on the temperature. At a temperature below $35°C$, the reaction starts with the formation of hydrogen bonds between the molecules and is followed by the ejection of a hydroxyl or water molecule. At higher temperatures, the reaction could start after a collision, since the activation energy for this reaction is positive. The reaction is again followed by the ejection of a hydroxyl or water molecule (Bischop and Bear, 1972).

Once a small amount of polymer has been formed, the monomer disappears very rapidly. The monomer reacts more rapidly with dimer and higher order oligomers than with other monomers, because the ionization constants of polymeric species are higher than those of monomeric silica (Gill, 1993; Bremere et al., 2000). The polymeric silica formed is unstable. The maximization of the number of Si-O-Si bonds and the minimization of the number of Si-OH groups is favored. The polymerization therefore continues through the formation of small ring structures (Milne et al., 2014). Eventually, internal cross links will be formed and the structures become particles with an shell of silanol groups that continue to grow (Bremere et al., 2000; Kley et al., 2014). As a result of this process, spherical particles are formed. The particles continue to grow, by means of the crystallization of more silica onto the surface of the particles or by a process called Ostwald ripening, which involves the growth of bigger particles at the expense of the smaller, more soluble, particles that dissolve (Salvador Cob, 2014).

When the particles have reached a certain size, they are called colloidal silica. There is no consensus over the definition of colloidal silica. Often the definition of Iler (1979) is used, that states that the minimal diameter of colloidal silica is 5 nm. However, according to IUPAC, the diameter ranges from 0.001 μm to 1 μm. The colloidal silica formed is stable (Bremere et al., 2000). The surface of the colloid contains many silanol groups, see Figure 2.3.

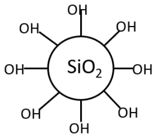

Figure 2.3: Schematic overview of the surface of colloidal silica with silanol groups (pH < 7)

These silanol groups are ionized when the pH is higher than 7. As a result, the overall charge of the colloid is negative (Bremere et al., 2000). Colloidal silica particles can grow without aggregation at a pH between 7 and 11, if no salts are present. Certain ions, such as polyvalent metal ions, cause the polymers or colloids to aggregate. The aggregates formed can be removed using filtration or through settling. Particulate silica is often defined as large particle size silica that can be separated by a $0.45\mu m$ filter (Milne et al., 2014).

2.2.2 Factors influencing the solubility of silica

The solubility (s) of amorphous silica is often calculated using Marshall's formula (Chan, 1989):

$$\log s = -0.1185 - \frac{1.1260 \cdot 10^3}{T} + \frac{2.3305 \cdot 10^5}{T^2} - \frac{3.6784 \cdot 10^7}{T^3} \quad T \text{ in } K,\ 298 < K < 573 \tag{2.2}$$

The resulting solubility at a temperature of 20-23 ℃ is $118 - 126\ mgSiO_2/L$. However, the solubility of silica is not only dependent on temperature, but also on pressure, pH and ionic strength (Ben Sik Ali et al., 2004). The solubility of silica has a minimum value of 100 mg/L between pH 7 and 8. When the pH increases, the solubility also increases. At a pH of 9 the solubility will already have increased to 138 mg/L. An explanation for the rapidly increasing solubility is the formation of the ionic types $H_3SiO_4^-$ and $H_2SiO_4^{2-}$. Other types that can form, such as $Si_2O_2(OH)_5^-$, increase the solubility even further. Thus, at pH below 9, the soluble form that is present is mainly monomer. With increasing pH the equilibrium shifts towards deprotonation (Milne et al., 2014; Sjöberg, 1996):

$$H_4SiO_4 \leftrightarrow H^+ + H_3SiO_4^- \qquad log\beta_{-1,1} = pK_1 = -9.473 \text{ at } 25°C,\ 0.6MNaCl \tag{2.3}$$

$$\begin{gathered} H_3SiO_4^- \leftrightarrow H^+ + H_2SiO_4^{2-} \qquad pK_2 \\ H_4SiO_4 \leftrightarrow 2H^+ + H_2SiO_4^{2-} \qquad log\beta_{-2,1} = pK_1pK_2 = -22.12 \text{ at } 25°C,\ 0.6MNaCl \end{gathered} \tag{2.4}$$

where the variation in formation constants $\beta_{-1,1}$ and $\beta_{-2,1}$ with ionic strength I follows the extended Debye-Hückel expressions: $log\beta_{-1,1} = log\beta^0_{-1,1} + \frac{1.022I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.11I$ and $log\beta_{-2,1} = log\beta^0_{-2,1} + \frac{3.066I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.31I$ (Sjöberg, 1996). The fraction of dimeric silica is never more than 5% of the total silica (Bremere et al., 2000; Sjöberg, 1996). The presence of these silicate ions also influences the kinetics of the polymerization of silica, because it is assumed that an ionic monomeric silica molecule is needed for the dimerization reaction (Milne et al., 2014). When the concentration of monomeric silica is higher than 200 $mgSiO_2/L$, the condensation reaction can occur. The pH is one of the most important factors influencing the presence of the different forms of silica and therefore the solubility.

The solubility of silica increases as the temperature increases. The effect of the change in temperature depends on the form of silica present. The solubility can also be influenced by the presence of multivalent cations. Hardness decreases the solubility, because calcium and magnesium silicates are formed or monomeric acid adsorbs on magnesium hydroxide and calcium carbonate. Hardness increases the polymerization rate. The presence of aluminum ions decreases the solubility. The formation of aluminum hydroxide could cause a large decrease in solubility (Milne et al., 2014). A reduction from 110 to

10 $mgSiO_2/L$ is reported by Iler (1979). The most probable reason for this reduction is the formation of aluminum silicates (Ning, 2002). However, adsorption of monomeric silica by aluminium hydroxide could also have contributed to this effect (Yokoyama and Tarutani, 1981; Milne et al., 2014). Iler (1979) also reported that even traces of ferric or aluminum can increase the polymerization rate by decreasing the solubility. The solubility is also significantly reduced in the presence of ferric. According to Bremere et al. (2000), iron silicates have a ten times lower solubility than amorphous silica. Ferric can help to destabilize supersaturated solutions (Bremere et al., 2000). Thus, multivalent cations can cause scale formation at concentrations below silica saturation (Milne et al., 2014).

Silica solubility also decreases when the ionic strength increases (Ben Sik Ali et al., 2004). Carbonate and sulphate seem to stabilize silica by forming salt complexes (Milne et al., 2014). The effect of the discussed factors is summarized in Table 2.1

Table 2.1: Overview of the factors influencing the solubility of silica. '-': low solubility, '+': higher solubility. The solubility at pH 7 and 25°C is $100 - 120$ $mgSiO_2/L$ (Bremere et al., 2000)

	low	high
pH (> 7-8)	-	+
pH (< 7-8)	+	-
Temperature	-	+
Conductivity	+	-
Hardness	+	-
ferric	+	-
Aluminum	+	-

2.3 Scale mitigation methods

When choosing an appropriate silica scale mitigation method, the main factors influencing silica scale formation and removal should be taken into account. These factors are pH, temperature, the presence of multivalent cations such as calcium and magnesium, aluminum, ferric and other metals as well as the ionic strength and anions present. The choice of a scale mitigation method is restricted by the aim to produce a good quality product in a cost-effective manner.

To prevent the formation of silica scale, operations can be changed, anti-scalants can be added or silica can be removed. Changing the operation often includes changing the pH or lowering the recovery of RO systems. In this way, the operation becomes more expensive and does not adhere to the restrictions for sustainable mitigation. The same holds for the addition of anti-scalants (Milne et al., 2014; Gabelich et al., 2010).

There are several methods that can be used to remove silica before treatment or in between stages. One way to remove silica is by adding lime or caustic to precipitate calcium and magnesium as well as silica. However, the sludge that is produced is highly complex and hard to dispose of (Rahardianto et al., 2007). Metal salt addition, such as aluminum or ferric, electrocoagulation and adsorption could also be used to remove silica. One drawback of these methods is the production of a waste sludge that needs to be treated and the presence of residual metal, making these methods less sustainable

(Milne et al., 2014). For example, precipitation with Al^{3+} seems to be very efficient for the removal of dissolved silica, however colloidal aluminosilicates are not removed from the brine (Salvador Cob et al., 2014). Thus, an additional ultrafiltration step is needed after the precipitation step. Low concentrations of aluminum and silica remaining in solution could also cause aluminosilicate scaling in RO membranes, since aluminosilicates have a 10 times lower solubility than silica. Residual aluminum could end up in the concentrated brine after the RO steps, making it harder to recover valuable compounds from the concentrated brine (Salvador Cob et al., 2012, 2014). Ion exchange and electrodialysis reversal can also be used to remove silica. However, ion exchange seems to be less suitable when other anionic species are present, since these species reduce the removal efficiency of silica (Milne et al., 2014; Ning et al., 2010). Finally, seeded precipitation, where silica-based seeds function as a precipitation surface, can be used to remove silica from solution. For an efficient removal process, a large crystallization surface is needed (Bremere et al., 2000). It is also important that the surface is receptive to the specific form of silica present in the solution (Milne et al., 2014). The driving force for the removal process at high silica concentrations of 400 and 530 $mgSiO_2/L$ is supersaturation (Bremere et al., 2000).

A promising seed material is silica gel, since it has a large specific surface. Silica gel beads of appropriate size could also be fixed in a column under gravity flow in order to maximize the contact surface and thus to increase the rate of precipitation.

2.4 Silica removal using silica gel

Silica gel consists of spherical particles of colloidal silica that are organized in a continuous network. A random packing of SiO_4 tetrahedrons determines the bulk structure. The surface of silica gel contains weakly acidic silanol groups (Tran et al., 1999). Well-known types of silica gel are chromatography silica gel and desiccant silica gel. Desiccant silica gel beads are cheaper and more readily available than chromatography silica gel, but it is not available in particle sizes smaller than $1-3\ mm$ and only few characteristics are given, such as particle size and a range of the specific surface area. Chromatography silica gel is available in various particle sizes up to $1-3\ mm$ and with various pore volumes. In all research on precipitation with silica gel chromatography silica gel has been used.

