

ÅBO AKADEMI UNIVERSITY

**COMPLEXATION OF SODIUM, CALCIUM, MAGNESIUM AND
ALUMINIUM IONS ON A SILICA GEL SURFACE**

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SUMMARY

All bioactive glasses and bioactive glass ceramics bond to bone in a similar way, *i.e.* through formation of a Ca-P rich layer situated on top of or within a Si-rich layer. For the formation of the Si-rich layer the structure of the glass and the leachability of certain components are of major importance. However, exact knowledge of the bone bonding mechanism and a possibility to predict effects of additions to the glasses prior to experiments on animals is unavailable until now.

In order to further unravel the mechanisms involved, a research project has been carried out to study the possible interactions between ions present in the glass used and surrounding body fluid with the Si-rich layer, which forms on all bioactive glasses and glass-ceramics *in vivo*.

Aldrich's 28,863-2 high purity grade gel is used as a model substrate. The BET surface area determined by N₂ adsorption equals 411 m²/g using the extended BET equation. The particle diameter is between 63 and 212 μm.

The ion exchange capacity of the gel is determined by adsorption of Na⁺ ions and is found to be 100 mM when 0.01 l fluid /g gel is present.

It has been shown that in the adsorption of cations on the gel, two types of hydroxyl groups should be taken into account. The fraction of most active groups equals 0.46.

Simple adsorption experiments of Ca²⁺ and Mg²⁺ ions at concentrations ranging from 0...33 mM at a constant ionic strength of 0.1N NaCl in a pH range 5.5...9.5 have been carried out. Preliminary adsorption experiments of Al³⁺ at a concentration of 10 mM at a ionic strength of 0.1 N NaNO₃ in a pH range 0..12 have been carried out as well.

It is found that Ca²⁺, Mg²⁺ and Al³⁺ ions form complexes at the gel surface with only one hydroxyl group involved. At low concentrations only the most reactive groups are involved in the complexation reaction. At higher concentrations two types of hydroxyl groups should be taken into account.

The apparent equilibrium constants at 293K for the different complexes formed were determined: The pK for =SiONa is found to be 6.4 and 9.6, respectively; the pK for =SiOCa⁺ is found to be in the range 7.1...7.4; for =SiOMg⁺ in the range 6.3...7.4; formation of =SiOAlOH⁺ gives a pK of 5.75 and for =SiOAl(OH)₂ the pK equalled 9.55 in the pH range considered.

The complexation of Ca^{2+} , Mg^{2+} and Al^{3+} ions is modelled by means of the Gibbs' energy minimisation software SOLGASWATER[®] and compared with experiments. Using equilibrium constants extracted from the experimental data gives a good agreement with direct SOLGASWATER[§] simulations.

The simulations also show that Mg^{2+} and Al^{3+} ions can have an inhibitory effect on the complexation of Ca^{2+} ions when present in competitive amounts. This is in agreement with the known inhibitory effect of aluminium and magnesium, when present in bioactive glasses, on the formation of the Ca-P rich layer on or within the Si-rich layer.

PREFACE

The work described here has been carried out at the Department for Inorganic Chemistry at Åbo Akademi University during the 1993-1996 period. The Finnish Technology Development Centre, TEKES, is kindly acknowledged for financial support.

I would like to thank Prof. Mikko Hupa for introducing me to Prof. Kaj Karlsson thereby initiating an inspiring period of research.

I am indebted to Prof. Paul Schindler, Bern University, Switzerland, for providing useful approximations of the equilibrium constants for the calcium and magnesium surface complexes.

Jörgen Rosenqvist, currently at the University of Umeå, and Bengt Skrifvars deserve a special word of thanks for all the time they spent in order to explain the world of complexation chemistry to me. Their patience has been remarkable. I also want to thank Jarl Ahlbeck and Henrik Saxén for helping me planning experiments and manipulating data in a proper way. Actually all colleagues within the department need to be mentioned. They helped me through difficult periods by keeping me company during coffee and lunchbreaks.

Last but not least I want to mention Ron, my husband. Without his enthusiasm for my work and inspiring discussions in the middle of the night this work was not completed.

Åbo, January 1998
Maria Zevenhoven

TABLE OF CONTENTS

INTRODUCTION	7
Silica gel and the bioactivity of certain glasses and glass-ceramics.....	7
Objectives	8
This thesis	9
SILICA GEL.....	10
The silica gel surface	10
Ionisation of the silica gel surface.....	11
Complexation theories of cations on a silica gel surface	12
Complexation of Calcium, magnesium and Aluminium ions	12
Calcium.....	12
Magnesium.....	13
Aluminium.....	14
COMPLEXATION OF METAL CATIONS: DEFINITION OF EQUILIBRIUM CONSTANTS.....	15
Hydrolysable ions	15
Non-hydrolysed ions.....	16
SIMULATION OF COMPLEXATION WITH SOLGASWATER®.....	18
Equilibrium constants	18
Simulation of the complexation of calcium ions.....	20
Simulation of the complexation of magnesium ions.....	22
Simulation of complexation of aluminium ions on silica gel.....	24
Simulation of simultaneous complexation of calcium and magnesium ions in concentrations as used in SBF.....	26
Simulation of simultaneous complexation of calcium and aluminium ions.....	28
Simultaneous complexation of calcium and aluminium ions in concentrations as used in bioactive glass and SBF.....	30
THE =SIOH-NA ⁺ SYSTEM	32
Titration of a silica gel	32
Determination of the capacity of the gel.....	35
Determination of the equilibrium constant and type of complex involved	36
SOLGASWATER® simulations compared with experimental values.....	40
Conclusions =SiO ⁻ -Na ⁺ system.....	43
THE =SIOH-CA ²⁺ -NA ⁺ SYSTEM.....	44
The ion exchange of Ca ²⁺ ions on Aldrich's 28,863-2 gel.....	44
Experimental procedure	44
Experimental results of adsorption of CaCl ₂ on the silica gel at 20°C	45
Influence of the associated ion on the adsorption on Ca ²⁺ ions on the silica gel.....	48
The influence of temperature on the adsorption of Ca ²⁺ ions on the silica gel.....	49
Determination of the type of complex involved in the adsorption of Ca ²⁺ ions.....	50
Determination of the apparent equilibrium constant.....	54
Comparison of SOLGASWATER simulations with experimental results.....	56
Conclusions =SiO ⁻ -Ca ²⁺ -Na ⁺ system	57
THE =SIOH-MG ²⁺ -NA ⁺ SYSTEM.....	58
The ion exchange of Mg ²⁺ ions on Aldrich's 28,863-2 gel.....	58
Experimental procedure	58
Experimental results of adsorption of MgCl ₂ on the silica gel at 20°C	59
Influence of the associated ion on the adsorption on Mg ²⁺ ions on the silica gel	62
The influence of temperature on the adsorption of Mg ²⁺ ions on the silica gel	63
Determination of the type of complex involved in the adsorption of Mg ²⁺ ions.....	65
Determination of the apparent equilibrium constant.....	67
Comparison of SOLGASWATER simulations with experimental results.....	69
Conclusions =SiO ⁻ -Mg ²⁺ -Na ⁺ system	70
THE COMPLEXATION OF CA ²⁺ AND MG ²⁺ IONS	71
The ion exchange of Ca ²⁺ and Mg ²⁺ ions on Aldrich's 28,863-2 gel.....	71
Experimental procedure	71
Experimental results.....	71
SOLGASWATER ^S simulation of the simultaneous adsorption of Ca ²⁺ and Mg ²⁺ ions	73
Conclusions =SiO ⁻ -Ca ²⁺ -Mg ²⁺ -Na ⁺ system.....	74
THE =SIOH-AL ³⁺ -NA ⁺ SYSTEM.....	75

The ion exchange of Al ³⁺ on Aldrich's 28,863-2 gel.....	75
Experimental procedure	75
Experimental results.....	75
Determination of the type of complex involved in the adsorption of Al ³⁺ ions	77
Determination of the apparent equilibrium constant.....	78
SOLGASWATER ^Š simulations of the adsorption of Al ³⁺ ions.....	80
Conclusions =SiO ⁻ -Al ³⁺ -Na ⁺ system.....	81
GENERAL DISCUSSION AND CONCLUSIONS	82
Gel characterisation	82
Determination of the type of complexes formed in the experiments	83
Determination of equilibrium constants.....	83
SOLGASWATER ^Š -simulations.....	84
This work and the bioactivity of glass	85
LITERATURE REFERENCES.....	86
APPENDICES	90
Input files as used in the SOLGASWATER [®] simulations.....	90
Simulation of complexation of sodium ions with two different surface active groups present.....	90
Simulation of complexation of calcium ions with two different surface active groups present.....	91
Simulation of complexation of magnesium ions with two different surface active groups present.....	92
Simulation of simultaneous complexation of calcium and magnesium ions with two different surface active groups present	93
Simulation of complexation of aluminium ions with two different surface active groups present.....	96
Reprint of the Proceedings of the 8th. International Symposium on Ceramics in Medicine	98

INTRODUCTION

Silica gel and the bioactivity of certain glasses and glass-ceramics

During the last twenty-five years bioactive materials such as Bioglass[®], Ceravital[®] and A-W glass ceramics were developed. Not only the United States and Japan, but also Finland plays an important part in both the development of and understanding the behaviour of bioactive materials.

All these bioactive materials bond to bone in a similar way, *i.e.* through formation of a Ca-P rich layer situated on top of or within a Si-rich layer. For the formation of the Si-rich layer the structure of the glass and the leachability of certain components are of major importance (Ducheyne 1988, Ohtsuki *et al.* 1991), whereas the presence of acid hydroxyl groups, such as =SiOH, =Si(OH)₂, and -Si(OH)₃, are of great importance for the formation of a Ca-P rich layer (Li *et al.* 1992, 1993a, 1993b, 1993c, Andersson *et al.* 1990, Hench *et al.* 1990). When the glass is submerged in Simulated Body Fluid (SBF) or in the body itself, these acid hydroxyl groups appear, first at surface defects such as scratches, which lead to the formation of nucleation sites for Ca-P crystals (Marshall *et al.* 1993).

The hydroxyl groups are formed due to the following sequential mechanisms (Hench *et al.* 1991):

1. Rapid exchange of Na⁺ or K⁺ ions leached from the glass with H⁺ or H₃O⁺ from the surrounding solution. This stage is usually diffusion-controlled and exhibits a \sqrt{t} dependence. During this stage hydroxyl groups are produced at the surface.
2. Loss of soluble silica to the solution resulting from breakage of Si-O-Si bonds and the formation of hydroxyl groups at the glass-solution interface. This stage is usually controlled by interfacial reaction and exhibits a linear t dependence.
3. Condensation of silanols and repolymerisation of a hydrated Si-rich layer on a surface site depleted in alkaline and alkaline earth ions.

Thus a silica rich layer similar to a **silica gel** is formed, which is proved to be of major importance in the bone bonding mechanism between bone and bioactive glass devices.

Objectives

The mechanism of the formation of the Ca-P rich layer has not been completely revealed. Recently two possible mechanisms were proposed *i.e.* polycondensation of phosphate with the silica network, or Ca-binding with the silica network (Andersson *et al.* 1990, Kangasniemi *et al.* 1993).

Also the composition ($\text{SiO}_2\text{-Na}_2\text{O-CaO-P}_2\text{O}_5$) of the first Bioglass[®] has been subject to addition of other components such as Al_2O_3 , K_2O , CaF_2 , MgO and B_2O_3 , to obtain better mechanical strength and workability during implantation, but also to provide a wider working range for the production of the glasses.

All these additions to the glasses, however, have their influence on the bioactivity of the glasses. Al_2O_3 has been found to be toxic if added in greater amounts than 1.5 %wt. (Andersson 1990). No Ca-P rich layer was found on glasses with additions of Al_2O_3 , CaF_2 or Fe_2O_3 (Ebisawa *et al.* 1990). Also additions of >8%wt MgO are found to retard formation of the Ca-P rich layer (Ishizawa *et al.* 1990). Other additions might also influence the formation of the Si gel layer or might react or interfere with the formation of the Ca-P rich layer.

To obtain more knowledge of the above mentioned reaction mechanism a fundamental research project has been started to study the possible interactions between ions present in the glass used and surrounding body fluid with the Si-rich layer. To simplify the system Aldrich's 28,863-2 high purity grade gel is used as a model substrate. The BET surface area determined by N_2 adsorption equals $411 \text{ m}^2/\text{g}$ using the extended BET equation. The particle diameter is between 63 and 212 μm .

The complexation of Ca^{2+} , Mg^{2+} and Al^{3+} ions is modelled by means of the Gibbs' energy minimisation software, SOLGASWATER[®] and complexation experiments are carried out to check experimental procedures and to make a comparison with the simulations and with what has been reported in literature.

Whereas for the body environment a pH of about 7 is an interesting area to study, knowledge of the behaviour of the cations in other pH ranges can be used in other applications such as the production of slow release pharmaceuticals.

The interaction of the gel with other anions, cations and/or mixtures of anions and cations will be also interesting and might be studied in the future. This will lead to a greater understanding of possible reactions at the glass implant surface when implanted, but will also provide knowledge that can be used in other applications of glasses or silica gels.

This thesis

This thesis describes the work done in the period October 1993-August 1996.

The thesis can be divided into different parts *i.e.*:

1. A short literature review
2. Computer simulations of complexation of Ca^{2+} , Mg^{2+} and Al^{3+} ions with SOLGASWATER[®]
3. The $=\text{SiOH}-\text{Na}^+$ system:
 - Titration of the gel with HCl/NaOH at a constant ionic strength of 0.1 N NaCl.
 - Determination of the ion exchange capacity of the gel.
 - Determination of the equilibrium constant of $=\text{SiONa}$.
 - Comparison of experimental results with SOLGASWATER[®] simulations.
4. The $=\text{SiOH}-\text{Na}^+-\text{Ca}^{2+}$ system:
 - The complexation of Ca^{2+} ions on the silica gel at various concentrations, pH values, associated anions and temperatures.
 - Determination of the kind of complex formed.
 - Determination of the equilibrium constant of $=\text{SiOCa}^+$.
 - Comparison of experimental results with SOLGASWATER[®] simulations.
5. The $=\text{SiOH}-\text{Na}^+-\text{Mg}^{2+}$ system:
 - The complexation of Mg^{2+} ions on the silica gel at various concentrations, pH values, associated anions and temperatures.
 - Determination of the kind of complex formed.
 - Determination of the equilibrium constant of $=\text{SiOMg}^+$.
 - Comparison of experimental results with SOLGASWATER[®] simulations.
6. The $=\text{SiOH}-\text{Na}^+-\text{Ca}^{2+}-\text{Mg}^{2+}$ system:
 - The complexation of Ca^{2+} and Mg^{2+} ions on the silica gel at concentrations as used in simulated body fluid and different pH values at 20°C
 - Comparison of experimental results with SOLGASWATER[®] simulations.
7. The $=\text{SiOH}-\text{Na}^+-\text{Al}^{3+}$ system:
 - The complexation of Al^{3+} ions on the silica gel.
 - Determination of the kind of complex formed.
 - Determination of the equilibrium constant of $=\text{SiOAlOH}^+$ and $=\text{SiOAl}(\text{OH})_2$.
 - Comparison of experimental results with SOLGASWATER[®] simulations.
8. General discussion and conclusions:
 - An overview is given of the results obtained.
 - The results are compared with literature and SOLGASWATER[®] simulations.
 - Conclusions are summarised.

- The relevance of this work for a better understanding of the bone bonding process at bioactive glass implant surfaces is evaluated.

Preliminary experiments of adsorption of Ca^{2+} ions at an ionic strength which was not kept constant have been presented as a poster at the 8th International Symposium on Ceramics in Medicine and were published in the proceedings:

Maria F.J. Zevenhoven-Onderwater, Jörgen Rosenqvist , Kaj H. Karlsson, "Complexation of calcium, magnesium and aluminium ions on silica gel, *Bioceramics*, Volume 8, 497-500

SILICA GEL

The silica gel surface

Hydrated silica gel contains a surface covered with hydroxyl groups which can react with cations in ion exchange reactions. For determination of formed complexes and equilibrium constants it is important to determine the amount of hydroxyl groups available for this ion exchange reaction. Since silica gel is rather porous and contains a large surface area, the surface area determined by, for example, the N_2 -BET method will not include the surface of small internal pores since these are not reachable for the adsorbing N_2 molecules. However, these internal pores might contain hydroxyl groups which are detected by another measurement technique, but which are not available for ion exchange.

The hydroxyl groups can be removed by dehydration of the gel at high temperatures. This leads to condensation of the hydroxyl groups in the internal pores and closure of the so-called micropores. If the gel is only heated up to 120°C most of the physically adsorbed water molecules will be removed. In the micropores water can remain physically adsorbed up to a temperature of about 180°C . The hydroxyl groups dehydrate extensively at temperatures above 170°C . At a temperature of $400\text{-}450^\circ\text{C}$ about half of the hydroxyl groups are removed leaving the surface with a sufficient amount of hydroxyl groups to allow for rapid rehydration of the surface accessible for ions in ion exchange reactions.

Rehydration first starts at the dehydrated oxide sites next to a remaining hydroxyl group. Thus if the dehydration temperature has been too high, almost all of the hydroxyl groups might have been removed, leading to an almost infinite rehydration time. Proper dehydration and rehydration leads to a fully hydrated surface structure of the silica gel similar to cristoballite containing $4.6 \text{ OH}^- \text{ nm}^{-2}$ (Iler 1979). However, it is found that not all the hydroxyl groups will be available for ion exchange reactions or titration. In a 0.1 M ionic medium only 2.4 OH^- groups per nm^2 have been found to be available (Schindler 1968).

Ionisation of the silica gel surface

Silica gel has a point of zero charge (pzc) at a pH of 2. At a higher pH the number of negative charges increases but remains rather low. Above pH=9 not only the negative charge concentration increases but also silicate ions (HSiO_3^-) dissolve. Extensive dissolution of the gel will take place at a pH above 9 due to the formation of $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$ and polysilicate complexes.

The pK_a varies from 6.8 to 9.2 depending on the neutralisation. Since the pK_a of the gel is much lower than the pK_a of monosilicic acid the gel is more acidic. However, the acidity of the surface area decreases when the degree of ionisation increases (Iler 1979).

An empirical equation for the number of SiO^- groups present in a completely hydroxylated gel as a function of pH was obtained by Schindler (1976) from potentiometric titrations of a silica gel H (Merck) with a surface area of 372 m/g in 1 M perchloric acid (HClO_4):

$$\log \text{SiO}^- (\text{nm}^{-2}) = 5.2 \log(\text{pH}) - 4.8$$

(1)

Figure 2.2.1 shows the number of hydroxyl groups present nm^{-2} .

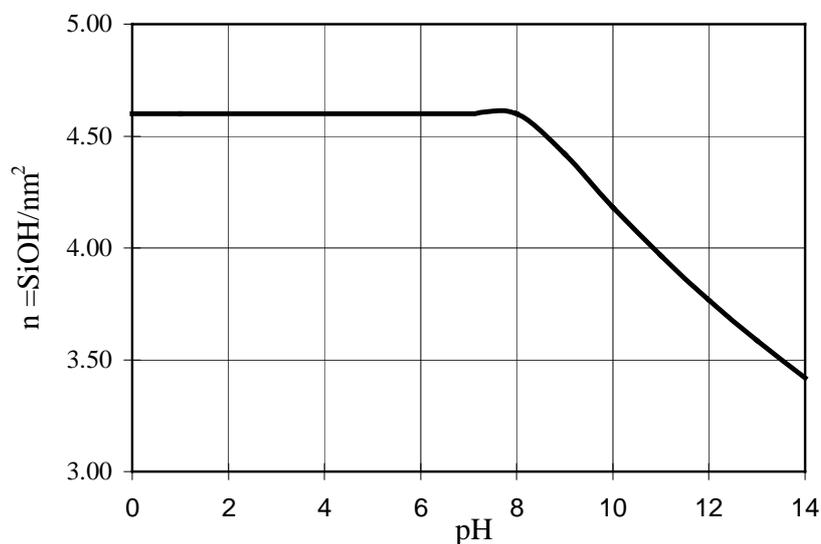


Figure 2.2.1. The number of hydroxyl groups nm^{-2} present at the surface of the H Merck gel as a function of pH (Schindler 1976).

Complexation theories of cations on a silica gel surface

Currently there are two main theories on the complexation of ions:

1. Classical theory, which is valid when the main forces involved are ionic
2. Site binding theory, which is valid even when other forces are involved.

The classical theory contains several elements such as :

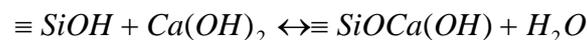
- The Nernst equation for the work done in transporting an ion from an infinite distance to a point at the solid surface.
- The double layer theory based on the Poisson-Boltzmann equations which describe the thermal energy that keeps the cation in motion near the surface to which they are attracted by corresponding negative charges.
- The compact double layer or Stern layer introduced to correct for ion size and describing a certain proportion of cations swarming near the surface to which they become essentially immobilised against the surface.
- Co-ordinated bounded layer within which cations become specifically bonded overcoming a specific adsorption potential.

The site binding theory describes the bonding of ions to a specific place on a surface with opposite charge and describes the behaviour of all oxides. This theory shows that the Nernst equation, which assumed that the opposite charge is spread randomly over the whole surface, is not valid (Iler 1979).

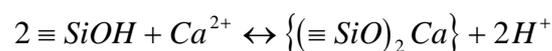
Complexation of Calcium, magnesium and Aluminium ions

Calcium

Von Böhm *et al.*(1959) proposed that Ca(OH)_2 is bonded to silica gel in the following manner:



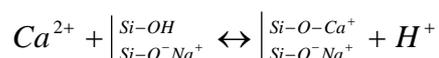
Dugger *et al.*(1964) and Stanton *et al.* (1963) assumed a different complexation mechanism for Ca^{2+} at $\text{pH} < 5$. They assumed $z = n$, where z is the charge of the cation and n is the number of hydroxyl groups involved in the complexation reaction, thus:



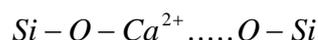
However Schindler *et al.* (1976) found that in this pH range no Ca^{2+} ions become adsorbed at all. Iler (1975) assumed that at a high pH initially only one H^+ ion will be formed. At a later stage a second H^+ ion might be exchanged. This is in

agreement with Allen *et al.* (1971) who assumed that the silica gel surface will contain two types of hydroxyl groups, one reactive and one less reactive.

Iler (1975) found that coagulation between colloidal silica gel (particle size, $d_p < 50\text{\AA}$) occurs in the presence of Ca^{2+} ions. At a pH from 8 to 9.5 one H^+ ion is generated by ion exchange and thus an additional negative site is generated at the colloid surface. This site is neutralised by one adsorbed Ca^{2+} ion that retains a single positive charge. Thus, when a Ca^{2+} ion is adsorbed on silica gel particles already bearing a negative surface charge with Na^+ counter ions, preferentially a further decrease in negative charge will occur according to:



Van der Waals forces seem unlikely to cause coagulation, due to the negative charge of the surface (repulsion between colloidal particles). According to Iler (1975) bridging according to the following mechanism seems more likely:



or



Iler (1975) also found that coagulation occurs when a critical fraction of the solid surface is covered by ions. The concentration of adsorbed Ca^{2+} ions per unit of surface area is independent of the particle size and depends only on the salt concentration in the solution and pH. At decreasing particle size a higher concentration of Ca^{2+} ions in solution is required to maintain the necessary concentration of Ca^{2+} ions at the particle surface to cause coagulation. This is due to the fact that Ca^{2+} ions tend to be repelled from the surface by their positive charged neighbours. A higher ion concentration in solution is necessary to overcome this repulsion.

Magnesium

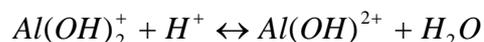
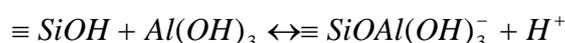
The Mg^{2+} ion is a cation much like Ca^{2+} ions and is expected to form the same kind of complexes as Ca^{2+} . Since the ion is more acidic, the complexation is believed to start at a lower pH than the complexation of Ca^{2+} ions. Thus $\text{Mg}(\text{OSi}=\text{O})_2$ and $=\text{SiOMg}^+$ will be formed at other values for concentration, ionic strength of the solution and pH.

Aluminium

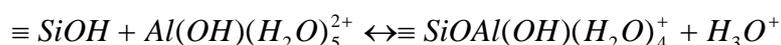
Also other soluble hydrolysable cations, such as Al^{3+} , can be adsorbed on a silica gel surface and, if present in excess, reverse the surface charge. This means that as the concentration of cations increases on the silica gel surface, the surface may eventually become totally covered. During this process the ζ -potential of the surface becomes less negative, going through zero ('charge reversal') to the final positive value of the metal ion as the surface becomes covered. (Iler 1979).

In colloidal systems this phenomenon can lead to coagulation starting at the charge reversal point. (James *et al.* 1977). This coagulation will show different stability regions depending on the aluminium concentration used, the associated anions and the pH.

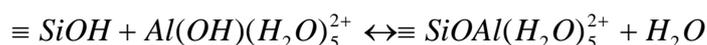
Adsorption of Al^{3+} ions may take place according to the mechanisms such as those proposed by Von Kohlschütter *et al.* (1964), who took the presence of Al^{3+} , $AlOH^{2+}$ and $Al(OH)_2^+$ into account. For $Al(OH)_2Cl$ the following three reactions were proposed since for every mole Al^{3+} adsorbed, one mole HCl is formed:



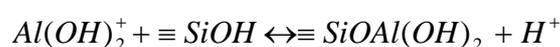
Another mechanism proposed is equivalent to the adsorption of lanthanum ions (Allen *et al.* 1971):



or



The first reaction is equivalent to the formation of $\equiv SiOAlOH^+$ as proposed by Charlet (1993). Another complex expected to be formed is $\equiv SiOAl(OH)_2$ according to (Rosenqvist 1994):



COMPLEXATION OF METAL CATIONS: DEFINITION OF EQUILIBRIUM CONSTANTS

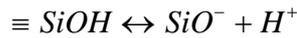
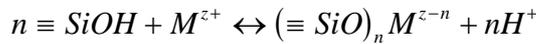
Hydrolysable ions

Ahrland *et al.* (1960) found that the amount of metal ions adsorbed on silica gel depends strongly on the pH of the solution. The adsorption of ions shifts to a lower pH at an increasing charge/size ratio of the ion. Zr^{4+} and Nb^{5+} will become adsorbed at a pH above

-1, U(IV) and Pu(IV) at a pH above 0, U(VI) above a pH of 2, Gd^{3+} at a pH above 2.5 (100% adsorption at pH 5.5) and Ca^{2+} , Ba^{2+} , and Na^+ above pH 6-8.5. Schindler *et al.* (1976) found that Fe^{3+} is adsorbed above a pH of 3; Pb^{2+} , Cu^{2+} in a pH range from 4 to 7.5 and Co^{2+} in the range from pH 4.5 to 9.

According to Schindler *et al.* (1976) in case of adsorption of strongly hydrolysed ions the equilibrium is only reached slowly while a sorption of low molecular non-hydrolysed ions is quite rapid *i.e.* hours vs. minutes. Ions like Na^+ , Ca^{2+} , Gd^{3+} and UO_2^{2+} are adsorbed quickly (95% in 5 minutes at ambient conditions) whereas ions formed by Zr^{4+} , Nb^{5+} and Pu^{4+} are taken up more slowly. The latter group contains those ions which are strongly hydrolysed even in rather acid solution.

Schindler *et al.* (1976) proposed that the surface complexation reactions can be described as follows:



which can be described by the intrinsic equilibrium constant, β_n which gives:

$$\beta_n = \exp\left(\frac{(z-n)F\phi}{RT}\right) \frac{[H^+]^n \{(\equiv SiO)_n M^{z-n}\}}{\{\equiv SiOH\}^n [M^{z+}]}$$
 where n is 1...z

(2)

Here \hat{u} is the potential difference between the sites of $(\equiv SiO)_n M^{(z-n)+}$ and the bulk solution

and

$$Z = \frac{\text{number of } H^+ \text{ released}}{\text{number of } M^{z+} \text{ adsorbed}} \quad (3)$$

Non-hydrolysed ions

As shown above, Schindler assumed that different kinds of complexes can be formed. If only one type of complex is formed between a non-hydrolysed ion and silica gel and if $\hat{u}=0$, according to Dugger *et al.* (1964) and Stanton *et al.* (1963) β_n can be written as:

$$\beta_n = \frac{\{(\equiv SiO)_n M\} [H^+]^n}{\{\equiv SiOH\}^n [M^{z+}]} \text{ where } z = n \text{ and } \hat{u}=0 \quad (4)$$

In infinitely diluted solutions the activity of the ions will be equal to their concentration and $\{..\}$ will be related to the mole fractions:

$$x_{SiOH} = \frac{n_{SiOH}}{n_{SiOH} + n_{SiO^-}} \text{ and } x_{SiO^-} = \frac{n_{SiO^-}}{n_{SiOH} + n_{SiO^-}}$$

If θ is the fraction of SiO^- groups in the hydrogen form *i.e.* $\theta = \frac{n_{SiOH}}{n_{SiO^-}}$

β_n can be written as:

$$\beta_n = \frac{1-\theta}{n\theta^n} \left[\theta + \frac{1-\theta}{n} \right]^{n-1} \frac{[H^+]^n}{[M^{z+}]} \quad (5)$$

Dugger *et al.* (1964) assumed that $z = n$ for all non-hydrolysed ions in indefinitely diluted solutions. θ is calculated from the number of H^+ ions released and the number of hydroxyl groups present at the surface, available for ion exchange.

In more concentrated solutions the activity, a , of the ions should be taken into account. This means for non-hydrolysed ions and $\hat{u}=0$ (Ahrland *et al.* 1960):

$$\beta_n = \frac{a_{H^+}^n \cdot a_{\{(\equiv SiO)_n M\}}}{a_{M^{z+}} \cdot a_{\{\equiv SiOH\}}^n} \quad (6)$$

using

$$a = f \cdot c \quad (7)$$

in which f is the activity coefficient and c is the concentration. This leads to

$$\beta_n = \frac{[H^+]^n \{(\equiv SiO)_n M\} f_{H^+}^n \cdot f_{\{(\equiv SiO)_n M\}}}{[M^{z+}] \{(\equiv SiOH)\}^n f_{M^{z+}} \cdot f_{\{(\equiv SiOH)\}}^n} \quad (8)$$

and

$$-\log f = 0.5 z_i^2 \sqrt{I} \quad (9)$$

and

$$I = 0.5 \sum c_i z_i^2 \quad (10)$$

SIMULATION OF COMPLEXATION WITH SOLGASWATER®

Equilibrium constants

Model calculations of metal complexation, *i.e.* complexation of Ca^{2+} , Mg^{2+} and Al^{3+} , were performed using the extended computer program SOLGASWATER®, version 1992 (Eriksson 1979). This version of SOLGASWATER® makes calculations of surface complexes possible. The equilibrium constants used were recalculated to the appropriate ionic strength using the Davies equation (Davies 1962)

$$\log \beta_{pqr} = \log \beta_{pqr}^0 + a_i \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

and

$$a_i = 0.5 \Delta Z^2 \tag{11}$$

Here β^0 is the formation constants at zero ionic strength, β is the constant at ionic strength I , a_i is the Debye Hückel constant and Z is the charge of the ions involved. The subscripts pqr represent the reactions involved, such that:

$$\beta_{pqr} = \frac{[A_p B_q C_r \dots]}{[A]^p [B]^q [C]^r \dots} \text{ in the reaction } p A + q B + r C + \dots \leftrightarrow A_p B_q C_r \dots \tag{12}$$

All calculations were made with equilibrium constants valid at 298 K and $I = 0.1$ M. The equilibrium constants used in the model are given in Table 5.1.1.

Table 5.1.1: Thermodynamic data used in the calculations. All $\log\beta_{\text{pqr}}$ values are valid at 298K and 0.1M (Davies 1962).

Species	Me ⁿ⁺			Silicates
	Ca ²⁺	Mg ²⁺	Al ³⁺	Si(OH) ₄ and =SiOH
SiO(OH) ₃ ⁻	-	-	-	- 9,52 ²⁾
SiO ₂ (OH) ₂ ²⁻	-	-	-	-22,26 ²⁾
Si ₂ O(OH) ₆	-	-	-	1,3 ⁴⁾
Si ₂ O ₂ (OH) ₅ ⁻	-	-	-	- 7,81 ³⁾
Si ₂ O ₃ (OH) ₄ ²⁻	-	-	-	-18,14 ³⁾
Si ₄ O ₆ (OH) ₆	-	-	-	-12,57 ¹⁾
MeOH ⁽ⁿ⁻¹⁾⁺	-12,50 ⁵⁾	-11,21 ⁵⁾	-5,43 ⁹⁾	-
Me(OH) ₂ ⁽ⁿ⁻²⁾⁺	-21,02 ⁵⁾	-14,09 ⁵⁾	-11,01 ⁹⁾	-
Me(OH) ₃ ⁽ⁿ⁻³⁾⁺	-	-	-16,93 ⁹⁾	-
Me(OH) ₄ ⁽ⁿ⁻⁴⁾⁺	-	-	-23,46 ⁹⁾	-
MeOSi(OH) ₃ ⁽ⁿ⁻¹⁾⁺	- 9,15 ⁶⁾	- 8,90 ⁶⁾	-	-
MeO ₂ Si(OH) ₂ ⁽ⁿ⁻²⁾⁺	-19,19 ⁶⁾	-18,11 ⁶⁾	-	-
Me(OSi(OH) ₃) ₂ ⁽ⁿ⁻²⁾⁺	-16,96 ⁶⁾	-15,23 ⁶⁾	-	-
=SiONa	-	-	-	- 6,97 ¹⁾
=SiOH ₂ ⁺	-	-	-	- 3,00 ¹⁾
=SiOMe ⁽ⁿ⁻¹⁾⁺	- 8,11 ¹⁾	- ,7,31 ¹⁾	-	-
(=SiO) ₂ Me ⁽ⁿ⁻²⁾⁺	-16,71 ¹⁾	-14,71 ¹⁾	-	-
(=SiO)Me(OH) ₂ ⁽ⁿ⁻³⁾⁺	-	-	-8,8/10,4 ⁷⁾	-
(=SiO)Me(OH) ⁽ⁿ⁻²⁾⁺	-	-	≈-5,8 ⁷⁾	-

- 1) Schindler P. (1995)
- 2) Sjöberg *et al.* (1981)
- 3) Sjöberg *et al.* (1985a)
- 4) Sjöberg *et al.* (1985b)
- 5) Critical stability constants (1976)
- 6) Schantschi *et al.* (1974)
- 7) Charlet L (1993)
- 8) Rosenqvist (1994)
- 9) Lövgren (1990)

Simulation of the complexation of calcium ions

Results of the SOLGASWATER[®] simulations are presented in Figures 5.2.1...5.2.3 shown below for a concentration of Ca^{2+} ions of 20 mM, a constant ionic strength of 0.1 M (NaCl) and different degrees of hydroxylation of the gel surface.