Seeded precipitation with silica gel as potential seed material in geothermal energy applications has been extensively studied. The seed method is based on the polymerization reaction at the silica gel surface. In this way, excess monomeric is removed. Silica gel has a high capacity because of the large surface area. It is confirmed by Sugita et al. (1999) that a high specific surface area is important for the removal efficiency. Research showed that silica can be removed up to saturation concentration $(328-340\ mg/L)$ from geothermal brine at a temperature of $82-85$ ℃ and using $5\ g/L$ silica gel or colloidal amorphous silica seeds (Sugita et al., 1998a) (Sugita et al., 1998b) (Sugita et al., 1999) (Sugita et al., 2000) (Sugita et al., 2003). According to Sugita et al. (1998a) direct deposition is enhanced at higher supersaturation, but increasing silica polymerization at higher concentrations reduces the silica removal efficiency at concentrations above 500 $mgSiO_2/L$. The silica precipitation rate depends on the specific surface area and the particle diameter. Sugita et al. (2000, 2003) showed that the kinetics of silica precipitation at a start concentration of 500 $mgSiO_2/L$ can be described by the following first order equation (Sugita et al., 2003).

$$-\frac{dC_T}{dt} = kA_s(C_M - C_x) \qquad [kgSiO_2/m^3s], \qquad C_x > C_e \tag{2.5}$$

where k is the apparent rate coefficient (m^3/sm^2), A_s is the seed surface area per unit liquid volume (m_s^2/m^3), C_T is the concentration of total silica ($kgSiO_2/m^3$), C_M is the concentration of monomeric silica ($kgSiO_2/m^3$), C_x is the pre-equilibrium silica concentration ($kgSiO_2/m^3$) and C_e is the amorphous silica solubility ($kgSiO_2/m^3$) (Sugita et al., 2003). The apparent rate coefficient k is dependent on the particle diameter of the seed (m), as well as on temperature, pH and the presence of other components. A_s can be represented by the product of the seed concentration in solution and the seed surface area per unit mass of seed. No prior research is done on the kinetics of silica precipitation on silica gel when no or very little polymerization takes place.

To make the removal of silica using silica gel more suitable for application, the dose of silica gel needed during operation needs to be lowered and the removal performance should be enhanced (Sugita et al., 2003; Nguyen et al., 2017). Only a few methods to increase the removal efficiency have been investigated, such as the combination of silica gel and ultrasonication or the addition of Fe^{3+} to the solution (Nguyen et al., 2017).

Removal of silica by silica gel has also been studied for RO brine. 2 g/L silica gel with a particle size ranging from 9.5 to 11 μm was tested on a solution of 200 $mgSiO_2/L$ silica with a pH of 8.5. After 6 hours 30% of the silica was removed. In the case where ferric was added (100 mg/L) 28% was removed. There was no difference between the addition of 2 or 3 g/L silica gel (Salvador Cob et al., 2014). Bremere et al. (2000) obtained a removal of 20% after 2h, starting with a concentration of 200 $mgSiO_2/L$ and using $2g/L$ silica gel with a particle size that ranges from $62 - 200$ μm at pH 7 and 21°C. Bremere et al. (2000) suggests that the amorphous silica solubility would be approached after 8-10h, however this was not tested. A removal of 50% was reported for the combination of silica gel and Fe^{3+} (Bremere et al., 2000).

The removal of silica using silica gel has only been tested in batch experiments using silica gel with a particle size smaller than 200 μm. However, silica gel beads can also be used in a fixed bed column. The use of larger beads than previously researched in a column could be beneficial from a practical point of view. It could allow for efficient operation and possibly for easy renewal of the beads. The size of the beads only influences the kinetics of removal and not the removal efficiency (Sugita et al., 2003). In a column, the contact surface is larger, which could result in a higher removal rate (Bremere et al., 2000).

The addition of small doses of aluminum or ferric (1 or 10 mg/L) to the silica solution could increase the removal efficiency, since the solubility of silica is decreased by those components (Milne et al., 2014). It has been suggested by Iler (1979) that traces of ferric or aluminum could increase and accelerate precipitation of silica. Furthermore, research on the type of scale on RO membranes showed that traces of ferric and aluminum can enhance scale formation (Bremere et al., 2000; Darton, 1999). Salvador Cob et al. (2012) reported concentrations of 0.1 $mgFe/L$ and 0.5 $mgAl/L$ in the RO concentrate as a result of pretreatment. However, enhancing the removal by adding small doses of ferric or aluminum has not yet been investigated. Further research is needed to determine whether silica gel in a fixed bed column is suitable for the treatment of RO brine and whether traces of ferric or aluminum can enhance the removal efficiency.

3 Materials and methods

Experiments were conducted to investigate the removal of silica using silica gel beads and the applicability of a column filtration process of RO brine using silica gel beads. Both the removal mechanism and kinetics were investigated.

3.1 Experimental setup

3.1.1 Batch experiments

During batch experiments, the most suitable experimental operational conditions and the influence of ferric and aluminum on the removal process were investigated. Firstly, the stability of the silica gel beads in solution and the stability of the silica solutions was investigated. Secondly, the effect of silica concentration, the dose of silica gel beads, pH and temperature on the removal process was investigated. Based on the results of these tests and the specifications of real RO brine (Evides demiwaterplant, Botlek), the experimental operational conditions were determined. Thirdly, the effect of ferric and aluminum on the removal was determined. These components can react with silica in solution and form complexes or precipitate directly, together with the silica in solution. The effect of the components was tested separately. The removal equilibrium was investigated by both measuring the silica concentration of demiwater to which silica gel was added and by measuring the silica concentration of a silica solution to which silica gel was added. The kinetics was investigated by measuring the removal over time.

The batch experiments were conducted using covered plastic 500 mL beakers. The pH of the model solution containing silica was measured (WTW multimeter 3430) and was adjusted to the preferred experimental level by adding HCl (1M, Sigma Aldrich) or $NaOH$ (1M, Sigma Aldrich). The temperature was measured continuously. The experiments were carried out at room temperature ($21°C$). In the experiments where the effect of temperature on the removal was tested, the beaker was placed in a water bath with a fixed temperature (C-MAG HS7, IKA). Two types of silica gel were tested, desiccant and chromatography silica gel. For the specifications, see Table 3.1. The desiccant silica gel was prepared. To this end, the silica gel was exposed to air for two weeks to moisturize the beads. Afterwards, the silica gel was flushed with demineralized water. The chromatography silica gel was only flushed with demineralized water (unprepared).

Table 3.1: Specifications of silica gel chromatography and desiccant

Type	chromatography	desiccant
Manufacterer	Carl Roth	Sigma Aldrich
Particle size range	1-3 mm	1-3 mm
Specific surface area	500-600 m^2/g	
Specific pore volume	0.8-1.0 m^3/g	
Pore diameter	53-80 Å	

The experiments started with the addition of $4g$ of silica gel beads to $500mL$ of the prepared solution. The solution was continuously mixed (110 rpm) on a shaker (Sea*Star 1.11, Heathrow Scientific). The pH was checked and, if necessary, adjusted every 15 minutes by adding HCl (1M, Sigma Aldrich) or $NaOH$ (1M, Sigma Aldrich). Samples were taken using a plastic syringe. The sample was filtered with a $0.45\mu m$ filter (Chromafil Xtra PES45/25, Macherey-nagel) in order to remove suspended insoluble silica. The first 2 mL were discarded to diminish the possible effect of adsorption of silica to the filter membrane. A portion of the sample was taken and diluted to the appropriate concentration for testing. All diluted samples were mixed using a vortex mixer. The sample was analyzed for reactive silica and total silica. The reactive silica analysis was performed shortly after sample collection. In order to preserve the sample for total silica analysis HNO_3 (65%, Carl Roth) was added. The runtime of the experiment investigating the stability of the silica gel beads was one week. The stability of the silica solutions was investigated to find out whether the silica polymerized or was removed. The runtime of these experiments was 48 hours. Samples were taken at the start and end of these experiments. The runtime of the experiments that were performed to investigate the kinetics was 8 hours. During these experiments samples were taken every 30 or 120 minutes. The runtime of the experiments that were used to investigate the removal after equilibrium seemed to be reached was 48 h. Samples were taken at the start and end of the experiment. All experiments were performed in duplicate.

3.1.2 Column experiments

Column experiments were conducted to determine the influence of the available contact surface on the removal efficiency and to investigate the kinetics. The conditions of the column experiments mimicked the selected conditions of the batch experiments, see Table 3.2. In the batch experiments, the solution was mixed using a shaker in order to prevent the silica gel beads from breaking as a result of fast mixing using a stirrer. Poor mixing could result in a smaller effective available contact surface. Thus, the first goal of the column experiments was to investigate whether the removal was affected by poor mixing. The second goal was to investigate the kinetics by using different doses of silica gel. The effect of an increased contact time was tested by using double and eight times the dose of silica gel ($8g/500mL$ and $32g/500mL$ respectively). The contact time is important to determine the suitability of fixed column filtration with silica gel beads for application. A schematic overview of the setup is also given, see Figure 3.1. The silica solution was placed in the beaker. The experiment started when the solution was first pumped through the column filled with silica gel. The solution was stirred in order to obtain a homogeneous concentration distribution in the beaker. The runtime of the experiment was 8 hours. Every 30 minutes or 1 hour a sample was taken from the beaker. The pH was measured continuously and adjusted in the beaker.