As expected from the theory a fully hydroxylated gel allows the Ca^{2+} ions to form complexes with hydroxyl groups of both the types $=\text{SiOCa}^+$ and $(=\text{SiO})_2\text{Ca}$. A reduction in the degree of hydroxylation significantly lowers the formation of the latter type and increases the formation of complexes with silicate ions present in the solution, due to slow dissolution of the silica gel. At higher pH values also $=\text{SiONa}$ complexes are formed. A lower degree of hydroxylation also allows formation of $\text{Ca}(\text{OH})_2$.

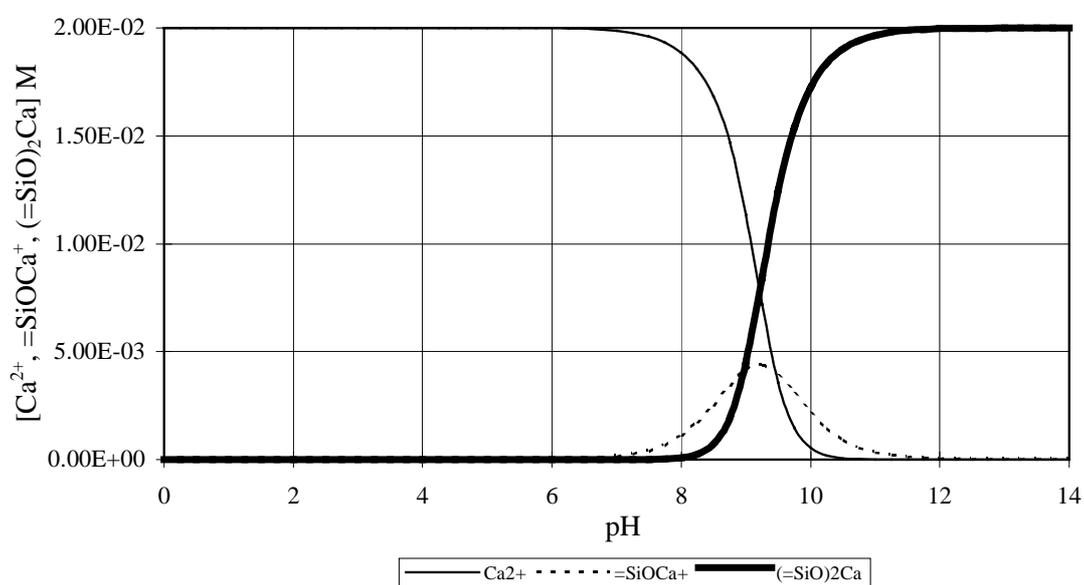


Figure 5.2.1 Complexation of Ca^{2+} ions on a completely hydroxylated silica gel

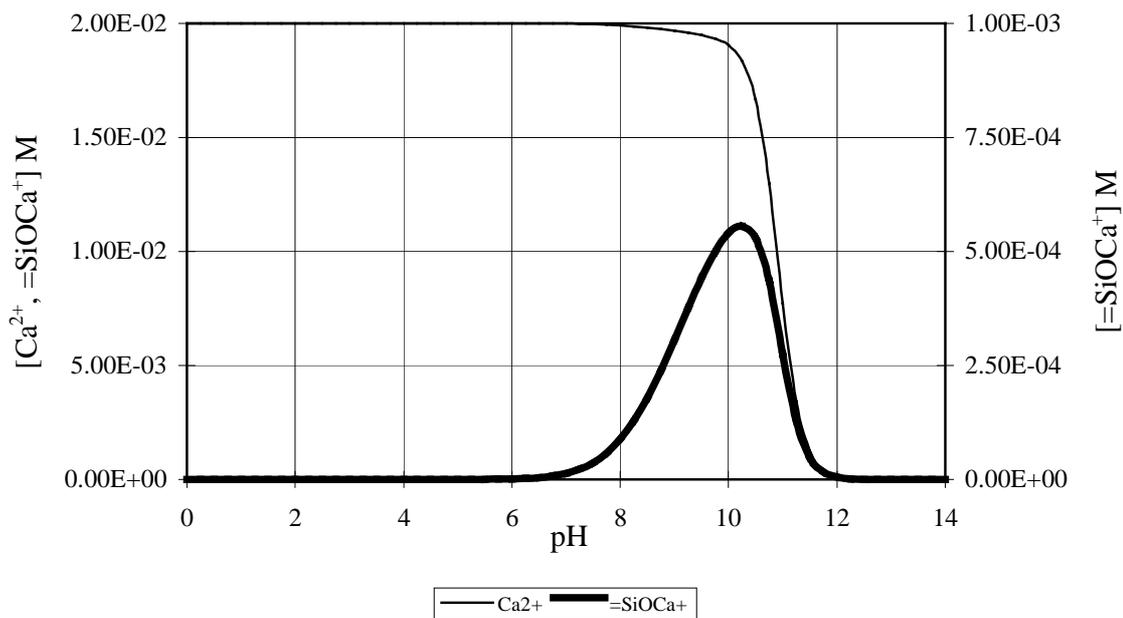


Figure 5.2.2. Complexation of Ca^{2+} ions on a 10% hydroxylated silica gel

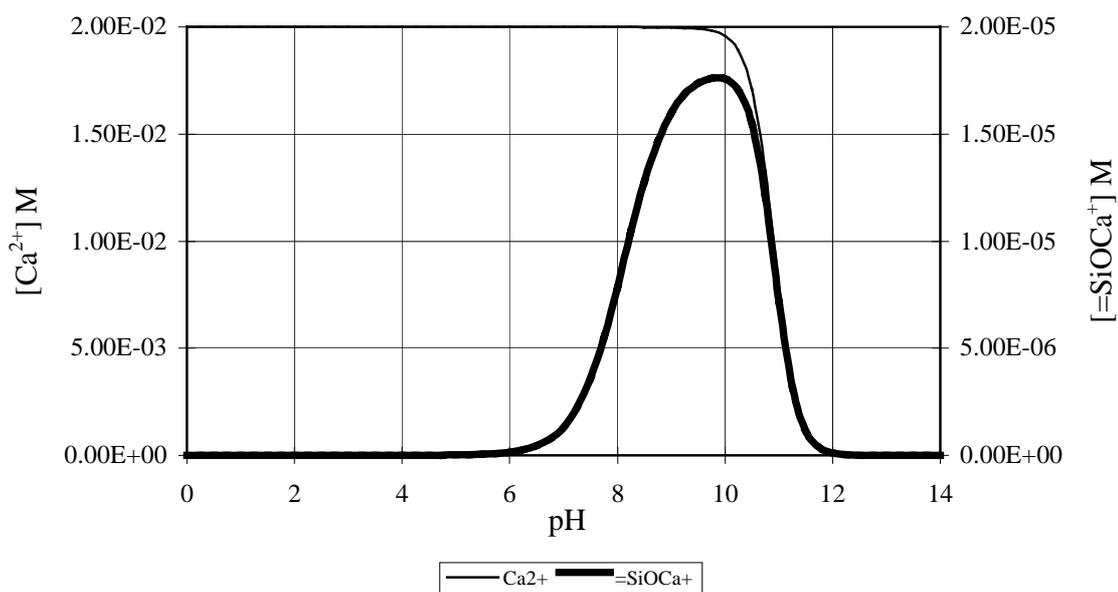


Figure 5.2.3. Complexation of Ca^{2+} ions on a 1% hydroxylated silica gel

Simulation of the complexation of magnesium ions

Results of calculations with SOLGASWATER[®] for the complexation of Mg^{2+} ions onto silica gel are shown in Figures 5.3.1....5.3.3. The concentration of Mg^{2+} ions is 20 mM, the ionic strength is 0.1 M (NaCl).

The figures show the differences in complexes formed influenced by the degree of hydroxylation of the silica gel. As gels with a lower degree of hydroxylation are used, the formation of $\text{Mg}(\text{OH})_2$ is possible at pH 8.25 and higher. At these higher pH values competition with Na-complexes also becomes more severe. At a higher pH also more soluble magnesium silicates are formed.

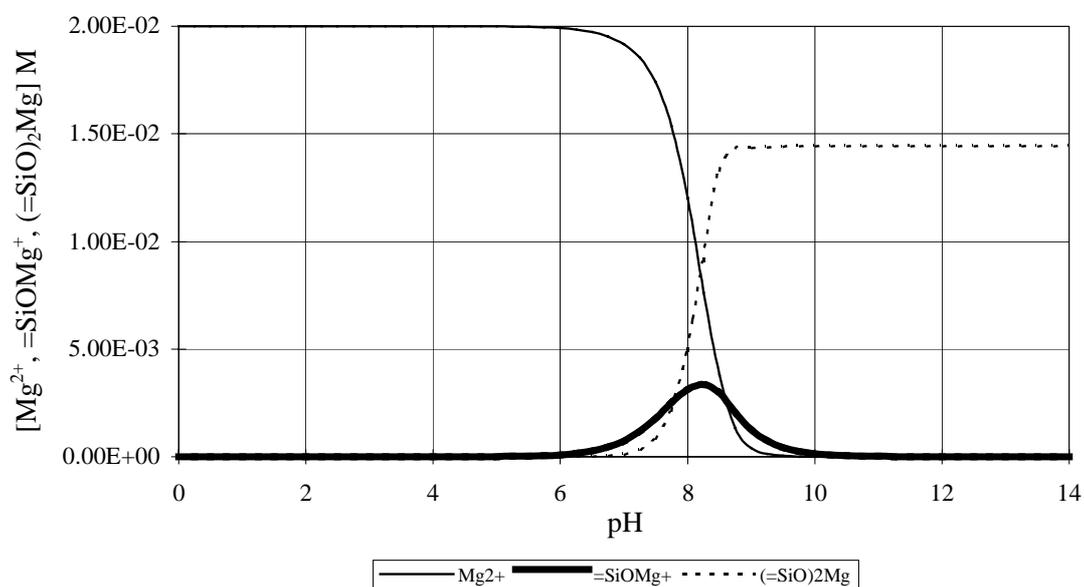


Figure 5.3.1. Complexation of Mg^{2+} ions on a fully hydroxylated silica gel

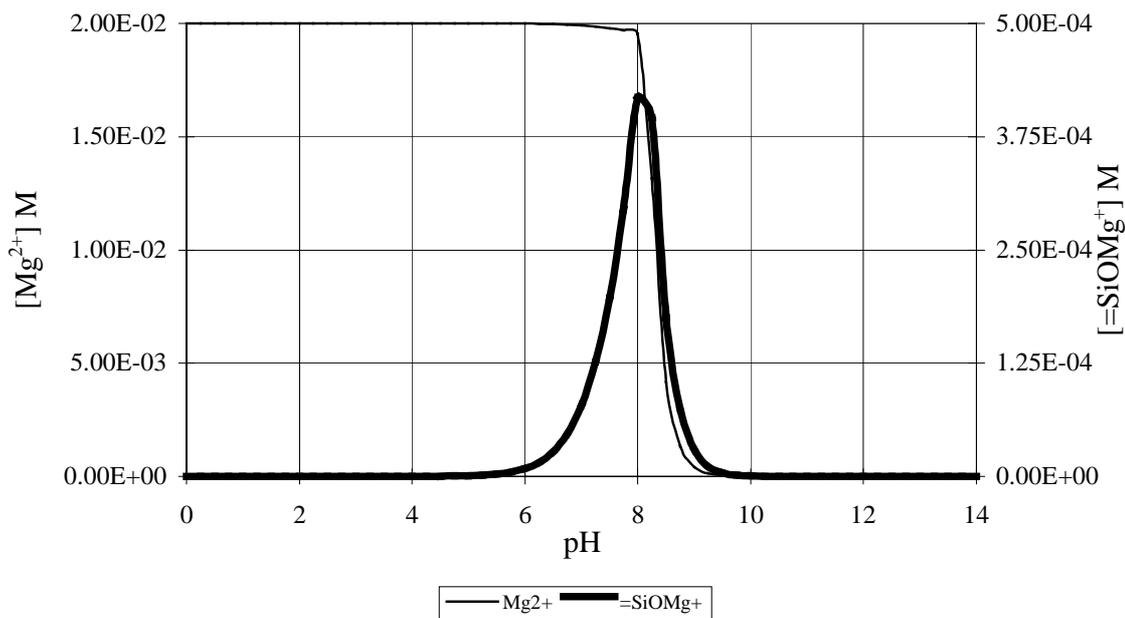


Figure 5.3.2. Complexation of Mg^{2+} ions on a 10% hydroxylated silica gel

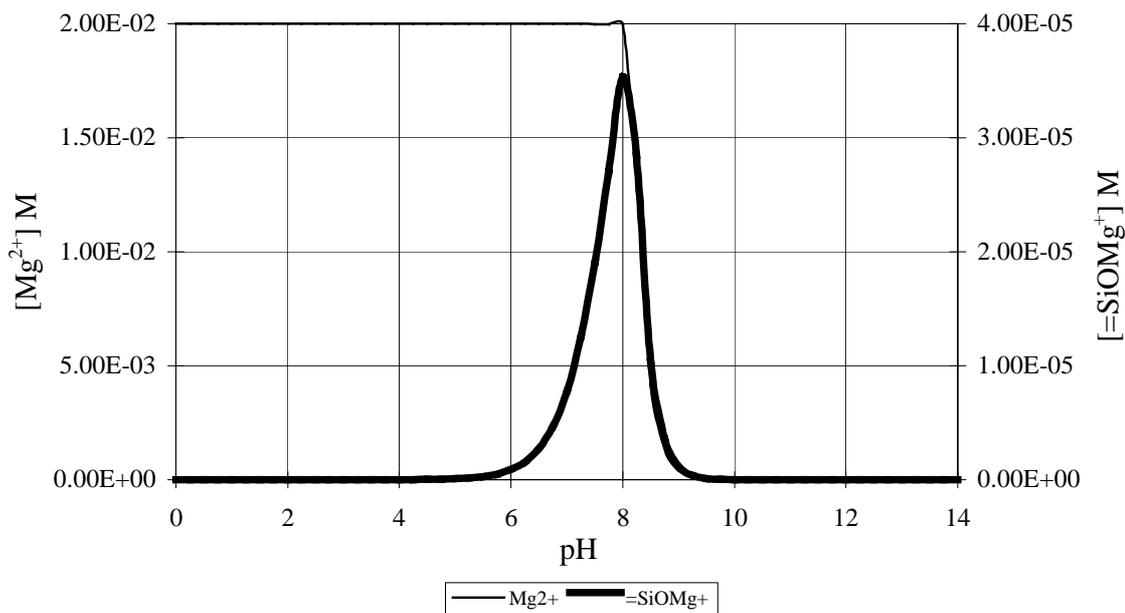


Figure 5.3.3. Complexation of Mg^{2+} ions on a 1% hydroxylated silica gel

Simulation of complexation of aluminium ions on silica gel.

Results of calculations with SOLGASWATER[®] for complexation of Al³⁺ ions on silica gel are shown in Figures 5.4.1....5.4.3. The concentration of Al³⁺ ions is 10 mM, the ionic strength is 0.1 M (NaCl). According to the simulation no Al(OH)₃ is formed. Since no equilibrium constants were available for the formation of soluble aluminium silicates these complexes have not been accounted for. The equilibrium constants available for the surface complexes are only rough estimations. The simulation results therefore can only be seen as an indication of the complexes formed as a function of pH.

At high pH, *i.e.* pH > 12, the surface is negatively charged and repels the present Al(OH)₄⁻ leading to a decrease in formation of surface complexes.