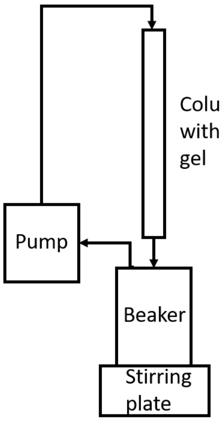

Figure 3.1: Schematic overview of the column experiment setup

Table 3.2: Specifications of the column experiment setup

Solution	
Type of water	demineralized water
Amount of solution	500 mL
SiO_2 concentration	180 mg/L
pH	8.5
Experimental setup	
Silica gel chromatography	4, 8 or $32g/500mL$
Diameter column	1.5 cm
Height column	40 cm
Height filter bed	3.9, 8.0 or 31.4 cm
Pump	Watson-Marlow 520S
Flow rate	318 mL/min
Contact time/hour	2.04, 4.19 or 16.45 min
Stirring plate	Labinco L23
Runtime	8 h

3.2 Silica solutions

Several silica solutions were prepared to investigate the removal process under different conditions, see Table A.3. The silica solutions were prepared by dissolving $Na_2SiO_3{\cdot}5H_2O$ (98% purity, Sigma Aldrich) in demineralized water. To investigate the effect of aluminum and ferric on the removal process, Al^{3+} (as $AlCl_3{\cdot}5H_2O$, 95% purity, Carl Roth) and Fe^{3+} (as $FeCl_3 \cdot 6H_2O$, 98% purity, Carl Roth) were added to the silica solution, respectively. The solutions with ferric and aluminum were used directly (within 45 minutes) or aged for more than 45 minutes.

3.3 Analyses

Total silica comprises reactive silica and non-reactive silica. Total silica was analyzed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS, PlasmaQuantMS, Analytikal Jena). The reactive silica was analyzed by a spectrophotometer at 452 nm wavelength (Hach-Lange DR3900), following the silicomolybdate Hach method 8185. In this method molybdate reagent is added. The rate of the staining reaction between monomeric silica and the reagent molybdic acid is fast. Dimeric silica also reacts completely within the ten minutes of test time. However, the reaction of higher order polymeric silica takes much longer. Polymeric silica is therefore not measured with this method. The removal efficiency can be obtained from the change in total silica concentration or from the change in the reactive silica concentration in a seeded batch. When the removal efficiency is determined by considering only the reactive silica, the change in concentration for the seeded batch has to be compared to the change in concentration in a similar unseeded batch. The comparison with the unseeded batch allows for compensation for the loss of reactive silica due to polymerization.

The standard deviation of the results of the Hach method 8185 was determined by diluting and measuring the same solution 10 times. The standard deviation was ±4 $mgSiO_2/L$. The results of ICP-MS were not accurate enough and are therefore not included in this report. A description of the procedure of the ICP-MS measurements can be found in appendix A.

The pH was measured continuously with WTW multimeter 3430.

4 Results

Two types of silica were tested in this research, desiccant and chromatography silica gel. Desiccant silica did not seem to be able to remove silica. With chromatography silica gel removal percentages up to 30% were obtained after 8 hours. Chromatography silica gel was therefore used to investigate the removal of silica under different conditions. All data on silica concentrations in this chapter was obtained by the Hach 8185 method. The values therefore represent the concentration of reactive silica (monomeric and dimeric silica). The standard deviation of all results is $\pm 4mg/L$.

4.1 Stability of silica gel in demineralized water

The chemical stability of silica gel in demineralized or ultrapure water was tested under different conditions. Desiccant silica gel seemed to be more stable than chromatography silica gel, because the concentration of reactive silica in solution after 1 week was approximately 53 $mgSiO_2/L$ for desiccant silica gel, whereas it was approximately 104 $mgSiO_2/L$ for chromatography silica gel (pH 8.5, 21℃), see Table B.2 and Table B.3. Chromatography silica gel dissolved more rapidly under all circumstances until equilibrium was reached. The increase in concentration of SiO_2 for standard conditions (pH 8.5, 4g chromatography silica gel/500mL, 21℃) was monitored regularly for the first 8 hours, see Figure 4.1. The experiment was left to run for another week. The resulting silica concentration was approximately 104 ± 4 $mgSiO_2/L$. The silica concentration after 2 days and 1 week for different conditions can be viewed in Figure 4.2. The pH had a minor influence on the dissolution of chromatography silica gel. Increasing the temperature to 35℃ for 48 hours resulted in a 13% higher silica concentration. After one month the concentration of silica in solution was still approximately 104 ± 4 $mgSiO_2/L$, which showed that equilibrium was reached (pH 8.5, 4g chromatography silica gel/500mL, 21℃).

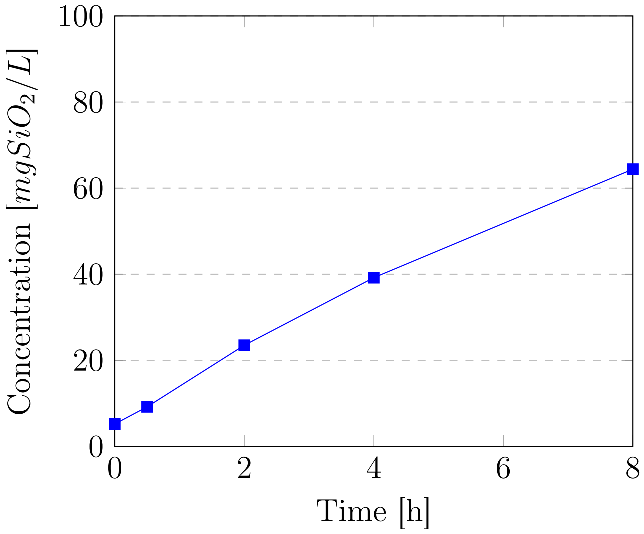

Figure 4.1: Concentration of reactive silica in solution over time after the addition of $4g/500mL$ chromatography silica gel to demineralized water at pH 7 and 21℃.

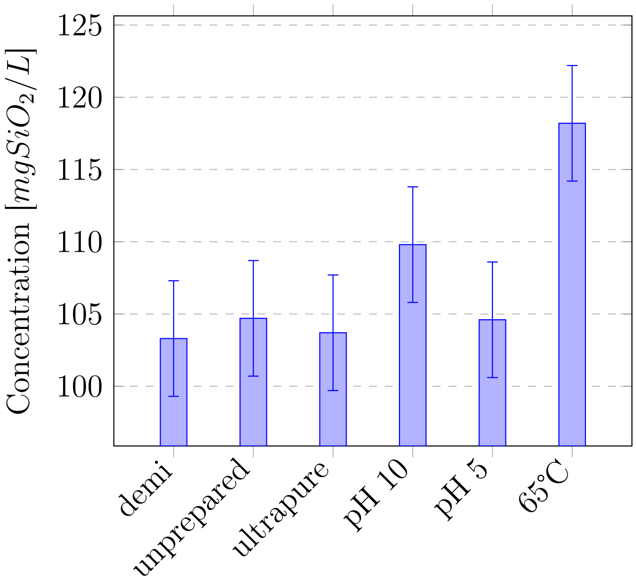

Figure 4.2: Concentration of reactive silica in solution after the addition of $4g$ chromatography silica gel to 500 mL demineralized or ultrapure water at various conditions measured after 1 week. The standard test conditions were: demineralized water, silica gel prepared by flushing with demiwater, pH 7, 21℃. The deviation from the standard conditions is indicated on the x-axis. Unprepared silica gel was not flushed with demineralized water.

4.2 Silica removal from silica solutions using silica gel beads in seeded batches

Chromatography silica gel was able to remove reactive silica up to 30% in 8 hours. The concentration of reactive silica in an unseeded batch did not change in this time-frame. This shows that polymerization did not occur under these conditions (Table B.1). The removal of reactive silica was therefore considered to be equal to the removal of total silica from solution.

The dose of silica gel that was required to get the most efficient removal of silica after 48 hours from a 180 $mgSiO_2/L$ solution was determined to be $8g/L$, see Figure 4.3.

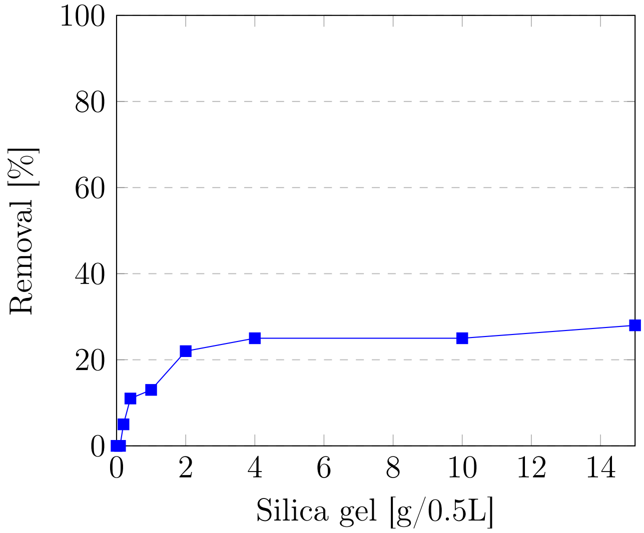

Figure 4.3: Removal efficiency of reactive silica after 48h using a batch system with different doses of silica gel at pH 8.5 and 21℃.

The removal of silica using chromatography silica gel was tested for solutions with initial concentrations of 100 to 200 $mgSiO_2/L$, pH varying from 5 to 10 and added concentrations of ferric and aluminum of 1 or 10 mg/L. The resulting removal efficiency after 48 hours is summarized in Figure 4.4. The removal efficiency was higher when the SiO_2 concentration was higher, seemed to be lower when the pH was higher or lower and was approximately the same if 1 or 10 mg/L of ferric was added or if 1 mg/L of aluminum was added. The removal seemed to be lower when 10 mg/L of aluminum was added. The removal was also investigated over time. When the temperature was decreased to 10℃ or increased to 35℃, the removal efficiency seemed to decrease. In the cases where ferric or aluminum were added, the removal efficiency was dependent on the aging time of the solution. If the solution was aged up to 45 minutes, the removal seemed to be equal or higher in comparison to a solution without ferric or aluminum. If the solution was aged for more than 45 minutes, the removal appeared to be lower.

The resulting removal from the solution under standard conditions was also measured after 1 month. The final silica concentration was 99.6 ± 4 $mgSiO_2/L$.

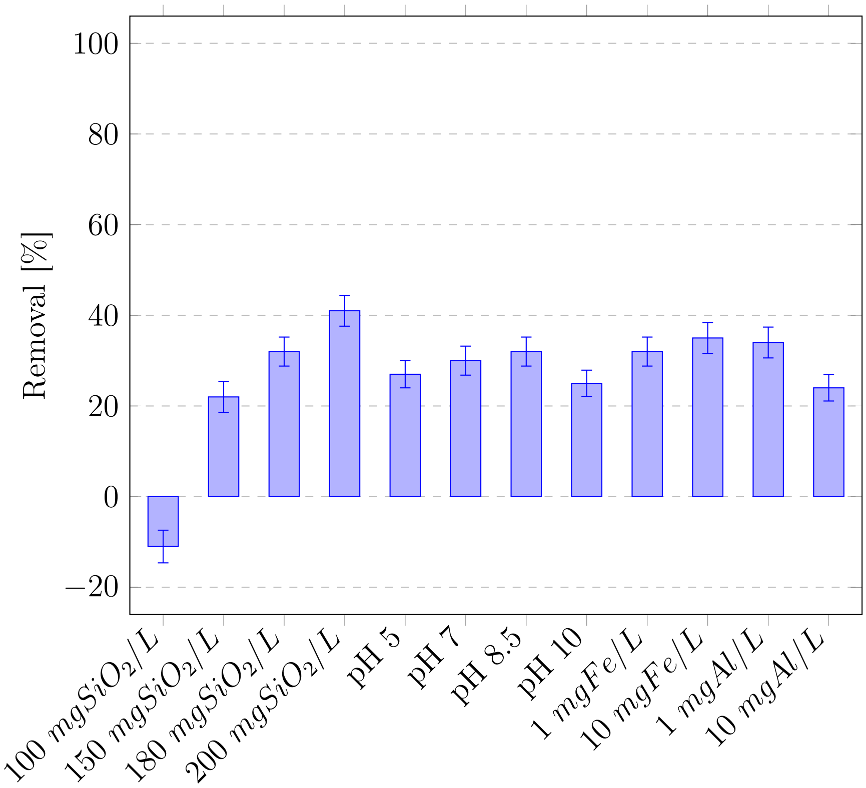

Figure 4.4: Removal efficiency of reactive silica after 48h using a batch system at various silica concentration, pH and with ferric or aluminum added. The standard test conditions were: demineralized water, silica gel prepared by flushing with demiwater, pH 8.5, 21°C. The deviation from the standard conditions is indicated on the x-axis.

4.3 Silica removal through fixed bed column filtration

4.3.1 Results of silica removal using fixed bed column filtration with silica gel beads

The removal of silica was also investigated in a fixed bed column filtration experiment in order to test the effect of mixing. The removal in a seeded batch and a mimicked fixed bed column filtration experiment was similar (Figure 4.5). Doubling the amount of silica gel increased the removal rate but not the removal efficiency after 8 hours. Increasing the amount of silica gel by 8 times seemed to give only a slightly higher removal rate compared to doubling the amount of silica gel.

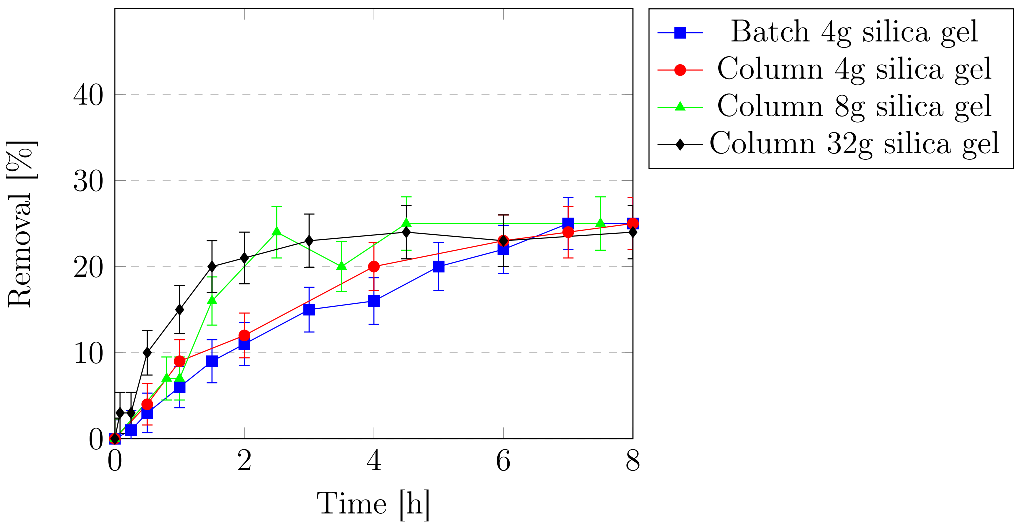

Figure 4.5: Removal efficiency of reactive silica over time using a seeded batch with $4g$ silica gel or fixed bed column filtration with $4g$, $8g$, or $32g$ $/500mL$ silica gel (pH 8.5, 21°C).

4.3.2 Kinetics of silica removal using fixed bed column filtration with silica gel beads

In order to quickly determine whether the rate law (Equation 2.5) also holds when there is only reactive silica present, the rate was calculated directly by $\Delta C/\Delta t$ and plotted against the reactive silica concentration, see Figure 4.6. The lines were determined using the least square method. The results for $4g$ and $32g$ silica gel clearly show a linear decrease, and thus show that the rate was first-order. The results for $8g$ do not reveal a clear trend due to measurement errors. The rate tended towards zero at a concentration of approximately 130 $mgSiO_2/L$. At this concentration the removal process seemed to have stopped and this was the final concentration that was reached when the experiment was stopped after 8 hours. Thus, it seemed that Equation 2.5 can be used to describe the kinetics up to a concentration C_x, in which the rate approached zero. Equation 2.5 does not describe the kinetics for the whole removal process, since the limit was set at C_x. In reality, the removal process will continue slowly until equilibrium is reached. Namely, in other experiments the concentration had decreased to approximately 125 $mgSiO_2/L$ after 48 hours and to approximately 100 $mgSiO_2/L$ after 1 month. However, for the application of column filtration with silica gel, the part of the removal process until C_x is reached seemed more useful.

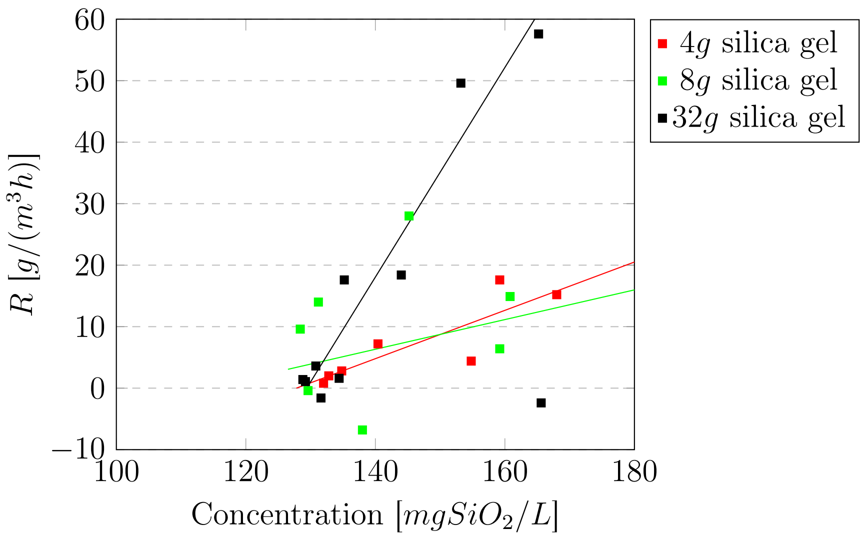

Figure 4.6: The rate of removal plotted against the concentration reactive silica for a column filled with $4g$, $8g$ or $32g$ chromatography silica gel (pH 8.5, 21℃). The lines were calculated using the least square method.

Based on the obtained silica concentrations and using Equation 2.5, the kinetic constant kA_s was determined using the least square method. The results can be found in Figure 4.7.

Table 4.1: Kinetic constants of removal using 4, $8g/500mL$ or $32g/500mL$ chromatography silica gel in a column (pH 8.5, 21℃, start concentration: 180 $mgSiO_2/L$, $S_w = 0.55m^2/kg$, t in h).

Kinetics							
		$4g/500mL$ silica gel		$8g/500mL$ silica gel		$32g/500mL$ silica gel	
		Experiment 1a	Experiment 1b	Experiment 2a	Experiment 2b	Experiment 3a	Experiment 3b
C_x	$mgSiO2/L$	122.3	128.9	126.5	131.2	129.3	129.6
kA_s	h^{-1}	0.293364	0.345064	0.520033	0.436785	1.039727	1.171412
A_s	m^2/m^3	4.4	4.4	8.8	8.8	32.5	32.5
k	m^3/hm^2	0.066674	0.078424	0.059095	0.049635	0.031992	0.036043

In Figure 4.7 the function

$$C(t) = C_x + (C_0 - C_x)e^{-kA_st} \qquad C_x > C_e, \quad t \text{ in } h \tag{4.1}$$

is plotted for experiment 1b, 2a and 3a, together with the measured values, because these functions gave the best fit or because these results were more trustworthy.