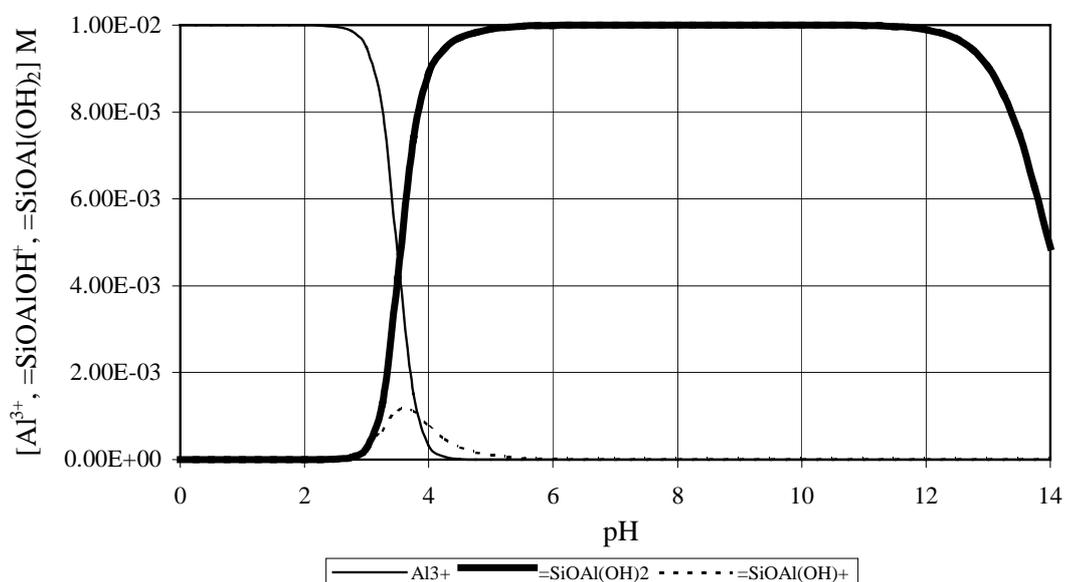


Figure 5.4.1. Complexation of Al³⁺ ions on a fully hydroxylated silica gel

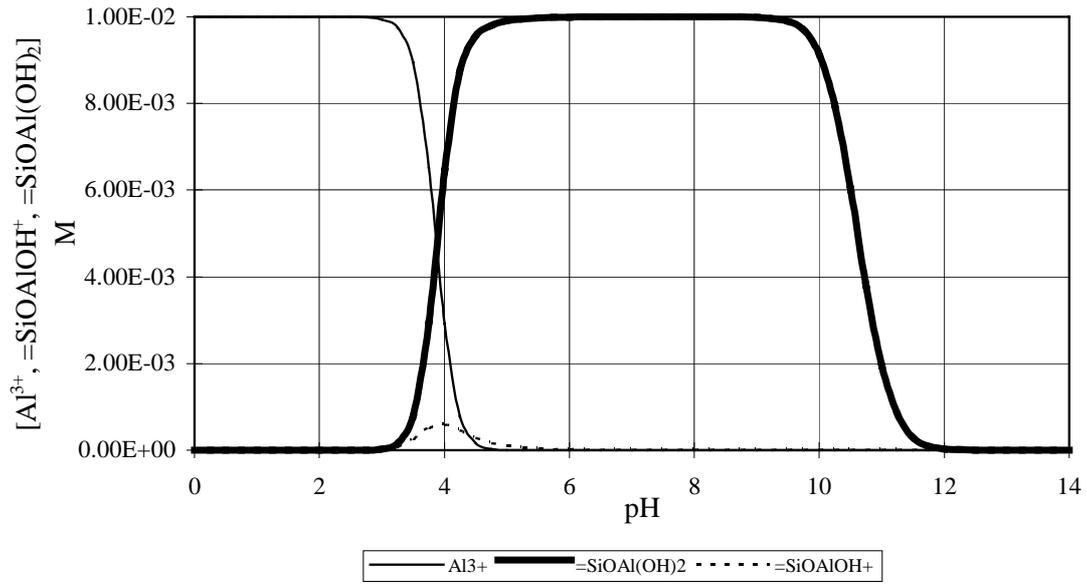


Figure 5.4.2. Complexation of Al^{3+} ions on a 10% hydroxylated silica gel

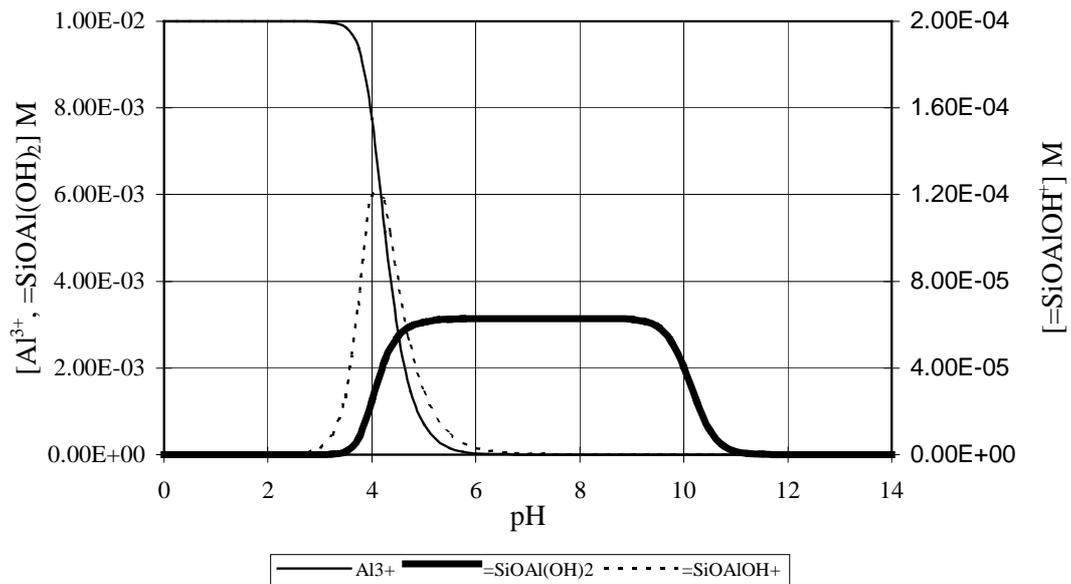


Figure 5.4.3. Complexation of Al^{3+} ions on a 1% hydroxylated silica gel

Simulation of simultaneous complexation of calcium and magnesium ions in concentrations as used in SBF

In the research for bone formation on bioactive glass a Simulated Body Fluid (SBF) is used generally. The fluid contains, among other ions, concentrations of 1.5 mM Mg^{2+} ions and 2.5 mM Ca^{2+} ions (Kokubo *et al.* 1992). These concentrations are used to simulate the behaviour in simultaneous complexation on silica gel with SOLGASWATER[®].

Results of the simulation at a constant ionic strength of 0.1 M are shown in Figures 5.5.1..5.5.3. As was also shown with complexation of Mg^{2+} ions and Ca^{2+} ions the hydroxylation of the gel surface determines the formation of the complexes and, in this case, also the type of complex.

On a fully hydroxylated gel enough hydroxyl groups are present to form complexes with both Mg^{2+} - and Ca^{2+} ions. At a lower degree of hydroxylation the ions will have to compete to form a surface complex. Since the $\log\beta$ value of magnesium complexes is greater than the $\log\beta$ value of calcium complexes the formation of magnesium complexes will be favoured over the formation of calcium complexes as shown in the figures given below.

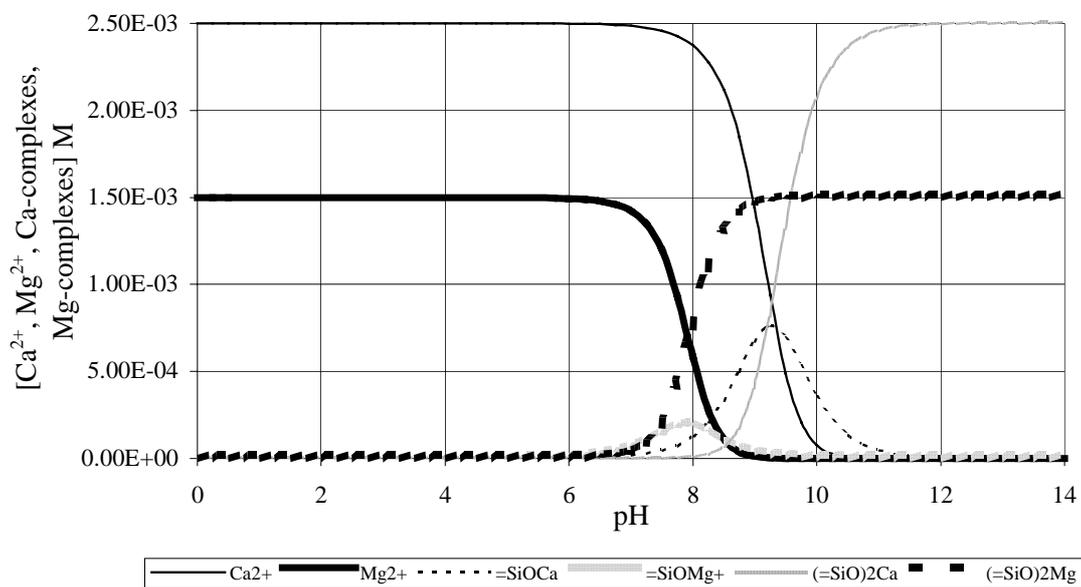


Figure 5.5.1. Simultaneous complexation of Ca^{2+} - and Mg^{2+} ions on a fully hydroxylated silica gel; $[\text{Ca}_{\text{tot}}]/[\text{Mg}_{\text{tot}}] = 1.67$

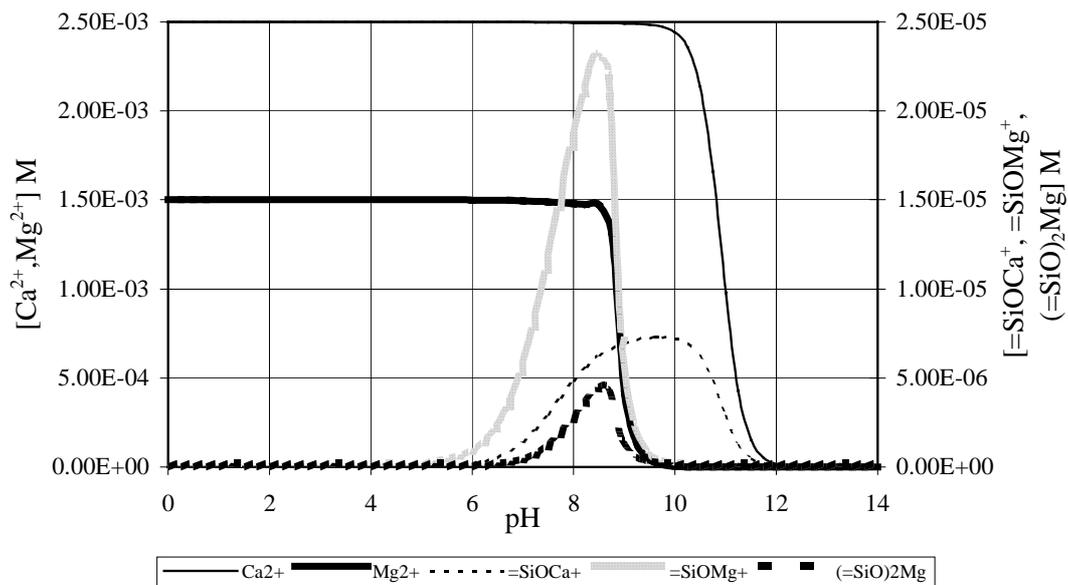


Figure 5.5.2. Simultaneous complexation of Ca^{2+} - and Mg^{2+} ions on a 10% hydroxylated gel; $[\text{Ca}_{\text{tot}}]/[\text{Mg}_{\text{tot}}] = 1.67$

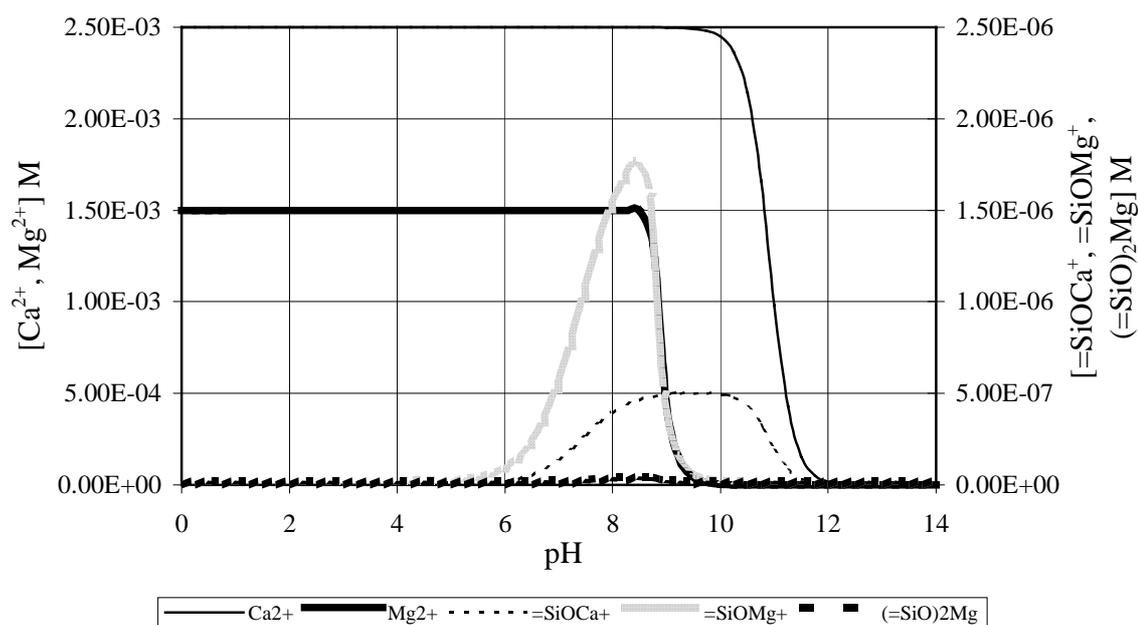


Figure 5.5.3. Simultaneous complexation of Ca^{2+} - and Mg^{2+} ions on a 1% hydroxylated silica gel; $[\text{Ca}_{\text{tot}}]/[\text{Mg}_{\text{tot}}] = 1.67$

Simulation of simultaneous complexation of calcium and aluminium ions

Results of the simulation of simultaneous adsorption of Al^{3+} ions and Ca^{2+} ions at a constant ionic strength of 0.1M are shown in Figures 5.6.1..5.6.3. As was shown with simultaneous complexation of Mg^{2+} ions and Ca^{2+} ions, the degree of hydroxylation of the gel surface determines the complexes formed. For a low hydroxylation degree formation of Al-complexes with the silica surface will inhibit the formation of Ca-complexes.

For simplicity, soluble silica complexes have not been accounted for since no constants were available for soluble aluminium silicates. The concentration of Ca^{2+} ions was 5 mM, the concentration of Al^{3+} ions was 1 mM.