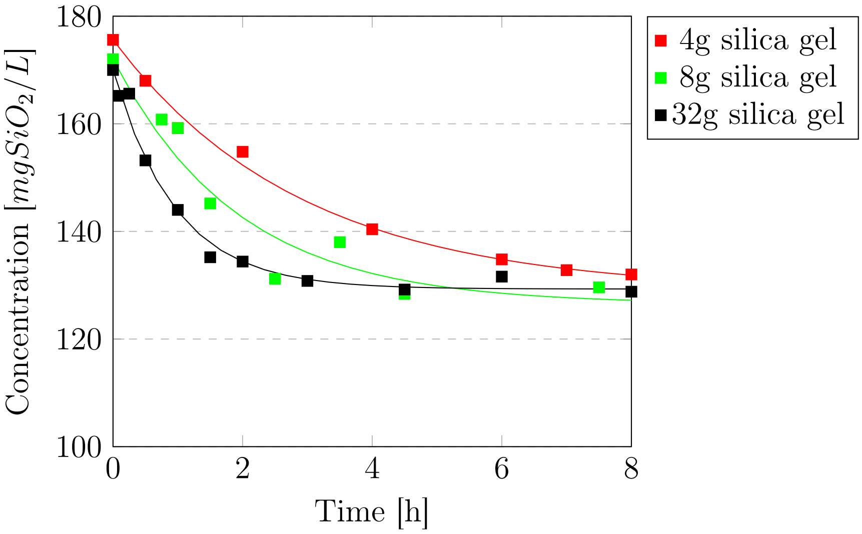

Figure 4.7: Measured concentration of reactive silica over time for a column filled with $4g$, $8g$ or $32g$ chromatography silica gel plotted together with the function $C(t) = C_x + (C_0 - C_x)e^{-kA_s t}$, where kA_s and C_x are determined with the least square method (pH 8.5, 21°C).

5 Discussion

5.1 Removal of silica using silica gel beads

In order to investigate the removal of silica using silica gel beads, experiments were performed that tested the effect of pH, temperature, a small dose of ferric or aluminum on the removal. Two types of silica gel were tested, desiccant silica and chromatography silica.

Desiccant silica gel did not remove reactive silica and was therefore not researched further. Only a few characteristics of the used desiccant silica gel were known. An explanation for the difference in removal capacity between the desiccant and chromatography silica gel could be the size of the available specific surface area or the functionality of the surface. However, without more research on the characteristics of both types of gel beads, a final conclusion on the reason for the difference and the characteristics that influence the removal capacity cannot be given.

5.1.1 Removal of silica using silica gel at pH 8.5 , 21°C

Chromatography silica gel was able to remove up to 30% of silica within 8 hours from a 180 $mgSiO_2/L$ solution. The concentration of reactive silica in the unseeded batch remained 180 $mgSiO_2/L$ for the entire experiment. This indicates that the decrease in concentration in the seeded batch can be attributed to the removal of reactive silica and not to polymerization. The chemical stability in the unseeded batch also showed that this concentration (180 $mgSiO_2/L$) is a pseudo-equilibrium point, since the concentration of reactive silica did not drop to the equilibrium concentration (Fleming, 1986; Bremere et al., 2000).

The obtained removal after 6 hours ($\sim$ 23%) was lower than the removal found by Salvador Cob et al. (2014) and Bremere et al. (2000). Salvador Cob et al. (2014) obtained a removal of 30% after 6 hours, starting with a silica concentration of 200 $mgSiO_2/L$ and using 2 or 3g/L silica gel at pH 8.5 (silica gel with particle size 9.5-11 μm and pore diameter 50-76 Å). There was no difference between using 2 or 3g/L of this type of silica gel (Salvador Cob et al., 2014). Bremere et al. (2000) found a slightly lower removal of about 28% using 2g/L silica gel 60 at pH 7 (200 $mgSiO_2/L$, silica gel with particle size 63-200 μm, mean pore diameter 60 Å). It was expected that the silica gel would have removed silica up to the amorphous silica solubility (118 $mgSiO_2/L$) after 8-10 hours

(Bremere et al., 2000). The measured lower removal efficiency after 6 hours could possibly be explained by the slower kinetics due to the particle diameter of the beads that were used and the lower initial concentration.

The results of the removal in the seeded batch under standard conditions are comparable to the results of the mimicked column, showing that the solutions were well-mixed during the batch experiments.

5.1.2 Effect of pH and temperature on the removal

Operating at pH 10 instead of 8.5 resulted in a lower removal. At pH above 9 silica ionizes, which leads to an increased solubility. The higher solubility of silica could be an explanation for the reduced removal. The reduced removal could also be explained by the receptiveness of the surface to polymeric silica. According to Sugita et al. (2003) silica gel only removes monomeric silica. This could be explained by the surface charge of silica gel and polymeric silica. Both are assumed to be negative at pH above 7 and therefore the polymeric silica is repelled from the surface (Bremere et al., 2000). At pH 5 the removal is comparable to the removal at pH 7 and 8.5, but was expected to be lower as a consequence of the higher solubility at this pH. Nguyen et al. (2017) showed that the removal efficiency at higher silica concentrations ($1100-1500$ $mgSiO_2/L$) is highest at pH 6, while the removal efficiency for initial concentrations of 500 $mgSiO_2/L$ is highest at pH 9. The pH seems to have a great influence on solutions with initial concentrations ≥ 500 $mgSiO_2/L$, but a low influence on solutions with initial concentrations of 180 $mgSiO_2/L$.

Increasing or decreasing the temperature has a negative influence on the removal efficiency. Based on the effect of temperature on the solubility, it was expected that a higher temperature would lead to lower removal efficiency, whereas a lower temperature would lead to a higher removal efficiency. Experimental difficulties during the experiments at lower and higher temperatures could have led to ill-mixing, resulting in a lower removal. However, it is not likely that this is the main reason. More research is needed to investigate the removal at lower and higher temperatures.

5.1.3 Effect of the addition of 1 or 10 mg/L of ferric or aluminum to the silica solution

Ferric and aluminum are known to decrease the solubility of silica. Even traces can increase the scaling potential greatly (Sugita et al., 1999). As a consequence, ferric and aluminum are often found in silica scale (Darton, 1999). It was therefore hypothesized that small doses of ferric and aluminum could be used to enhance the removal efficiency with silica gel beads. However, adding 1 or 10 mg/L of ferric or aluminum to the silica solution and letting the solution age for more than 45 minutes resulted in no removal from the moment the experiment was started (45 minutes after the solution was prepared). If the solution was aged shorter than 45 minutes, silica was removed. In this case, the removal can be attributed to the formation of colloidal iron silicates or aluminosilicates that were removed subsequently by filtering the sample ($0.45\mu m$ filter). This removal process also explains the higher removal efficiency found by Bremere et al. (2000) and Salvador Cob et al. (2014). Using $2g/L$ silica gel in combination with 100 $mgFe/L$ results in a removal of 28%, after 6 hours at a pH of 8.5 (Salvador Cob et al., 2014). Bremere et al. (2000)

obtained approximately 50% removal in 6 hours at pH 7 using $2g/L$ silica gel 60 and 100 $mgFe/L$. In these researches, silica is probably not removed with precipitation on silica gel, but due to application of ferric and filtration.

More research is needed to determine why traces of ferric or aluminum in RO feed increase the silica scaling potential, whereas small doses do not seem to improve the removal of silica with silica gel. The observed absence of removal could be explained by the characteristics of the surface. The surface might not be receptive to the metalsilicates or the larger metalsilicates could block the pores of silica gel, resulting in a very small specific surface area. Without pore blockage, the specific surface area per bead is 0.82 m^2 on average, whereas it is only $0.00031 - 0.00282$ m^2 per bead when all pores are blocked. Furthermore, the doses of ferric and aluminum used in this research are higher than the traces found in real brines. A different mechanism could occur when only traces are present, such as precipitation without aggregation, that in membrane systems, results in metalsilicate scale (Iler, 1979; Rigali et al., 2016).

5.1.4 Limitations of the removal of silica with silica gel

The removal capacity seemed to have a lower bound, since silica was not removed below a concentration of approximately 102 $mgSiO_2/L$. An explanation could be that silica gel is not chemically stable in water. The concentration of reactive silica (SiO_2) increased rapidly after the addition of chromatography silica gel to demineralized water. After 1 week the equilibrium concentration of approximately 102 $mgSiO_2/L$ was reached (standard conditions), but after 8 hours the concentration was already 64.4 ± 4 $mgSiO_2/L$. The dissolution of silica gel under standard conditions implicates that silica cannot be removed to concentrations below this equilibrium concentration of 102 $mgSiO_2/L$. The removal was thus limited because of the dissolution of silica gel.

The difference between the concentration of silica in solution and the amorphous silica solubility is considered to be a driving force for the removal (Bremere et al., 2000). (Bremere et al., 2000) found that a concentration of 200 $mgSiO_2/L$ dropped steadily to 160 $mgSiO_2/L$ in 2h. (Bremere et al., 2000) suggests that the amorphous silica solubility would be approached after 8-10h. However, results from this research showed that the removal rate tends toward zero at a concentration of approximately 130 $mgSiO_2/L$. The concentration seemed to stay constant within the runtime of the experiments, but was probably decreasing very slowly. After one month the equilibrium concentration of 102 $mgSiO_2/L$ was reached, however it could be that this concentration was reached earlier. The removal process after the first 8 hours was not researched. For application in practice, a runtime of one month is not feasible. Based on practical considerations, the removal process can therefore be divided into two different regions, that are separated at the concentration C_x at which the rate first tends towards zero. In the first region, in this research from $180 - 130$ $mgSiO_2/L$, the reaction is relatively fast and the removal seems to be almost linear. In the column experiments different doses of silica gel were used. Doubling the amount of silica gel that was used increased the removal rate in the first 2.5 hours. Using 8 times more silica gel increased the removal rate even more for the first 1.5 hour. Thus, the available contact surface seemed to be a limiting factor until the concentration of silica had dropped to 130 $mgSiO_2/L$. However, the increase in removal rate seemed to not be linear, which is a factor that should be considered when scaling up. In the second region, from $130 - 102$ $mgSiO_2/L$, the reaction was very slow. The removal process in this region was not a topic of research. Further research aimed at application should thus focus on increasing the removal rate in the first region. However, research on factors that influence the solubility and the dependence of the concentration C_x on the equilibrium concentration remains interesting, in order to understand the complete removal mechanisms and maybe even find methods to increase the total removal by lowering C_x.

Saturation of the beads could also decrease the removal efficiency. The lifetime of the beads is not yet determined. Especially when polymerization takes place, pores of the silica gel beads could become blocked. Pore blockage decreases the available surface area and thus the removal efficiency.

5.1.5 Equilibrium constant

The equilibrium constant of the dissolution-removal reaction can be calculated from the measured equilibrium concentration. The dissolution-removal reaction can be simplified as follows (Morey et al., 1964):

$$SiO_2(s) + nH_2O \leftrightarrow SiO_2(l) \tag{5.1}$$

If it is assumed that the amount of solid silica is not limiting, the equilibrium constant K is equal to the molar equilibrium concentration. Thus, K is 0.0017 $molSiO_2/L$.

In computer programs, often a higher K is used. For example, in the database PRHEEQC.DAT of software PhreeqC the standard K is 0.00195 $molSiO_2/L$, which gives a solubility level of 117 $mgSiO_2/L$ at 25°C. Before using these programs to model the dissolution of silica gel or the removal of silica, it should be checked that a correct temperature and pH dependent solubility level is used.

5.2 Suitability of fixed bed column filtration with silica gel for application

The effect of increasing the contact time gives an indication of the suitability of this technique for application in brine treatment. Increasing the contact time could decrease the time that was needed to obtain a 30% removal. However, both the final removal and the improvement due to the use of more silica gel seemed to be limited.

The obtained removal efficiency might be too low for application of fixed bed column filtration with silica gel beads as interstage silica removal technique in a RO system that is used to concentrate brine. The found limitations make it more difficult to increase the removal efficiency. Methods that overcome these limitations or increase the removal rate are needed to make fixed bed column filtration with silica gel beads more suitable for application (Nguyen et al., 2017). The mode of operation, such as increasing the flow velocity or using a different filtration method can also influence the kinetics. Factors that improve the kinetics in application are not thoroughly researched. Modelling and optimizing design parameters, such as the mode of operation or the removal conditions, is useful in order to find the most efficient removal operation (Bremere et al., 2000).

Methods that can improve the removal rate and thus the required time to reach a certain concentration, are interesting for application. One method that could be used to increase the removal rate is ultrasonication. Nguyen et al. (2017) showed that ultrasonication at alternating frequencies $500kHz$ and $28kHz$ increased the removal rate in the first 90 minutes, starting with a concentration of 1100 $mgSiO_2/L$. The effect of ultrasonication at lower initial concentrations is not yet researched. Increasing the pore size or decreasing the particle diameter have also been shown to increase the removal rate (Sugita et al., 2003; Nguyen et al., 2017). Adding traces of compounds that are known to influence the scaling process might also increase the removal rate or maybe even decrease the lower limit. Lowering the temperature did not result in a higher removal efficiency, however, there were some experimental difficulties. It therefore remains interesting to test a lower temperature could lead to a higher removal rate.

The initial concentration has a large influence on the removal. When an initial concentration of 200 $mgSiO_2/L$ is used, a higher removal efficiency can be obtained. Bremere et al. (2000) found that the silica concentration decreased faster when the initial concentration was higher: from 400 to 240 $mgSiO_2/L$ and from 500 to 290 $mgSiO_2/L$ in 2h. According to Sugita et al. (1998a) starting at concentrations higher than 500 $mgSiO_2/L$ decreases the removal efficiency, due to increased polymerization. In order to make the removal of silica using silica gel beads fixed in a column more suitable for application, it could be an idea to increase the concentration of silica in solution up to 500 $mgSiO_2/L$ beforehand. One method to increase the concentration of silica without increasing the scaling potential is by using semi-batch or batch RO systems instead of continuous RO to concentrate the brine. Using time-varying batch processes the liquid residence time is 3-4 times shorter. Batch RO systems have therefore the potential to concentrate brine further (Warsinger et al., 2018). Using silica gel to remove silica when the concentration has become limiting, the brine could possibly be concentrated even more. It might even be possible to reduce the need for evaporation techniques and thus make the final step of the brine treatment more energy-efficient. The silica concentration that would be limiting batch RO is much higher than the concentration that is limiting continuous RO (Warsinger et al., 2018). The removal with silica gel is therefore more efficient when batch RO is used to concentrate the brine. The silica gel after it is used to remove silica, is a potential valuable product, since it is assumed to have a high purity (Sugita et al., 1998a).

The combination of batch RO and fixed bed column filtration with silica gel could be a sustainable option for the treatment of waste brine streams, however more research on both technologies is needed. A high salinity, hardness or the presence of components such as barium could influence the removal and their effect should therefore be investigated.

5.3 Preliminary design calculations

The size of a column that can be used to remove silica in a batch RO setup, can be calculated using the mass balance:

$$C_0 \cdot Q - C \cdot Q - V \cdot R = 0 \tag{5.2}$$

where C is the chosen final concentration. In this calculation of the volume the column is considered to be a completely mixed reactor. The volume is calculated by dividing the removal over reactors that each remove 2 $mgSiO_2/L$, because this situation is more similar to plug flow. The rate from the $32g$ column experiment is used to calculate the mass balance. It is assumed that there is a linear increase in removal with the dose of the silica gel beads. It is also assumed that the beads do not get saturated. The total volume that is required for a flow of 0.318 L/min, an initial concentration of 170 $mgSiO_2/L$ and a final concentration of 140 $mgSiO_2/L$ is 25.83 L, see Table 5.1. A column of this size seems small enough to be implemented in a (batch) RO system. The column can be used to remove silica interstage. In this calculation, it was chosen to remove silica up to 140 $mgSiO_2/L$, because this can be done quite effectively in a relatively small column. In this way silica is removed from levels that are problematic to levels that do not give problems in a RO unit.

Table 5.1: Values used to calculate the volume of a column filled with chromatography silica gel (pH 8.5, 21℃).

C_0	$mgSiO_2/L$	170
C	$mgSiO_2/L$	140
Q	L/min	0.318
C_x	$mgSiO_2/L$	129.3
kA_s	h^{-1}	1.039727
V	m^3	0.02583
τ	min	81.22

6 Conclusion

Starting with a silica concentration of 180 $mgSiO_2/L$ a removal up to 30% was obtained after 8 hours (pH 8.5, 21°C). The removal of silica using silica gel beads was limited, because silica gel dissolves. The equilibrium concentration was approximately 102 $mgSiO_2/L$, obtained by both measuring the final silica concentration in a dissolution experiment and in a removal experiment after one month. The removal rate was influenced by the difference between the concentration of silica in solution and the equilibrium concentration. Using a higher dose of silica gel only increased the removal rate to a certain extent. Column experiments with different doses of silica gel indicated that the available contact surface was the main limiting factor until the concentration of reactive silica had dropped to 130 $mgSiO_2/L$. After this concentration was reached, the removal seemed to be have stopped in the observed time-frame. However, after one month the equilibrium concentration was reached, indicating that the removal process must have continued at a very small rate.

Increasing the pH to 10 seemed to decrease the removal efficiency. Lowering the pH to 7 or 5 did not decrease the removal efficiency. Changing the temperature to 10 or 35°C or adding 1 or 10 mg/L of ferric or aluminum did not increase the removal efficiency, but even seemed to decrease the efficiency.

The obtained removal efficiency might be too low for direct application of fixed bed column filtration with silica gel beads as interstage silica removal technique in a RO system that is used to concentrate brine. To make this technology more suitable for application in practice, it seemed most useful to find options that increase the removal rate before the concentration has decreased to 130 $mgSiO_2/L$. Options that could improve the removal rate include increasing the flow velocity, adding traces of ferric or aluminum, adding other components that are known to influence silica scale formation or methods such as ultrasonication. Previous research shows that a higher removal efficiency can be obtained at higher silica concentrations. A combination of filtration with silica gel and a technology that can concentrate the brine further without scaling could be an interesting solution to make brine treatment energy-efficient, since the need for an evaporation step is minimized. Preliminary calculations showed that only a relatively small column (26L) is required to decrease the silica concentration from 170 to 140 $mgSiO_2/L$. A column of this size could be implemented in the recirculation stream of a semi-batch or batch RO system.

7 Recommendations

Fixed bed column filtration with silica gel could be an option to remove silica from a brine with a low silica concentration, however more research on this technique is needed in order to find options to enhance the removal. The recommendations given in this chapter are focused on application and thus include factors that can improve the removal rate and design considerations. However, in order to understand the removal mechanisms and increase the maximum removal that is possible, it remains interesting to research factors that can influence the solubility and thus the final concentration. More insight into the mechanisms involved in the removal of silica using silica gel beads could help to find and improve methods to enhance the removal efficiency.

- **Enhancing the removal efficiency**
  - In this research simple fixed bed column experiments were performed using relatively large silica gel beads. The operation of the column and type of beads have effects on the removal efficiency and should be further researched. The mode of operation, including the flow velocity, should be optimized for efficient removal (Bremere et al., 2000). The most important factors when choosing the type of beads that is most suitable are the particle size, the specific surface area, the receptiveness of the surface to silica and the costs. The choice for a particular particle size can be a practical consideration, since larger beads are more easily separated from the liquid phase, while smaller beads have a faster kinetics (Nguyen et al., 2017). The costs of the type of beads that is used in this research is €$203/2.5kg$. For application, a less expensive industrial grade might be more suitable.
  - Lowering the temperature did not seem to have a positive influence on the removal efficiency, however there were some experimental difficulties that could have prevented obtaining a positive result. Since a lower temperature leads to a lower solubility, the removal could be enhanced by applying a lower temperature. However, the effect might be very small at the low initial concentrations used in this research. The effect of temperature for solutions with a low silica concentration therefore remains an interesting research topic.
  - The results of this research showed that adding 1 or 10 mg/L of ferric or aluminum did not enhance, but even seemed to lower the removal efficiency. However, traces of aluminum and ferric enhance scaling and remain therefore interesting options that could enhance the removal under certain circumstances.
  - Increasing the silica concentration, for example with batch RO, could enhance the removal using silica gel. The combination of batch RO and fixed bed column filtration with silica gel could be a sustainable option for the treatment of waste brine streams,

however more research on both technologies is needed. However, at silica concentrations above 180 $mgSiO)2/L$ polymerization can occur in the used conditions. Thus, the effect of polymerization on the removal efficiency needs to be researched for this type of bead in these conditions.