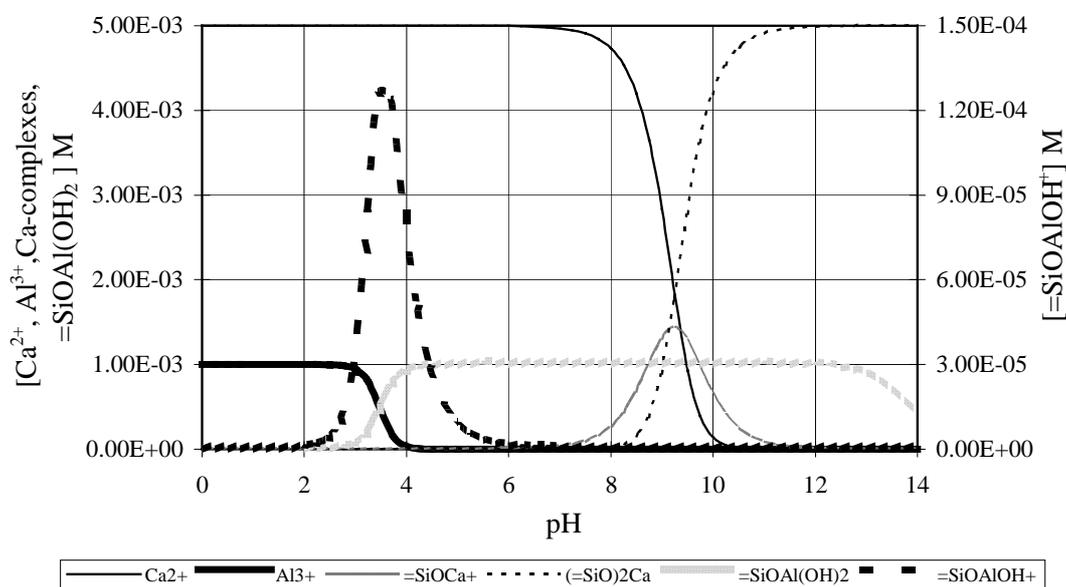


Figure 5.6.1. Simultaneous complexation of Ca^{2+} - and Al^{3+} ions on a fully hydroxylated silica gel; $[\text{Ca}_{\text{tot}}]/[\text{Al}_{\text{tot}}] = 5$

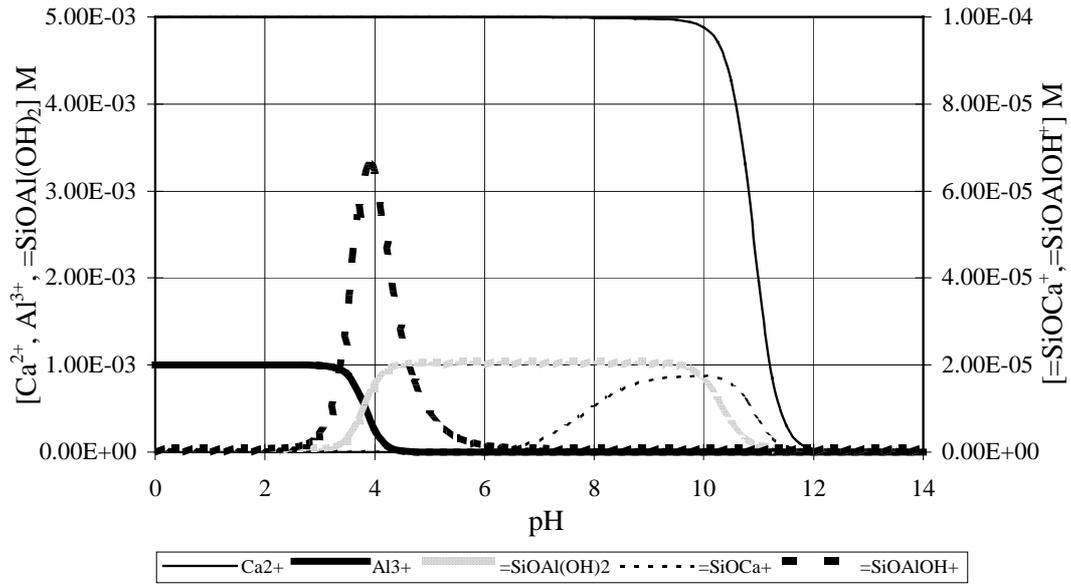


Figure 5.6.2. Simultaneous complexation of Ca^{2+} - and Al^{3+} ions on a 10% hydroxylated silica gel; $[\text{Ca}_{\text{tot}}]/[\text{Al}_{\text{tot}}] = 5$

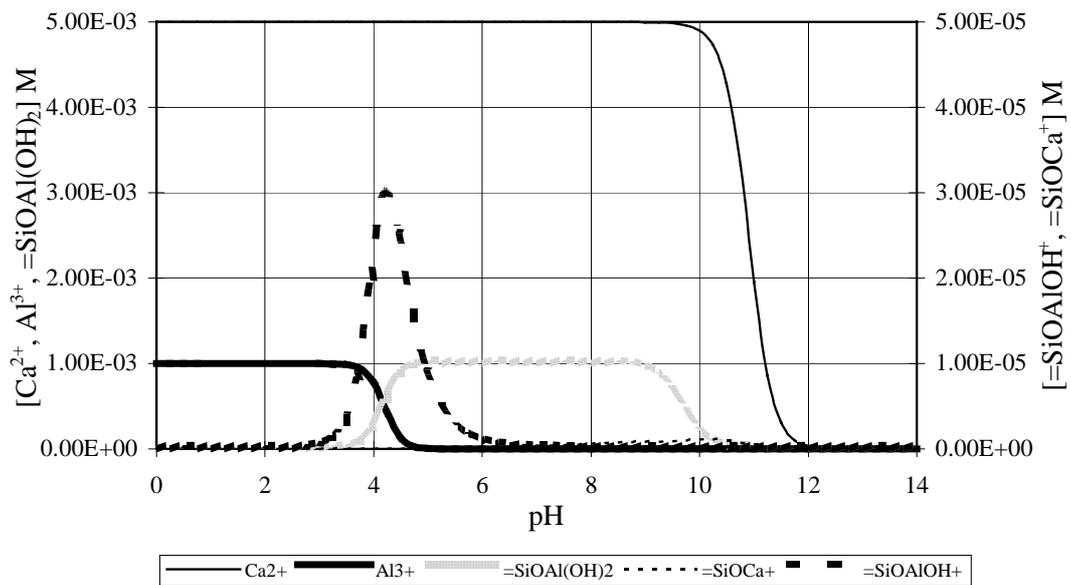


Figure 5.6.3. Simultaneous complexation of Ca^{2+} - and Al^{3+} ions on a 1% hydroxylated silica gel; $[\text{Ca}_{\text{tot}}]/[\text{Al}_{\text{tot}}] = 5$

Simultaneous complexation of calcium and aluminium ions in concentrations as used in bioactive glass and SBF

A more biologically realistic simulation is the simultaneous complexation of 2.5 mM Ca^{2+} ions and 1% Al^{3+} ions at a constant ionic strength of 0.1M. This means 25 μM Al^{3+} ions.

The results of this simulation are shown in Figures 5.7.1..5.7.3.

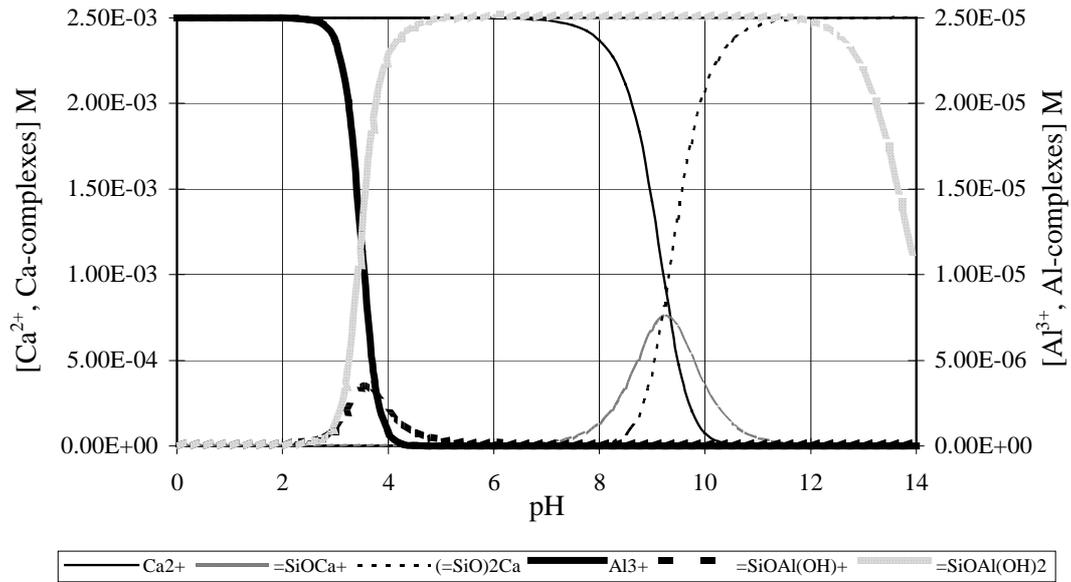


Figure 5.7.1. Simultaneous complexation of Ca^{2+} - and Al^{3+} ions on a fully hydroxylated silica gel; $[\text{Ca}_{\text{tot}}]/[\text{Al}_{\text{tot}}] = 100$

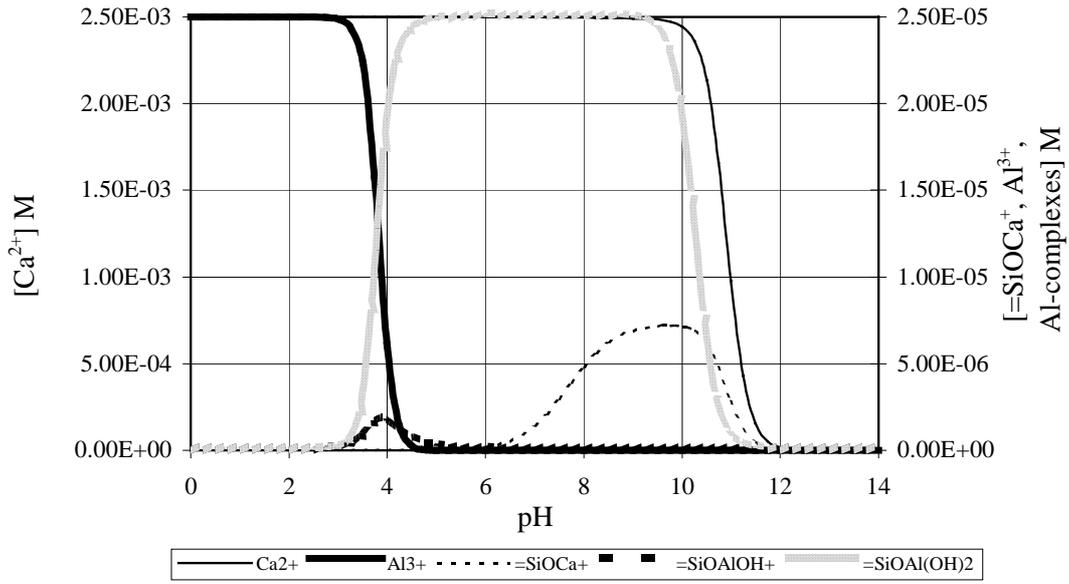


Figure 5.7.2. Simultaneous complexation of Ca^{2+} and Al^{3+} ions on a 10% hydroxylated silica gel; $[\text{Ca}_{\text{tot}}]/[\text{Al}_{\text{tot}}] = 100$

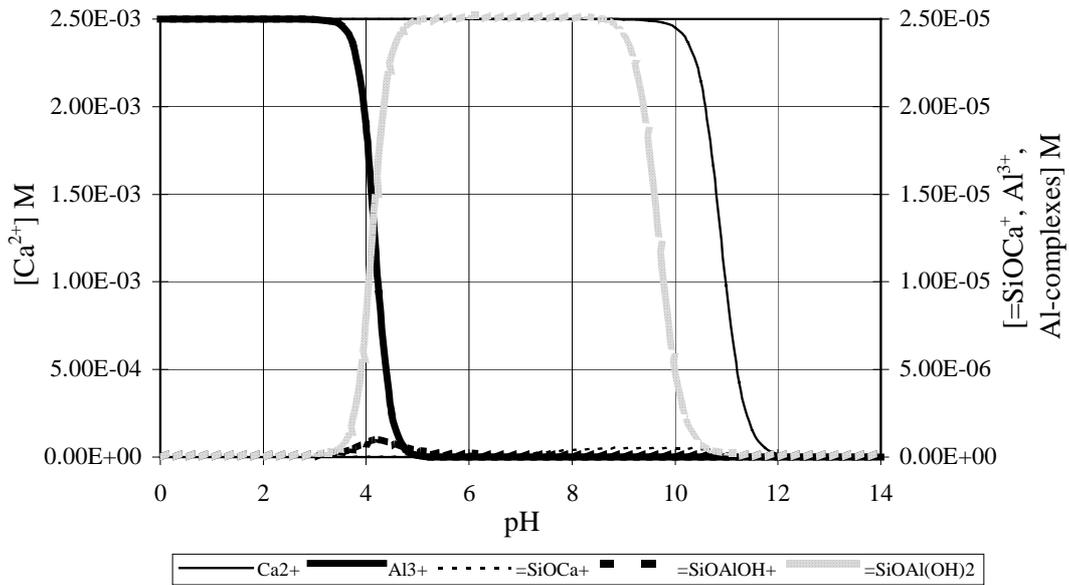


Figure 5.7.3. Simultaneous complexation of Ca^{2+} and Al^{3+} ions on a 1% hydroxylated silica gel; $[\text{Ca}_{\text{tot}}]/[\text{Al}_{\text{tot}}] = 100$

THE =SIOH-NA⁺ SYSTEM

Titration of a silica gel

In order to investigate the behaviour of a silica gel, a gel is titrated with hydrochloric acid (HCl) and sodium hydroxide (NaOH). Aldrich's 28,863-2 high purity grade gel is used. The BET surface area determined by N₂ adsorption equals 411 m²/g using the extended BET equation. The particle diameter is between 63 and 212 μm. The pore size distribution is shown in Figure 6.1.1, the pore specific volume is 0.74 cm³/g.

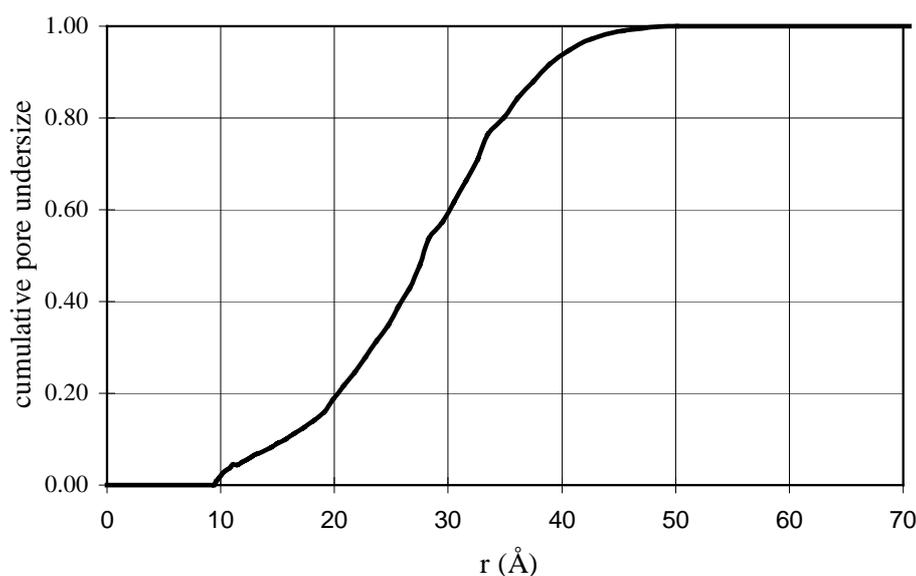


Figure 6.1.1. Measured cumulative pore size distribution

The gel was shaken with solution of various concentrations of either H⁺ or OH⁻ ions containing a constant initial concentration of Na⁺ ions of 0.1N. This initial Na⁺ concentration is obtained by adding extra NaCl to the hydroxide solution into such an extent that the total initial concentration of Na⁺ ions and the ionic strength equals 0.1 M.

The ratio between the volume, V, of the solution and the amount of gel, m, was 0.01 l/g. All chemicals used in the experiments were of the highest purity grade available. Water used in the experiments was distilled and deionised.

After 24h reaction time at 20°C the samples were stirred and the pH was measured.

The results from the titration are shown in Table 6.1.1 and Figure 6.1.2.

Table 6.1.1. Experimental results of titration of the gel at a constant ionic strength of 0.1N

No	Na ⁺ _{initial} mM	meq OH ⁻ /g	pH _{after}
1	100	1	10.97
2	100	0.8	10.42
3	100	0.7	10.35
4	100	0.6	10.00
5	100	0.4	9.34
6	100	0.3	8.77
7	100	0.2	8.22
8	100	0.1	6.80
9	100	0.05	6.97
10	100	0.01	5.86
11	100	0	5.68
12	100	-0.005	6.05
13	100	-0.01	5.27
14	100	-0.02	3.36
15	100	-0.03	2.82
16	100	-0.04	2.59
17	100	-0.05	2.45
18	100	-0.07	2.26
19	100	-0.08	2.20
20	100	-0.1	2.09
21	100	-0.5	1.38
22	100	-1	1.09

* Negative values represent addition of H⁺ ions.