- **Removal from brine or other waste streams**
  Knowledge of the effect of salinity and various components (e.g. TOC, calcium, magnesium, barium) on the removal is needed to determine the effectiveness of removal with silica gel from a certain type of brine or other waste streams.

- **Lifetime of the silica gel beads and possibilities for reuse in other industries**
  The lifetime of the beads is an important property, because it has a large influence on the costs of operation. During the experiments in this research there was no indication of saturation of the beads when only a silica solution was used. It is possible that pores become blocked, which will enhance saturation en thus shorten the lifetime of the beads. Pictures made with a scanning electron microscope (SEM) can be used to investigate whether pores are blocked. The amount of pore blockage that occurs could be researched by measuring the pore volume before and after use with, for example, a mercury intrusion porosimeter (MIP). The number of times that the beads can be reused effectively is currently unknown, but is very important in assessing the suitability of fixed bed column filtration for application. Used silica gel beads could possibly be a valuable product, because it is a high-quality silica resource (Sugita et al., 2003). Research on the mechanisms at the surface of the silica gel beads and the composition of the beads after use is needed to investigate these options.

- **Design of a column**
  In the preliminary design calculations in chapter 5, a number of assumptions were made that should be verified before a final design can be made. In order to calculate the volume based on the obtained results, it was assumed that the removal efficiency increases linearly with increasing doses of silica gel. However, the results of the column experiments with different doses of silica gel seemed to indicate that this is not the case. More experimental research with different doses of silica gel is needed in order to determine the effect of the doses of silica gel on the removal, before the design and mode of operation can be modelled and optimized. Based on the chosen application, the optimal final concentration can be determined. To design an efficient silica removal step, it can be useful to model and optimize the design parameters, next to carrying out experimental (pilot) research. A more accurate design can be obtained when the column is modelled in a way that resembles plug flow more accurately.

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A Material & Methods specifications

A.1 Overview of the used materials

Table A.1: Overview of the materials used during the experimental research

Item	Company	Type	Conditions
Shaking plate	Heathrow Scientific	Sea*Star 1.11	rpm: 110
Pump	Watson-Marlow	520S	Q: 318.1mL/min
Stirring plate	Labinco	L23	
Heater	IKA	C-MAG HS7	
Spectrometer	Hach-Lange	DR3900	Standard test Silica HR
ICP-MS	Analytikal Jena	PlasmaQuantMS	see section A.4

A.2 Contact time during column experiments

Table A.2: Calculated empty bed contact time during the fixed bed column filtration experiments (Q: 318.1 mL/min, d: 1.5cm, 500mL, solution flows 1.57x through the column/minute)

# silica gel	L_{bed}	V_{bed}	τ/min	$\tau/hour$
$g/500mL$	cm	m^3	min	min
4	3.9	6.89E-06	0.034	2.04
8	8.0	1.41E-05	0.070	4.19
32	31.4	5.55E-05	0.274	16.45

A.3 Composition of the prepared solutions

Table A.3: Specifications of the prepared silica solutions (per 500mL). The pH is adjusted to 5, 7, 8.5 or 10 by adding HCl.

Solution	$Na_2SiO_3 \cdot 5H_2O$	$FeCl_3 \cdot 6H_2O$	$AlCl_3 \cdot 5H_2O$
100 $mgSiO_2/L$	0.1801 g		
150 $mgSiO_2/L$	0.2702 g		
180 $mgSiO_2/L$	0.3242 g		
200 $mgSiO_2/L$	0.3602 g		
180 $mgSiO_2/L$ + 1 $mgFe/L$	0.3242 g	0.0025 g	
180 $mgSiO_2/L$ + 10 $mgFe/L$	0.3242 g	0.0247 g	
180 $mgSiO_2/L$ + 1 $mgAl/L$	0.3242 g		0.0047 g
180 $mgSiO_2/L$ + 10 $mgAl/L$	0.3242 g		0.0471 g

A.4 ICP-MS

In this section the measurement procedure to obtain results of total silica is elaborated in detail.

A.4.1 Preparation

Calibration

The standard solutions for calibration are prepared based on a single element Si solution. The original Si solution (1000 $mgSi/L$) was diluted to a concentration of 1 $mgSi/L$. This diluted solution was used to make a four points calibration series, see Table A.4. All solutions were mixed using a vortex mixer. The Si samples were diluted until the concentration was lower than 1 $mgSi/L$, which is within the range of the calibration series. In this way, the risk of Si adsorption on the glass components of the ICP-MS is minimized. The use of glass during Si analysis is not recommended. The use of an inert system is better, however the components for this system were not available.

Table A.4: Calibration series for Si analysis

Concentration Si in calibration solution	mg/L	0.05	0.1	0.5	1.0
Dose of Si in stock	mL	0.5	1	5	10
Dose of acidified ultrapure water (1%HNO_3)	mL	9.5	9	5	-

Heating of plasma and instrument tuning

The pumping tubes were tightened and clamped. After air was sucked in shortly, the front of the air bubble was followed, in order to evaluate whether the front was moving smoothly. If the front was not moving smoothly, the pumping tubes were changed.

After starting the water cooler, the plasma was activated, while the instrument sucked in acidified ultrapure water ($1\% HNO_3$). The used heating period was 60 minutes. At the end of the heating period the acidified ultrapure water was changed to a tuning solution of 1 $\mu g/L$ Be, In, Pb, Ce, Ba, Th. With this solution the sensitivity of the instrument was tested. It was also checked whether the formation of oxides (Ce/P) and double ionization (Ba^{++}) stayed within limits. Be, In and Th need to give a higher signal (in c/s) than the minimum specification, and the formation of oxides and double ionized elements needs to be lower than 2% of the total Ce and 3% of the total Ba, respectively. The minimum specifications can be found in Table A.5

Table A.5: Minimum specifications during ICP-MS tuning

	Be	In	Th	Ce/O	Ba^{++}
Prerequisites	$> 2 \cdot 10^4 c/s$	$> 5 \cdot 10^5 c/s$	$> 3 \cdot 10^5 c/s$	$< 2\%$	$< 3\%$

A.4.2 Analysis

It was observed that, in order to measure the relatively Si concentrations, the isotope Si^28 gave the most stable values when it is measured when adding H_2 gas. The specifications of the method can be found in Table A.6

Table A.6: Method specifications ICP-MS

Internal standards		Li, Sc, Y, In
Plasma flow	L/min	9.0
Auxiliary flow	L/min	1.1
Nebulizer flow	L/min	1.1
Sampling depth	mm	6.5
R/F power	kW	1.3
H_2 flow	mL/min	80
Stabilization delay	s	45
Dwell time Si	μs	20000
Attenuation Si		medium

Every analysis was build up from five individual replicates. Every replicate was the result of 25 scans. This means that for every analysis result 125 scans were carried out.

A.4.3 Setup of list of measurements

The measurement list started with at least 8 times a "rinse" sample. This "rinse" sample consisted of ultrapure water with 1% HNO_3. The goal of the rinsing step was to flush all Si from the system, in order to minimize drift during the analyses. If there was still a strong drift after the rinsing step, the analyses were stopped and started again.

The rinsing step was followed by the calibration series and the verification samples. Afterwards, the measurement series was started. The verification samples consisted of a reference solution with 5.1 $mgSi/L$ that was diluted 10 times, a standard addition of

Si and a repeated series of the calibration samples. In between each type of verification samples the system was rinsed with the rinse samples. The complete measurement series was carried out two times in quick succession.

A.4.4 Checks after measurements

The drift of the Si concentrations can be determined by comparing the following values:

- The rinse samples at the start and end of the run (difference in c/s)
- The concentrations of the reference solution at the start and end of the run (difference in mg/L)
- The concentrations of the calibration solutions that are measured again at the end of the run (in mg/L)
- The change in ratios of the internal standards compared to the blank measurement at the start of the run

The calibration line itself is also examined. Deviating values are not included. The results of the measurement from the first and second measurement are also compared.

The difference between these measurements was sometimes large and could not be explained. Other deviations that were found in the checks could not be explained or prevented. For this research, it was decided that the results were not accurate enough to be used.

B Overview of results

All data in this chapter is obtained by the Hach 8185 method. The values therefore represent the concentration of monomeric and dimeric silica. The standard deviation of all results is $\pm 4 mg/L$.

B.1 Batch experiments: stability of the solution

Table B.1: Concentration over time of solutions with an initial concentration of 400, 100 and 200 $mgSiO_2/L$ (pH 8.5, 21°C)

Time h	Time min	400 $mgSiO_2/L$ $mgSiO_2/L$	100 $mgSiO_2/L$ $mgSiO_2/L$	200 $mgSiO_2/L$ $mgSiO_2/L$
0	0	412	95.6	189.3
0.08	5	392	-	-
0.17	10	399	90.8	192
0.33	20	-	96.4	192.9
0.5	30	385	95.4	198.6
1	60	342	96.2	194.4
1.5	90	298	-	-
2	120	268	96.2	194.7
5	300	215	-	-

B.2 Batch experiments: dissolution of silica gel

Table B.2: Concentration of reactive silica in solution two days and 1 week after the addition of $1g$ desiccant silica gel to $100mL$ of demineralized or ultrapure water (pH 8.5, 21℃). The beads are pretreated by placing them into contact with air for two weeks and flushing them with demi or ultrapure water.

Pretreated?	Water type	2 days $mgSiO_2/L$	1 week $mgSiO_2/L$
yes	demi	23.6	52.9
no	demi	54.0	85.3
yes	ultrapure	23.6	52.6

Table B.3: Concentration of reactive silica in solution two days and 1 week after the addition of $1g$ chromatography silica gel to $100mL$ of demineralized or ultrapure water (pH 8.5, 21℃). The beads are pretreated by placing them into contact with air for two weeks and flushing them with demi or ultrapure water.

Pretreated?	Water type	Additional conditions	2 days $mgSiO_2/L$	1 week $mgSiO_2/L$
yes	demi		88.8	103.3
no	demi		98.8	104.7
yes	ultrapure		84.4	103.7
yes	demi	pH 10	99.6	109.8
yes	demi	pH 5	82.0	104.6
yes	demi	35 ℃	140.0	118.2

After one month the concentration of silica in solution was 103.6 ± 4 $mgSiO_2/L$ (pH 8.5, 4g chromatography silica gel/500mL, 21 ℃)

Table B.4: Concentration of reactive silica in solution over time after the addition of $4g$ chromatography silica gel to $500mL$ of demineralized water (pH 8.5 or 7, 21℃).

Time h	Time min	Result $mgSiO_2/L$
0	0	5.2
0.50	30	9.2
2.00	120	23.5
4	240	39.2
8	480	64.4

B.3 Batch experiments: removal equilibrium

Table B.5: Concentration of reactive silica in solution after the addition of $4g/500mL$ desiccant silica gel to $500mL$ solution of 200 $mgSiO_2/L$ (pH 8.5 or 7, 21℃)

Time h	Time min	pH 8.5 $mgSiO_2/L$	pH 7 $mgSiO_2/L$	pH 7 duplex $mgSiO_2/L$
0	0	197.0	195.6	192.8
0.17	10	198.0	185.2	190.0
0.33	20	204.5	194.0	187.6
0.5	30	202.0	188.0	188.0
1	60	191.0	178.8	186.0
1.5	90	199.0	192.8	190.4
2	120	199.0	182.8	184.0
4	240	-	-	181.6
5	300	-	190.4	-

Table B.6: Concentration and removal efficiency of reactive silica in solution after the addition of different doses of chromatography silica gel to $500mL$ solution of 200 $mgSiO_2/L$, measured after 48h (pH 8.5, 21℃)

	Experiment 1		Experiment 2	
$\#gel/0.5L$ g	Result $mgSiO_2/L$	Removal %	Result $mgSiO_2/L$	Removal %
0	181.2	0	177.6	0
0.1	173.6	4	178.4	0
0.2	168.0	7	168.4	5
0.4	160.4	12	158.8	11
1	158.8	12	154.8	13
2	154.8	15	138.4	22
4	140.4	23	132.4	25
10	140.0	23	132.4	25
15	133.6	26	128	28

Table B.7: Concentration and removal efficiency of reactive silica under different conditions, measured after 48 hours (21℃, start concentration: 180 $mgSiO_2/L$, $4g/500mL$ chromatography silica gel). A: removal compared to a standard solution (180 $mgSiO_2/L$), B: removal compared to the concentration of the solution that is measured.

					Experiment 1		Experiment 2			
					Result	Removal A	Result Solution	Result silica gel	Removal A	Removal B
	mg SiO_2/L	pH	mg Fe/L	mg Al/L	mg SiO_2/L	%	mg SiO_2/L	mg SiO_2/L	%	%
1	100	8.5			114.8	-15	103.6	110.8	-11	-7
2	150	8.5			116.4	22	152.4	117.2	22	23
3	180	8.5			130	28	179.2	123.2	32	31
4	200	8.5			136	32	196.4	118.4	41	40
5	180	5			138.8	23	180.4	131.6	27	27
6	180	7			130	28	174.8	126.4	30	28
7	180	10			161.2	10	178.8	135.6	25	24
8	180	8.5	1		135.6	25	174.8	123.2	32	30
9	180	8.5	10		134.4	25	167.6	117.6	35	30
10	180	8.5		1	139.6	22	164.8	118.4	34	28
11	180	8.5		10	151.6	16	133.6	136	24	-2

B.4 Batch experiments: removal kinetics

Table B.8: Concentration and removal efficiency of reactive silica using chromatography silica gel at pH 8.5 (21℃, start concentration: 180 $mgSiO_2/L$, $4g/500mL$ chromatography silica gel).

		Experiment 1		Experiment 2		Experiment 3	
Time h	Time min	Result $mgSiO_2/L$	Removal %	Result $mgSiO_2/L$	Removal %	Result $mgSiO_2/L$	Removal %
0	0	179.6	0	199.6	0	188.0	0
0.17	10	-	-	188.4	2	183.6	2
0.33	20	-	-	188.0	2	186.4	1
0.5	30	174.4	3	176.0	8	179.6	4
1	60	169.6	6	179.2	7	170.0	10
1.5	90	163.2	9	172.0	10	168.0	11
2	120	160	11	163.2	15	168.0	11
3	180	152.8	15	160.0	17	-	-
4	240	150	16	155.2	19	-	-
5	300	144	20	152.0	21	-	-
6	360	140.8	22	141.6	26	-	-
7	420	135.2	25	142.0	26	-	-
8	480	134.4	25	-	-	-	-
10	600	-	-	131.2	32	-	-
24	1440	-	-	-	-	120.8	36
29	1740	-	-	116.4	39	-	-

Table B.9: Concentration and removal efficiency of reactive silica using chromatography silica gel at pH 7 (21°C, start concentration: $180mgSiO_2/L$, $4g/500mL$ chromatography silica gel).

		Experiment 1		Experiment 2	
Time *h*	Time *min*	Result $mgSiO_2/L$	Removal %	Result $mgSiO_2/L$	Removal %
0	0	194.8	0.0	189.6	0
0.5	30	190.4	2	178.8	6
1	60	176.0	10	176.4	7
1.5	90	173.6	11	171.6	9
2	120	168.8	13	168.8	11
3	180	172.8	11	-	-
4	240	161.6	17	-	-
5	300	161.6	17	155.2	18
6	360	155.6	20	-	-
8	480	143.2	26	-	-
27	1620	127.2	35	130.4	31

Table B.10: Concentration and removal efficiency of reactive silica using chromatography silica gel at 10°C and 35°C (pH 8.5, start concentration: 180 $mgSiO_2/L$, $4g/500mL$ chromatography silica gel).

		T=10 °C				T=35 °C			
		Experiment 1		Experiment 2		Experiment 1		Experiment 2	
Time *h*	Time *min*	Result $mgSiO_2/L$	Removal %	Result $mgSiO_2/L$	Removal %	Result $mgSiO_2/L$	Removal %	Result $mgSiO_2/L$	Removal %
0	0	178.4	0	179.2	0	184.4	0	181.2	0
0.5	30	178.0	0	174.4	3	183.2	1	181.2	0
1	60	-	-	174.0	3	-	-	181.2	0
1.5	90	172.8	3	-	-	183.6	0	-	-
2	120	-	-	173.6	3	-	-	181.2	0
3	180	166.8	7	-	-	-	-	-	-
4	240	156.4	12	173.2	3	178.8	3	174.4	4
5.5	330	-	-	-	-	174.0	6	-	-
6	360	157.2	12	168.0	6			175.2	3
7.5	450	-	-	-	-	158.8	14	-	-
8	480	146.0	18	164.8	8	-	-	172.0	5

Table B.11: Concentration and removal efficiency of reactive silica using chromatography silica gel with 1 $mgFe/L$ and 1 $mgAl/L$ (pH = 8.5, 21°C, start concentration: 180 $mgSiO_2/L$, $4g/500mL$ chromatography silica gel).

		1 $mgFe/L$				1 $mgAl/L$			
		Experiment 1		Experiment 2		Experiment 1		Experiment 2	
Time	Time	Result	Removal	Result	Removal	Result	Removal	Result	Removal
h	min	$mgSiO_2/L$	%	$mgSiO_2/L$	%	$mgSiO_2/L$	%	$mgSiO_2/L$	%
0	0	178.4	0	139.2	0	173.2	0	136.0	0
0.5	30	178.4	0	139.2	0	174.4	-1	136.4	0
1	60	175.2	2	136.8	2	160.4	7	136.4	0
2	120	-	-	136.0	2	-	-	137.6	-1
3.5	210	160.0	10	-	-	160.0	8	-	-
4	240	-	-	136.4	2	154.0	11	137.2	-1
5.5	330	154.0	14	-	-	-	-	-	-
7	420	-	-	-	-	144.0	17	-	-
7.15	429	146.8	18	-	-	-	-	-	-
8	480	-	-	132.8	5	-	-	135.2	1

B.5 Column experiments

Table B.12: Concentration of reactive silica using 4, $8g/500mL$ or $32g/500mL$ chromatography silica gel in a column (pH 8.5, 21°C, start concentration: 180 $mgSiO_2/L$).

Concentration of reactive silica							
		$4g/500mL$ silica gel		$8g/500mL$ silica gel		$32g/500mL$ silica gel	
Time	Time	Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2
h	min	$mgSiO_2/L$	$mgSiO_2/L$	$mgSiO_2/L$	$mgSiO_2/L$	$mgSiO_2/L$	$mgSiO_2/L$
0.0	0	173.2	175.6	172.0	175.6	170.0	172.3
0.08	5	-	-	-	-	165.2	167.3
0.25	15	172.0	-	-	-	165.6	162.1
0.5	30	170.4	168.0	-	167.6	153.2	152.0
0.8	45	-	-	160.8	-	-	-
1.0	60	158.8	159.2	159.2	161.2	144.0	146.4
1.5	90	-	-	145.2		135.2	135.4
2.0	120	147.6	154.8	-	145.6	134.4	130.9
2.5	150	-	-	131.2	-	-	-
3.0	180	-	-	-	-	130.8	132.5
3.5	210	-	-	138.0	-	-	-
4.0	240	139.6	140.4	-	142.8	-	130.3
4.5	270	-	-	128.4	-	129.2	-
6.0	360	-	134.8	-	134.4	131.6	129.1
7.0	420	128.4	132.8	-	-	-	-
7.5	450	-	-	129.6	-	-	-
8.0	480	-	132.0		131.2	128.8	130.0
Kinetics							
kA_s	h^{-1}	0.293364	0.345064	0.520033	0.436785	1.039727	1.171412
A_s	m^2/m^3	4.4	4.4	8.8	8.8	32.5	32.5
k	m^3/hm^2	0.066674	0.078424	0.059095	0.049635	0.031992	0.036043