A typical S-curve is found, similar to those of weakly acidic ion exchangers (Ahrland *et al.* 1960). The S-curve as drawn in Figure 6.1.2 has been calculated using a neural network containing two hidden sigmoidal nodes (Saxén 1996):

$$pH_{after} = 1.06 + \frac{3.25}{1 + \exp(-4.39 + 2.640 * [OH^-])} + \frac{6.41}{1 + \exp(0.918 - 61.2 * [OH^-])} \quad (13)$$

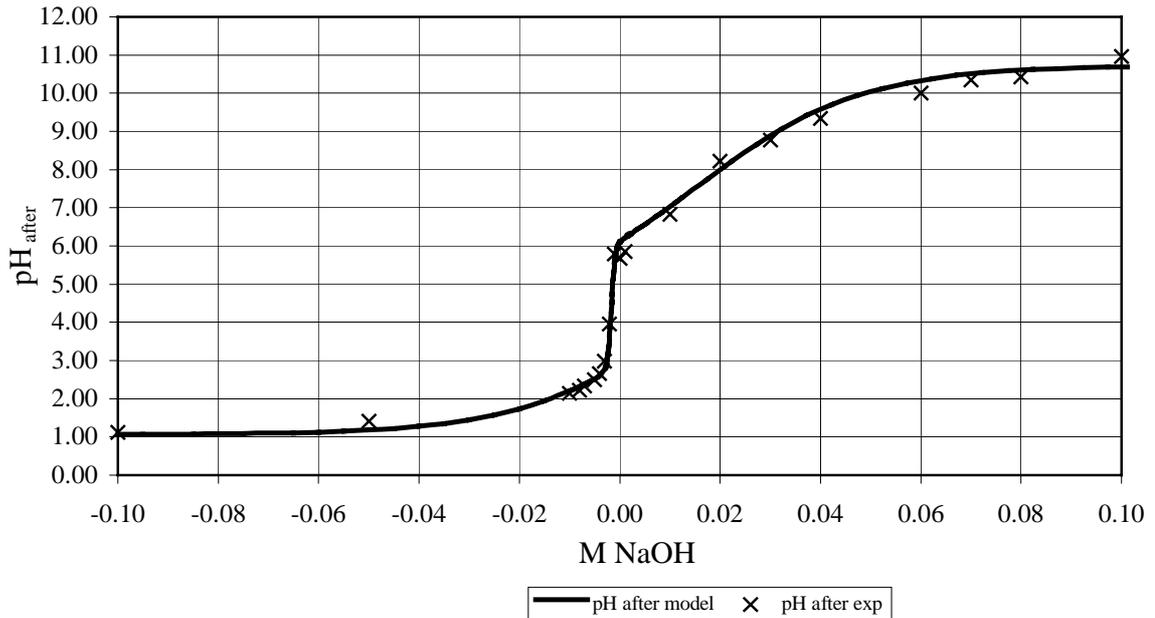
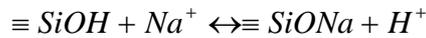


Figure 6.1.2. pH of the outer solution as a function of concentration NaOH. Negative values should be read as positive amounts of H⁺ ions added.

Ahrland *et al.* (1960) proved an equivalence between the amount of sorbed Na⁺ and the amount of H⁺ ions released. This means that the sorption is assumed to be an ion exchange reaction:



This ion exchange reaction and the polynomial as described in Equation 13 are used to calculate the amount of Na⁺ adsorbed to the gel as a function of measured pH as shown in Figure 6.1.3. This figure shows that at a pH of 11 all Na⁺ ions have become adsorbed. The drawn curve represents a calculated sigmoidal using a least sum of squares curve fitting procedure.

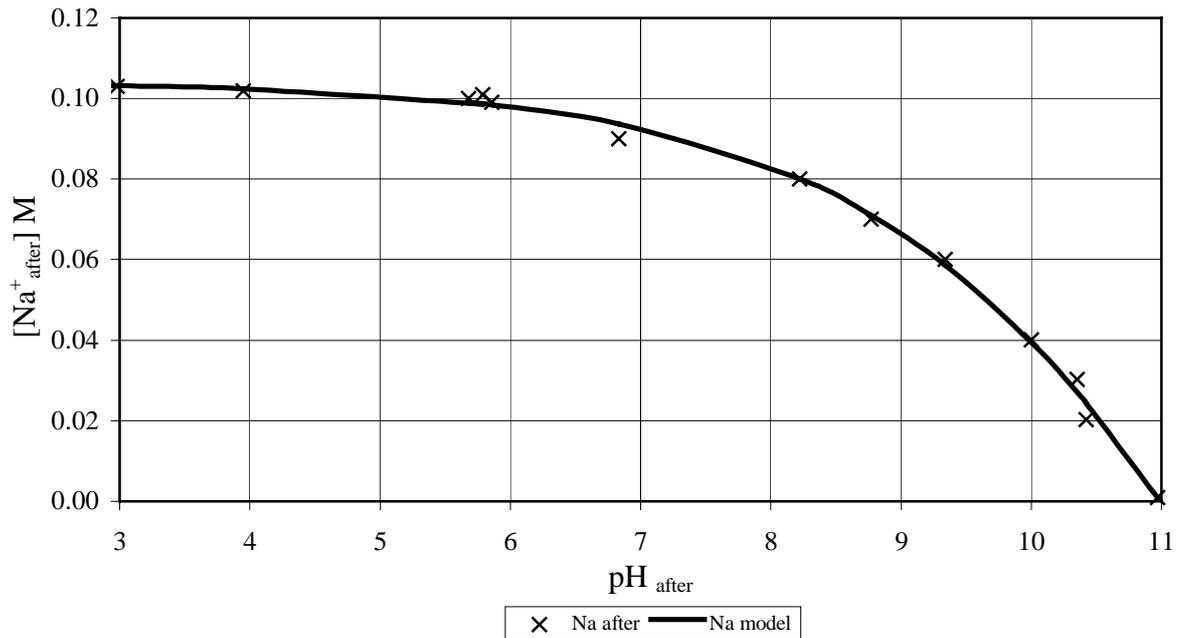


Figure 6.1.3. Concentration of adsorbed Na⁺ ions as a function of the pH in the solution.

Determination of the capacity of the gel

In order to determine the ion exchange capacity of the gel adsorption experiments have been carried out with different initial Na⁺ ion concentrations in the range up to 5 M.

According to Heston *et al.* (1960) and Allen *et al.* (1969), the surface is in its completely exchanged form at pH =12 and at a NaCl concentration of 4 mM. Figure 6.1.3 shows clearly that all Na⁺ ions are adsorbed at a pH above 11. An even higher pH value, *i.e.* pH=13, has been used in order to determine the ion exchange capacity of the gel.

Figure 6.2.1. shows the amount of H⁺ ions released from the gel, which equals the amount of Na⁺ ions adsorbed as a function of the initial Na⁺ concentration at pH=13

A maximum amount of 99.95 mM, *i.e.* ≈100 mM of Na⁺ ions have been found to become adsorbed. This means that the ion exchange capacity of the gel is about 100 mM, which equals 1.5 =SiOH nm⁻².

Schindler *et al.* (1968) reported a value of 2.4 =SiOH nm⁻² in a 0.1N ionic medium. The theoretical maximum amount of =SiOH nm⁻² has been calculated by Iler (1979), which equals 4.6 =SiOH nm⁻². This would mean that the surface of the gel as

used in the experiments is only partly hydroxylated, *i.e.* 33% of the theoretical maximum amount.

It should be noted here that at the concentration OH⁻ ions as used the maximum amount of 100 mM surface groups can become ionised leading to a gel capacity of 100 mM. However Heston and Allen stated that already at a pH 12 *i.e.* at a OH⁻ concentration below of 0.1M **all** the possible reactive groups will be ionised thus leading to a usable calculated capacity. If the assumption of Heston and Allen would not be valuable, using a higher OH⁻ concentration could possibly lead to a higher capacity of the gel

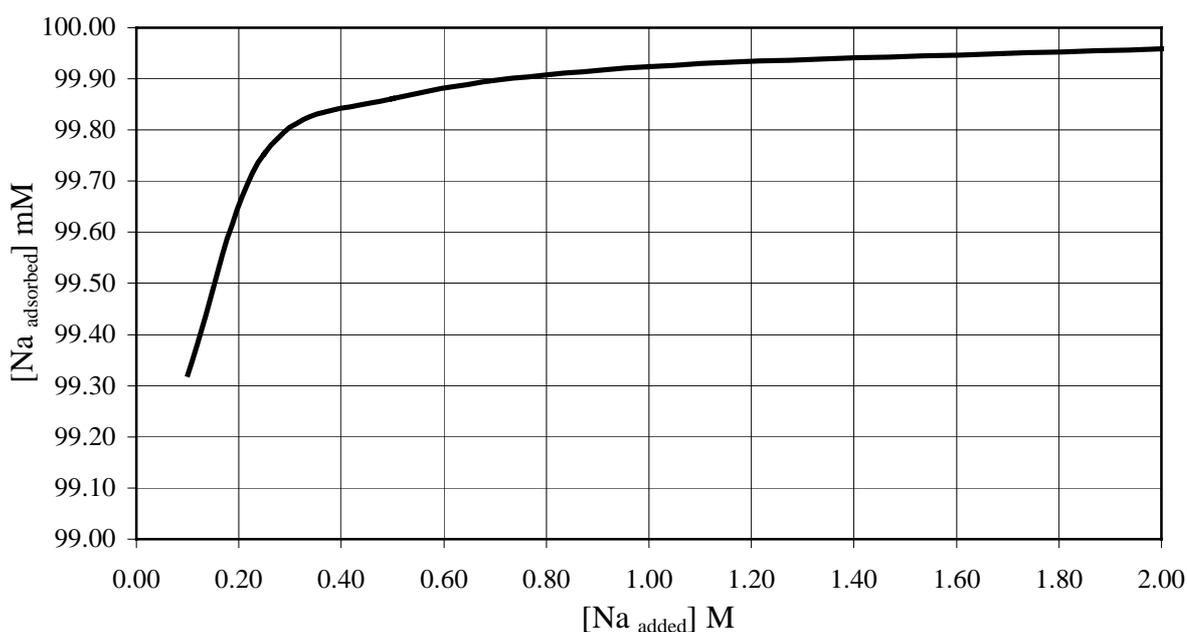


Figure 6.2.1. The amount of Na⁺ ions adsorbed as function of the initial Na⁺ concentration at pH=13

Determination of the equilibrium constant and type of complex involved

Using Ahrland's (1960) equation for the intrinsic equilibrium constant, β_{intr} , for non diluted solutions, the number of hydroxyl groups, n , involved and the equilibrium constant, β , for the $(=\text{SiO})_n\text{Na}^{(1-n)+}$ complex formed can be estimated (see Section 4.2):

$$\beta = \frac{[H^+]^n \{(\equiv \text{SiO})_n M\} f_{H^+}^n \cdot f_{\{(\equiv \text{SiO})_n M\}}}{[M^{z+}] \{(\equiv \text{SiOH})^n\} f_{M^{z+}} \cdot f_{\{(\equiv \text{SiOH})^n\}}} \quad (8)$$

Ahrland assumed that the potential difference, \hat{u} , between the surface complex and the bulk solution can be neglected, hence the intrinsic equilibrium constant equals the apparent equilibrium constant.

Defining D as:

$$D = \frac{\{(\equiv SiO)_n M\}}{[M^{z+}]} \quad (14)$$

and assuming that the activity coefficient, f , equals 1, gives

$$\beta = \frac{[H^+]^n}{\{SiOH\}^n} \cdot D \quad (15)$$

thus

$$-\log D = -n \log [H^+] + Cst \quad (16)$$

The number of hydroxyl groups involved in the ion exchange, n , follows from a $\log D$ vs. pH plot, giving a straight line with slope n . The apparent equilibrium constant, $\log K$, follows from the intercept.

According to Ahrland *et al.* (1960), the sorption is important only when the pH has exceeded a certain value. To the left of a $\log D$ curve very little of the metal ion is sorbed whereas to the right almost complete sorption occurs. Therefore ions with curves sufficiently apart can, by a suitable choice of pH , be separated from each other.

The adsorption of Na^+ ions at low pH as reported by Allen *et al.* (1970) seems, however, unlikely since among others Ahrland *et al.* (1960) stated that the Na^+ ion is adsorbed only at a pH above 13. Also the experiments as carried out and described in Section 6.1 showed that Na^+ ions are adsorbed at a pH above ≈ 6 .

Using the above described procedure for the titration, Figure 6.3.1 shows a slope of $n=0.31$ at a pH above 6.5 where the adsorption is supposed to become significant. Allen *et al.* (1970) reported a value for n equal to 0.26 at a pH range above 6.

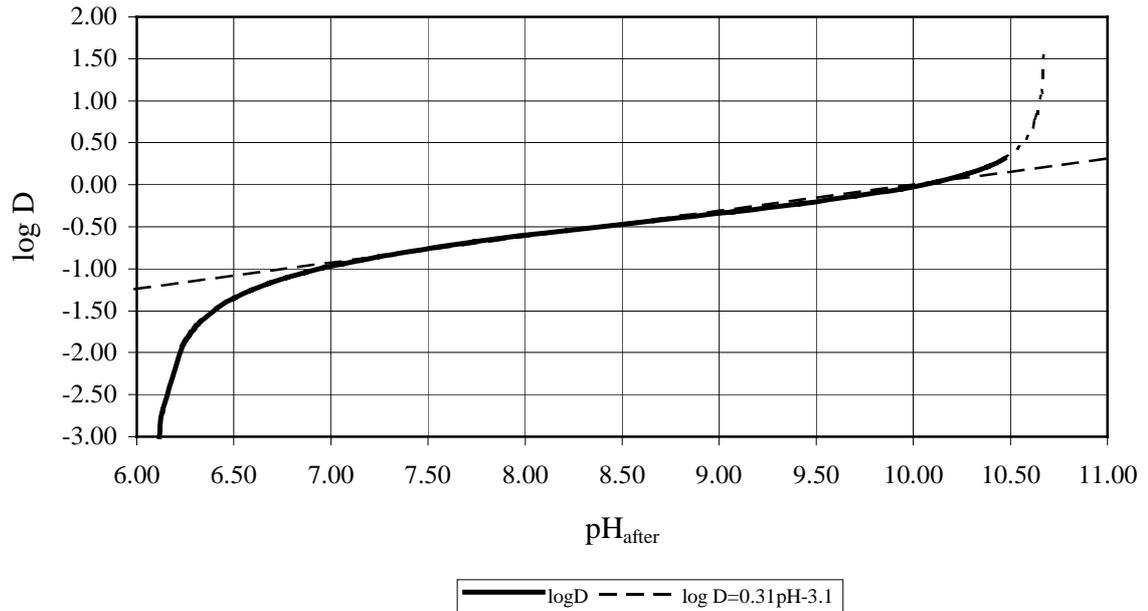


Figure 6.3.1. Log D as a function of the measured pH in solution.

Schindler *et al.*(1976) also found that n is very sensitive to experimental errors and that at higher pH the measured n will be smaller than the initial charge of the ion, z . In the case of Fe^{3+} , $n \leq 3$, and for Cu^{2+} , Cd^{2+} and Pb^{2+} , $n \leq 2$, respectively. Schindler proposed that these values are found due to steric hindrance on the silica gel surface which makes it impossible for the ions to exchange the maximum possible amounts of H^+ ions. Stanton *et al.* (1963) and Dugger *et al.* (1964) reported the same phenomenon, *i.e.* at higher ion concentration ion exchange is inhibited.

Allen *et al.*(1971) found that the slope of the plotted line for Na^+ only represents n for low pH ($\text{pH} < 5$); at higher pH the slope decreases. Allen suggests that this is due to the presence of two different hydroxyl groups on the surface having their own reactivity towards ion exchange. A second assumption he made was that as the extent of ion exchange increases, the reactivity of the surface decreases.

Allen's assumption of the presence of two different types of hydroxyl groups and decrease in reactivity of the surface might explain the discrepancy between the slope, n , as expected and the slope as found in reality.

Rosenqvist (1994) determined an intrinsic equilibrium constant for an $=\text{SiONa}$ complex, in which n is supposed to be $n=1$ by means of potentiometric titrations at an ionic strength of 0.1 N NaCl. This gave $-\log K = 7.441$ using the colloidal silica Ludox[®] TM, with a reported surface area of $125 \text{ m}^2/\text{g}$.

Schindler *et al.* (1968) reported a $-\log K = 6.8$ determined by coulometric titration of the silica gel H (Merck) with a surface area of $372 \text{ m}^2/\text{g}$ at 25°C and an ionic strength of 0.1 N NaClO_4 .

As mentioned above, Allen *et al.* (1971) derived a model for determining the apparent equilibrium constant, K, which combines two models, *i.e.* one within which the surface is assumed to consist initially of two types of hydroxyl groups with widely different reactivities and a second within which the apparent equilibrium constant for the exchange process is assumed to vary as the reaction progresses.

The first part of the model describes the law of mass action as derived in equations 14-16. Instead of one type of hydroxyl groups more types, such as =Si(OH)₂, -Si(OH)₃ and =SiOH, can be taken into account. However, which type is taken into account by Allen is unclear. For simplicity all three types are written =SiOH.

In the second part of the model it is assumed that that the difference between the free energies of a H⁺ and a Na⁺ ion at the surface increases linearly with the quantity *x* defined by Equation 17:

$$\log x = \log \frac{[\equiv SiO_I Na] + [\equiv SiO_{II} Na]}{[\equiv SiO_I H]_0 + [\equiv SiO_{II} H]_0} \quad (17)$$

Where the indices I and II indicate type I and type II hydroxyl groups, respectively.

Then the free-energy change in the exchange process may be described by:

$$\Delta G = -RT \ln K_0 / Q + Ax \quad (18)$$

in which Q is a concentration quotient and A is a constant of proportionality.

Using this model and assuming only one type of hydroxyl groups at the surface, Allen described a pK₀ value, which corresponds to a variation of pK₀ from 6.4 for a surface entirely in the hydrogen form to 9.6 for a surface completely in the sodium form.

Using two types of hydroxyl groups, from which one reacts more rapidly, Allen derived three equations, within which *x_i* describes the fraction of groups on which protons have been replaced by Na⁺ ions and *ù* describes the fraction of type I, the most reactive sites.

$$\log \frac{x_I}{1 - x_I} + \frac{A_I x_I}{2.303RT} = pH + \log K_{I,0} + \log [Na^+] \quad (19)$$

$$\log \frac{x_{II}}{1-x_{II}} + \frac{A_{II}x_{II}}{2.303RT} = pH + \log K_{II,0} + \log[Na^+] \quad (20)$$

$$x = x_I\phi + x_{II}(1-\phi) \quad (21)$$

Allen derived for the Ludox HS gel with a BET surface area of 200 m²/g values for A/RT=4.27, pK_{I,0}=5.55, pK_{II,0}=9.05 and \dot{u} =0.152 by means of a general multiparameter least sum of squares curve-fitting method.

Using Allen's total model and assuming two types of hydroxyl groups one with the pK₀ for a surface in the hydrogen form *i.e.* 6.4 and one with a pK₀ equivalent to a surface in the sodium form, *i.e.* 9.6, \dot{u} could be derived for the experiments as carried out, here giving \dot{u} =0.46. A/RT was kept at 4.3. The mean deviation in log *x* was 0.03 units in the pH range 6.5...10.5

Figure 6.3.2. shows the log *x* values using different pK values *i.e.* pK_{I,0}=5.505, pK_{II,0}=9.05, A/RT=4.3, \dot{u} =0.152 derived by Allen *et al.* (1971), and pK_{I,0}=6.4, pK_{II,0}=9.6, A/RT=4.3 and \dot{u} =0.46 as derived from the experiments.

SOLGASWATER[®] simulations compared with experimental values

In order to compare experimental values with SOLGASWATER[®] simulations, simulations have been carried out using the equilibrium constant as determined above.

Equation 2, Section 4.1, describes the intrinsic equilibrium constant as a function of the apparent equilibrium constant:

$$\beta_n = \exp\left(\frac{(z-n)F\phi}{RT}\right) \frac{[H^+]^n \{(\equiv SiO)_n M^{(z-n)}\}}{\{(\equiv SiOH)\}^n [M^{z+}]} \quad \text{where n is } 1 \dots z \quad (2)$$

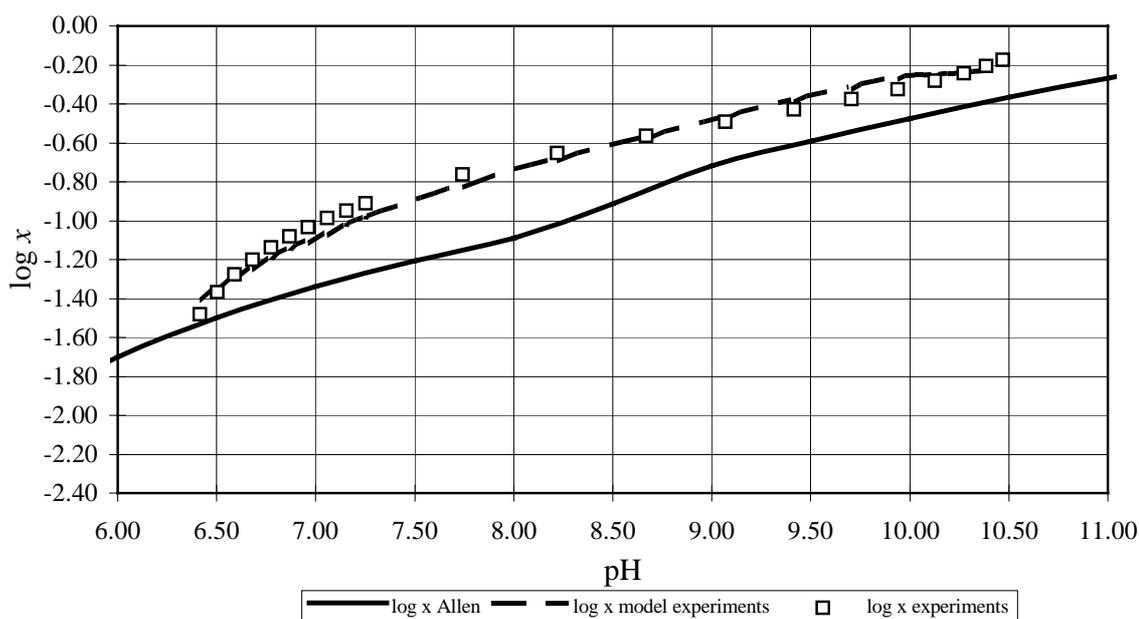


Figure 6.3.2. Plot of the logarithm of the fraction of the number of exchange sites occupied by Na^+ as a function of pH. The bold line shows the lines as computed using the equilibrium constants as derived by Allen *et al.* (1971). The data points and the dashed line show the experiments and the model derived from the experiments. All lines are calculated with $A/RT=4.3$

Since in the case of complexation of Na^+ ions on silica z equals n , the apparent equilibrium constant, K , equals the intrinsic equilibrium constant, $\hat{\theta}$, and can thus be used in the SOLGASWATER[§] simulations. Figures 6.4.1 and 6.4.2. show the simulations using the apparent equilibrium constant as derived by Allen *et al.* (1971), $\text{p}K_{\text{I},0}=5.05$, $\text{p}K_{\text{II},0}=9.05$, $\hat{\nu}=0.152$ and as determined from the experiments in Section 6.3.

Figure 6.4.2 shows that the approach of Allen *et al.* (1971) as described in the former section is very useful for describing the $=\text{SiO}^-$ - Na^+ system.

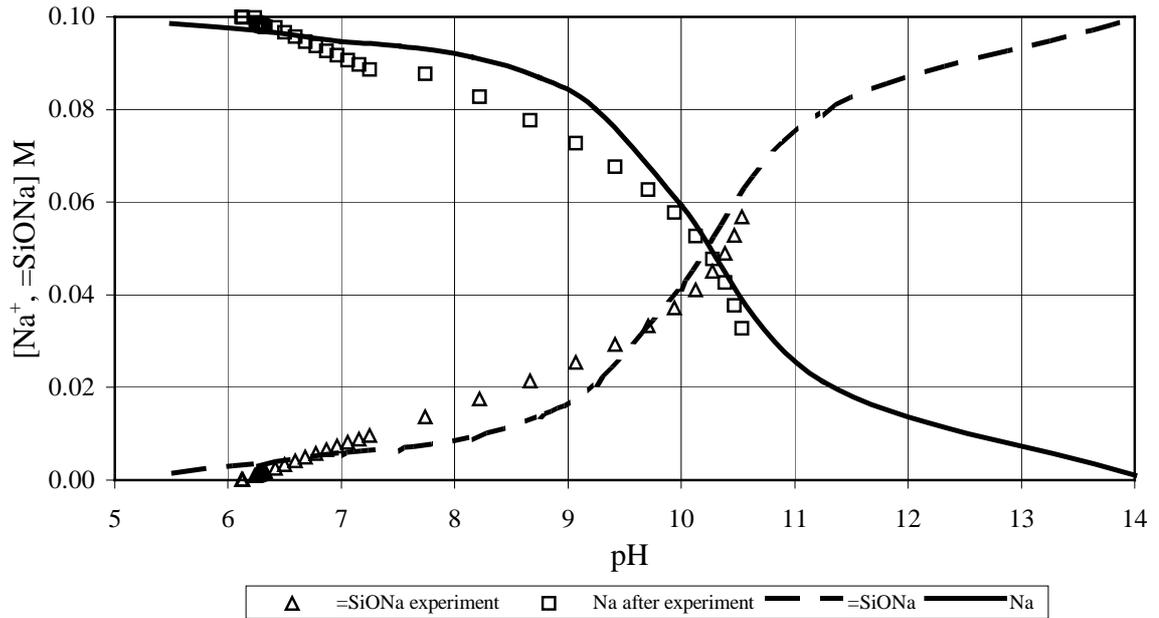


Figure 6.4.1 SOLGASWATER[®] simulations using the equilibrium constant for =SiONa as determined by Allen *et al.* (1971) compared with experimental datapoints.

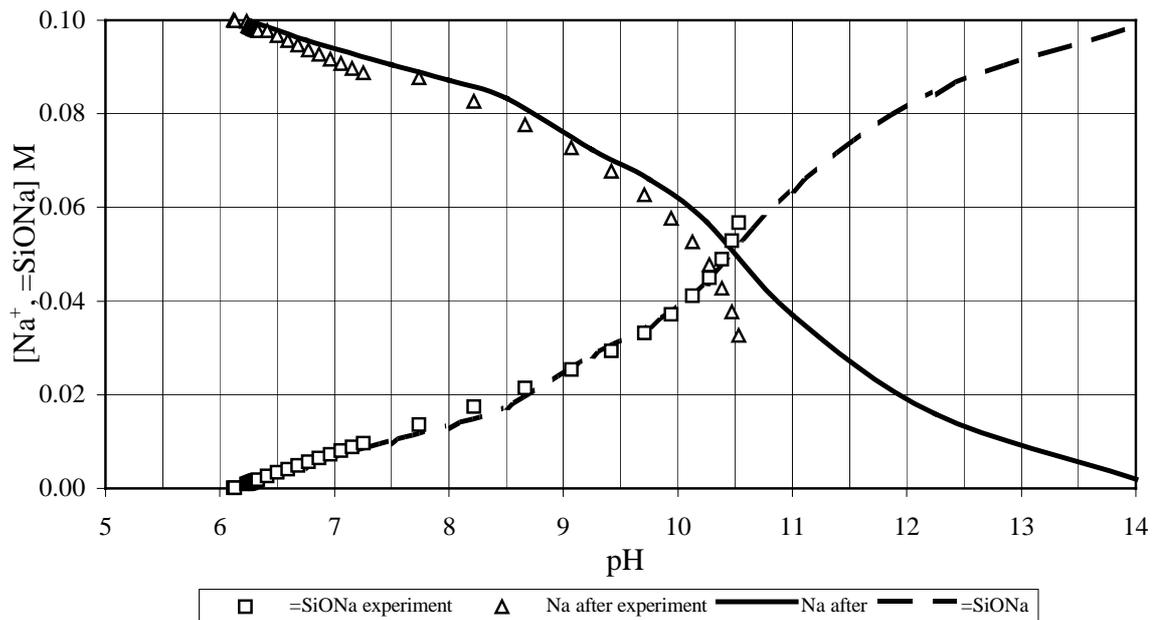


Figure 6.4.2 SOLGASWATER[®] simulations using the equilibrium constant for =SiONa as determined in this work, Section 6.3, compared with experimental datapoints.

Conclusions =SiO⁻-Na⁺ system

1. Aldrich's 28,863-2 silica gel is comparable with other weakly acidic ion exchangers.
2. The capacity of the gel as used in the experiments is ≈ 100 mM. This equals 1.5 OH/nm².
3. The adsorption of Na⁺ ions on the silica gel can be described using Allen's *et al.* (1971) approach giving: $\bar{u}=0,46$, $pK_{I,0}=6.4$, $pK_{II,0}=9.6$

THE =SIOH-CA²⁺-NA⁺ SYSTEM

The ion exchange of Ca²⁺ ions on Aldrich's 28,863-2 gel

Experimental procedure

The ion exchange of Ca²⁺ ions on silica gel has been investigated by titration of the gel as described in Section 6.1.

Apart from Na⁺, OH⁻ or H⁺ ions, Ca²⁺ ions in different concentrations and having different associated ions were added to the suspension. The ionic strength of the solution was adjusted to 0.1N by addition of NaCl.

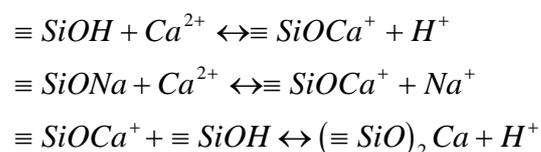
The ratio between the volume, V, and the amount of gel, m, was V/m = 0.01 l/g. All chemicals were of the highest chemical purity grade available. The water used was deionised and distilled.

Ion exchange is studied in the range from 0.02 meq H⁺/g gel to 0.47 meq OH⁻/g gel, *i.e.* in a pH-range from 5 to 9.5, if the initial pH is considered to be that pH value at which the gel is in equilibrium with a certain amount of H⁺ or OH⁻ ions added. Using Figure 6.1.2, it can be read that a pH of 5 equals to an addition of 0.02 meq H⁺/g gel and that a pH of 9.5 equals an addition of 0.47 meq OH⁻/g gel. In this pH range the amount of Ca(OH)₂ present is supposed negligible.

Experiments have been carried out at initial Ca²⁺ ion concentrations of 2.5 mM, 20 mM and 33 mM. In all but one case the associated ion was Cl⁻. In one series NO₃⁻ is used as the associated ion to study the possible difference in the ion exchange of Ca²⁺ ions. One series with Cl⁻ as the associated ion has been carried out at 37°C.

Experiments were planned in the concentration range 0...33 mM using a computer program (code name FPLAN) modified by Ahlbeck (1996). This program distributes the variables regularly in the parameter space. Two selected experimental variables, *i.e.* pH and ion concentration were varied across each other.

After 24h reaction time, when equilibrium was assumed to be reached, the samples were stirred and the pH measured. Part of the Ca²⁺ is supposed to exchange H⁺ ions of the silica gel and another part will replace Na⁺ ions according to Iler (1975):



Therefore the difference in OH⁻ concentration could not be used to calculate the adsorbed amount of Ca²⁺ ions. The Ca²⁺ concentration after reaction is determined separately by EDTA titration of the decanted solution.

Data analysis was carried out with a linear regression method using backwards elimination with computer programs (code names REGMAT and MULTREG) (Ahlbeck 1996).

Experimental results of adsorption of CaCl₂ on the silica gel at 20°C

Experimental results are summarised and shown in Tables 7.1.1 and 7.1.2 and Figures 7.1.1...7.1.3

Table 7.1.1. Results of the adsorption of Ca²⁺ ions on the silica gel: Initial Ca²⁺ concentrations of 2.5 mM, 20 mM and 33 mM respectively.

No	Ca ²⁺ _{initial} mM	pH _{initial}	meq OH ⁻ /g*	pH _{after}	Ca ²⁺ _{after} mM
1	2.5	5	-0.02	3.62	2.5
2	2.5	5.5	0	5.71	2.5
3	2.5	6	0.01	6.01	2.5
4	2.5	7	0.05	6.85	2.5
5	2.5	7.5	0.1	7.56	2.5
6	2.5	8	0.15	7.92	1.8
7	2.5	8.5	0.23	8.45	0.5
8	2.5	8.75	0.3	8.86	0.8
9	2.5	9	0.35	9.12	0.3
10	2.5	9.5	0.47	6.64	0.5
11	20	5	-0.02	3.99	20
12	20	5.5	0	6.06	20
13	20	6	0.01	6.32	19.75
14	20	7	0.05	7.03	19.5
15	20	7.5	0.1	7.51	17.5

* Negative values represent addition of H⁺ ions.

Table 7.1.1. continued

No	Ca ²⁺ _{initial} mM	pH _{initial}	meq OH ⁻ /g*	pH _{after}	Ca ²⁺ _{after} mM
16	20	8	0.15	7.83	15
17	20	8.5	0.23	8.22	12.5
18	20	8.75	0.3	8.53	9.5
19	20	9	0.35	8.72	6.75
20	20	9.5	0.47	9.05	4.5
21	33	5	-0.02	4.14	33
22	33	5.5	0	6.09	33
23	33	6	0.01	6.28	33
24	33	7	0.05	6.92	33
25	33	7.5	0.1	7.33	30.25
26	33	8	0.15	7.62	28
27	33	8.5	0.23	7.99	24.25
28	33	8.75	0.3	8.27	21
29	33	9	0.35	8.52	17.75
30	33	9.5	0.47	8.75	14

* Negative values represent addition of H⁺ ions.

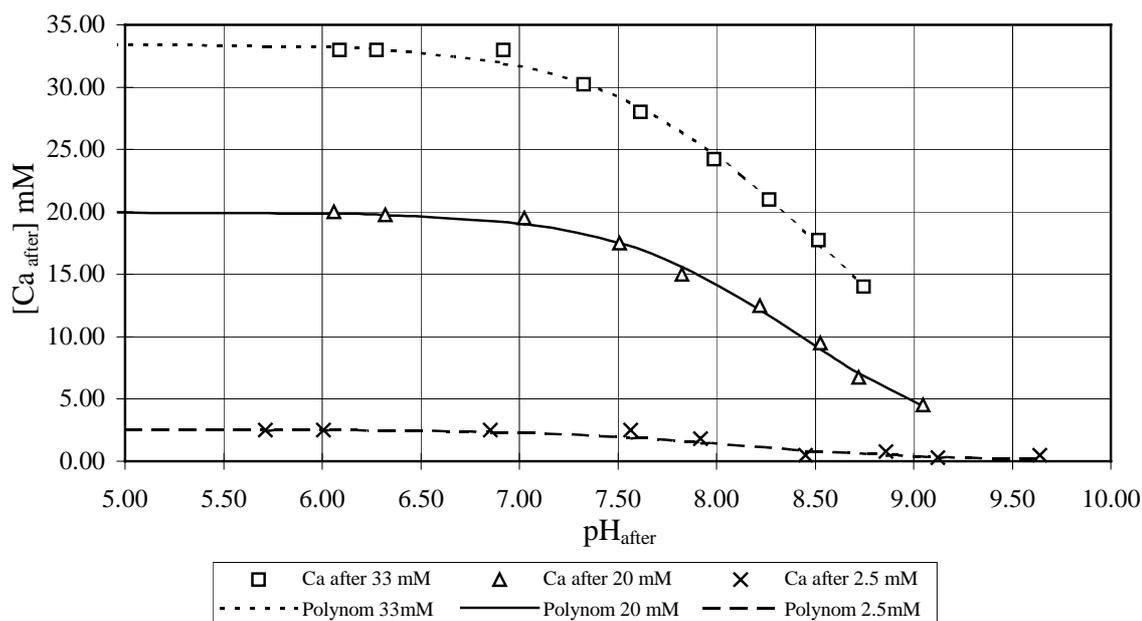


Figure 7.1.1. Measured concentration of Ca²⁺ ions, Ca_{after}, as a function of pH_{after}. The drawn lines represent a calculated sigmoidal using a least sum of squares curve fitting procedure.

Figure 7.1.2 and Table 7.1.2. show the experimental results from the experiments carried out following the experimental plan as described above. The drawn lines in Figure 7.1.2 represent the model derived by the linear regression model described above.

Linear regression showed that the experiments can be described using the polynomial:

$$Ca_{after}^{2+} = -0.359638 + 1.07537 * Ca_{initial}^{2+} - 0.117819 * 10^{-3} Ca_{initial}^{2+} \exp pH_{after} \quad (22)$$

$$R^2 = 0.9959$$

Figure 7.1.3. gives an indication of the validity of the used model.

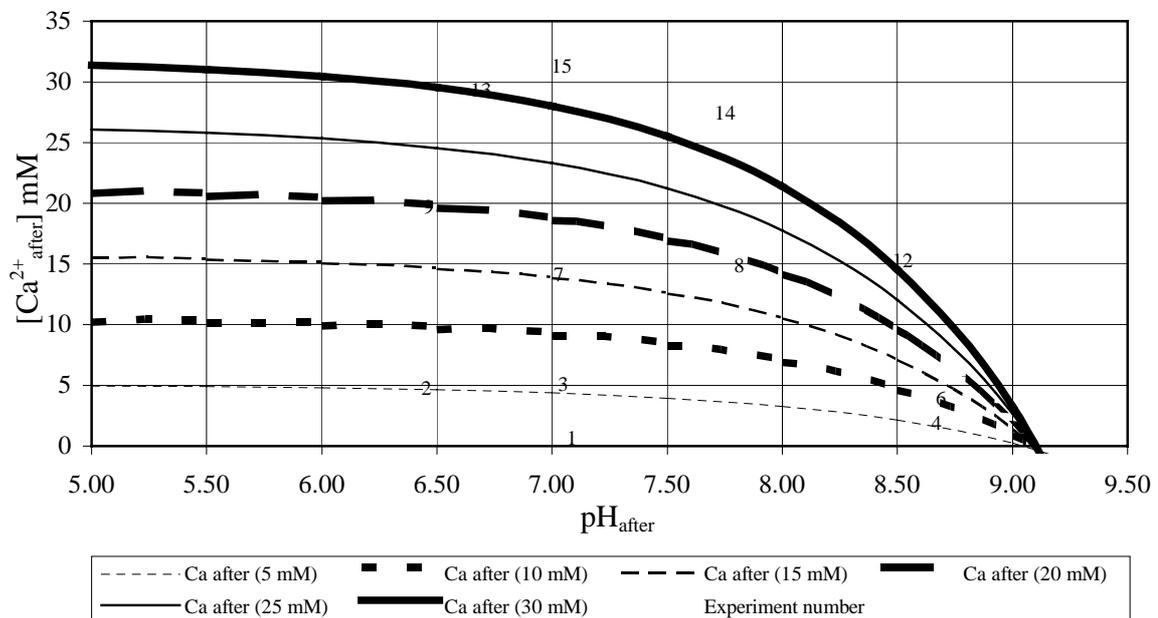


Figure 7.1.2. Experimental results and model lines as derived with the linear regression method described above. Ca_{after}^{2+} is plotted as a function of pH_{after} .

The figures shown above show that Ca^{2+} ions become adsorbed at a $pH > 7$. This is in good agreement with what other researchers have found. Iler (1975) stated that ions become adsorbed at some pH values below the value where metal hydroxides are formed. Ahrlund *et al.* (1960) report adsorption of Ca^{2+} ions in the pH range 6.5...9, which is in excellent agreement with the results found here.

Table 7.1.2. Results of the adsorption of Ca^{2+} ions on the silica gel at different initial concentrations and pH values as planned in the experimental planning procedure.

No	Ca^{2+} initial mM	pH _{initial}	meq OH^- /g*	pH _{after}	Ca^{2+} after mM
1	0	7	0.05	7.10	0.2
2	5	6	0.01	6.45	4.7
3	5	8	0.15	7.05	5.0
4	10	9	0.35	8.66	1.9
5	10	5	-0.02	4.08	10.5
6	15	9	0.35	8.69	3.9
7	15	7	0.05	7.02	14.0
8	20	8	0.15	7.79	14.8
9	20	6	0.01	6.47	19.7
10	20	5	-0.02	4.15	20.5
11	25	5	-0.02	4.17	24.9
12	30	9	0.35	8.52	15.1
13	30	6	0.01	6.69	29.3
14	33	8	0.15	7.74	27.3
15	33	7	0.05	7.04	31.2

* Negative values represent addition of H^+ ions.

Influence of the associated ion on the adsorption on Ca^{2+} ions on the silica gel

Figure 7.1.4. and Table 7.1.3 show that there is a small difference between the adsorption if different associated anions are present. Probably the presence of Cl^- ions reduces the amount of adsorbed Ca^{2+} ions slightly, due to metal-solution-anion interactions (Dugger *et al.* 1964). These interactions are more common for Cl^- ions than for NO_3^- ions.

Table 7.1.3. Adsorption of 20 mM Ca^{2+} ions on the silica gel: The associated ion is NO_3^- .

No	Ca^{2+} initial mM	pH _{initial}	meq OH^- /g*	pH _{after}	Ca^{2+} after mM
1	20	5	-0.02	3.92	20
2	20	6	0.01	6.28	18.75
3	20	7	0.05	6.91	18.25
4	20	8	0.15	7.77	14.75
5	20	9	0.35	8.67	6.50

* Negative values represent addition of H^+ ions.

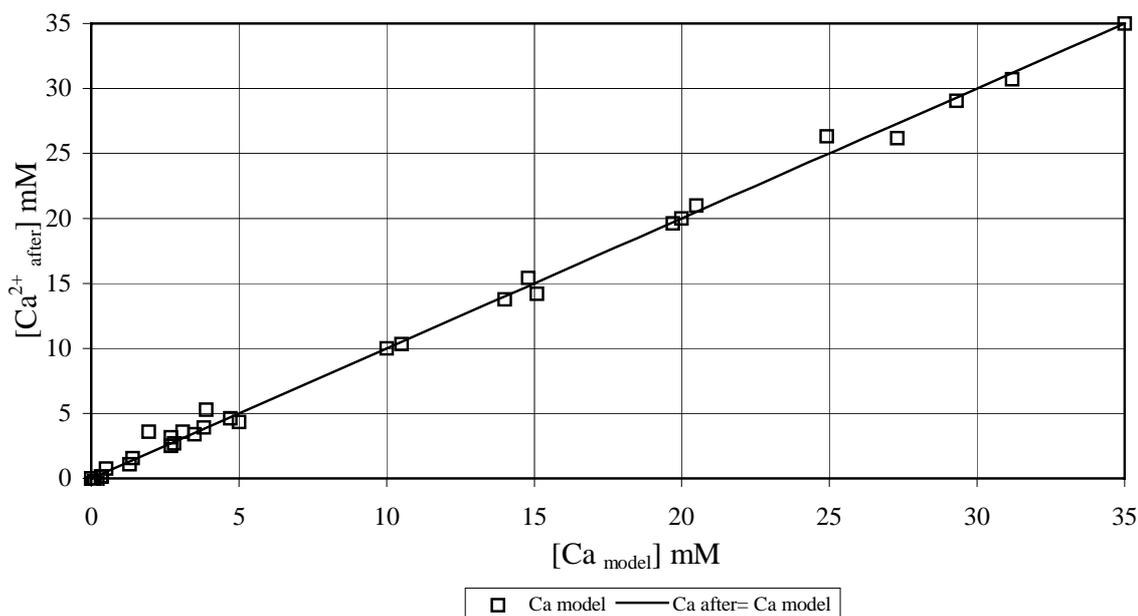


Figure 7.1.3. Measured Ca^{2+} concentration, $\text{Ca}^{2+}_{\text{after}}$, as a function of the calculated concentration of Ca^{2+} ions after adsorption, $\text{Ca}^{2+}_{\text{model}}$.

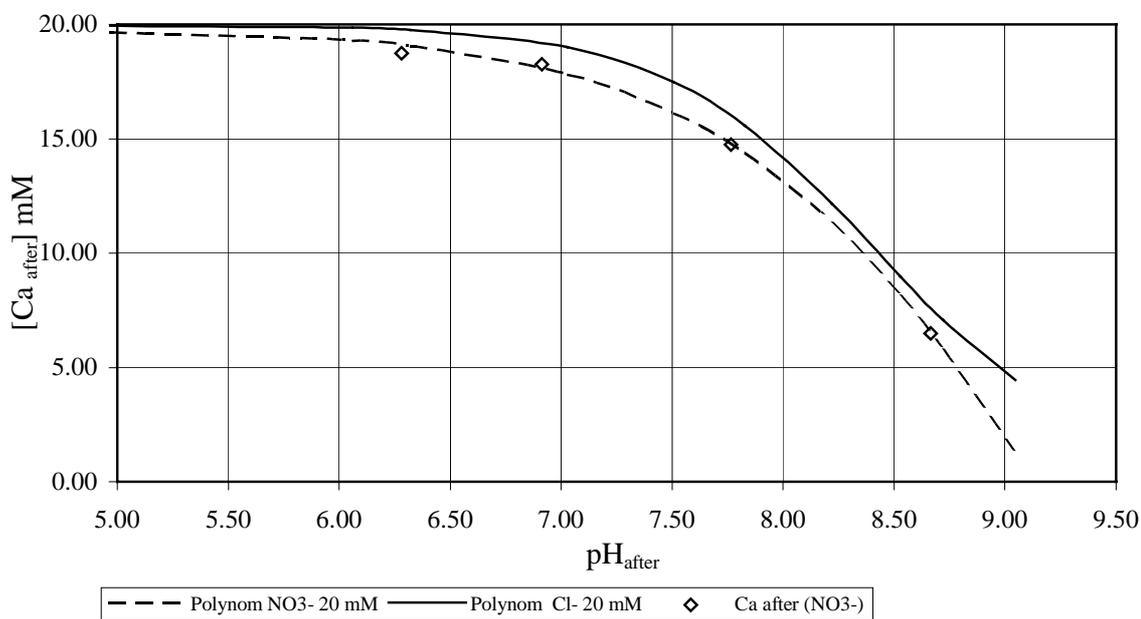


Figure 7.1.4. Comparison of different associated anions in adsorption of 20 mM Ca^{2+} ions on the silica gel. $\text{Ca}^{2+}_{\text{after}}$ is plotted as a function of pH_{after} .

The influence of temperature on the adsorption of Ca^{2+} ions on the silica gel

Figure 7.1.5. and Table 7.1.4. show the temperature dependency of the adsorption of Ca^{2+} ions. It shows that at a higher temperature more ions become adsorbed. Probably

a slightly higher temperature causes greater mobility among the Ca^{2+} ions and thus a greater chance to reach the surface and form silica complexes successfully.

Table 7.1.4. Adsorption of 20 mM Ca^{2+} ions on the silica gel at 37°C.

No	Ca^{2+} initial mM	pH _{initial}	meq OH^- /g	pH _{after}	Ca^{2+} after mM
1	20	7	0.05	7.04	19.25
2	20	8	0.15	7.66	16
3	20	9	0.35	8.51	6.5

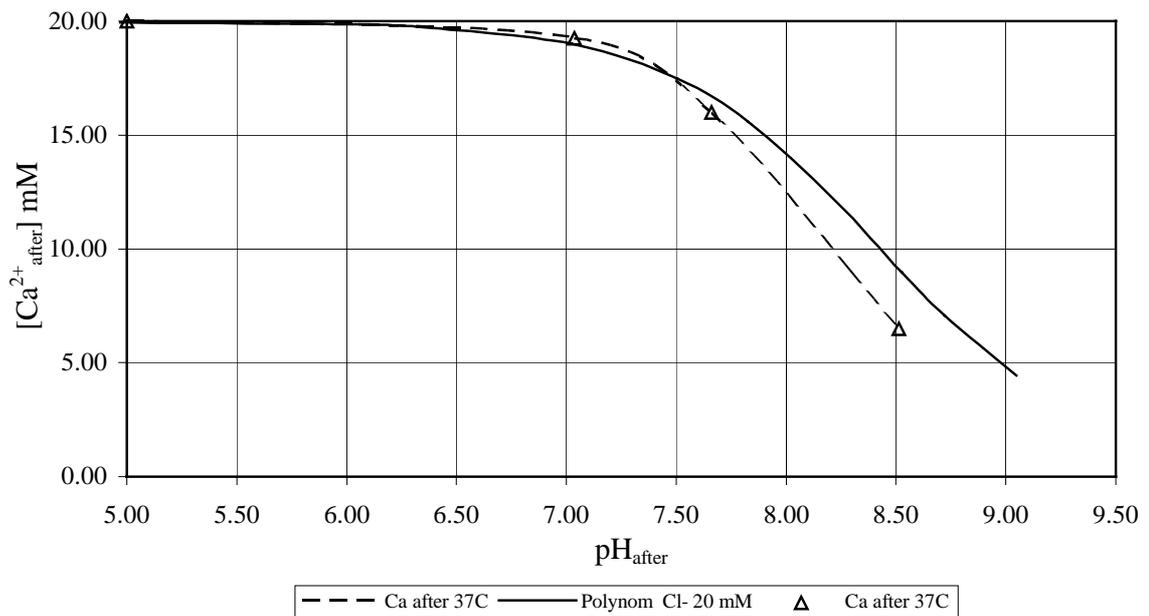


Figure 7.1.5. Comparison of the adsorption of Ca^{2+} ions on the silica gel on 25°C and 37°C respectively

Determination of the type of complex involved in the adsorption of Ca^{2+} ions

The method as derived by Ahrlund *et al.* (1960) can be used also in the ion exchange of Ca^{2+} . As described earlier in Section 6.3 the equation for the equilibrium constant for non-diluted solutions can be used in order to estimate the number of hydroxyl groups, n , involved in the complexation and the apparent equilibrium constant, K , for the

$(=\text{SiO})_n\text{Ca}^{(2-n)+}$ complex formed:

$$K = \frac{[\text{H}^+]^n \{(\equiv \text{SiO})_n \text{M}\} f_{\text{H}^+}^n \cdot f_{\{(\equiv \text{SiO})_n \text{M}\}}}{[\text{M}^{z+}] \{(\equiv \text{SiOH})\}^n f_{\text{M}^{z+}} \cdot f_{\{(\equiv \text{SiOH})\}}^n} \quad (8a)$$

Defining D as:

$$D = \frac{\{(\equiv SiO)_n M\}}{[M^{z+}]} \quad (14)$$

and assuming that the activity coefficient equals 1, gives

$$K = \frac{[H^+]^n}{\{\equiv SiOH\}^n} \cdot D \quad (15a)$$

thus

$$\log D = -n \log [H^+] + Cst \quad (16)$$

The number of hydroxyl groups involved in the ion exchange, n, follows from a log D vs. pH plot, giving a straight line with slope n. The apparent equilibrium constant, log K, follows from the intercept.

Figure 7.2.1. shows the log D curves as derived from the model lines as shown in Figure 7.1.2, and described by Equation 22 (lines) and the log D for the adsorption of 2.5 mM, 20 mM and 33 mM Ca²⁺ ions on the silica gel (points), at 20°C.

Above a pH value of 6.5, where adsorption becomes relevant, the slope of the log D-curve for the experimental values (points) is one or slightly under one *i.e.* 0.85..1. This means that most probably a complex like =SiOCa⁺ is formed. This is in agreement with Iler (1975) who stated that only in a later stadium, when enough hydroxyl groups are available a second H⁺ ion will be exchanged with the Ca²⁺ ion leading to a complex of the type (=SiO)₂Ca. Also Ahrland *et al.* (1960) found a complex with one hydroxyl group.

Above pH=8.5 the log D curve calculated from the model equation (22) deviates from the experimental values, *i.e.* in reality adsorption is slightly lower than calculated.

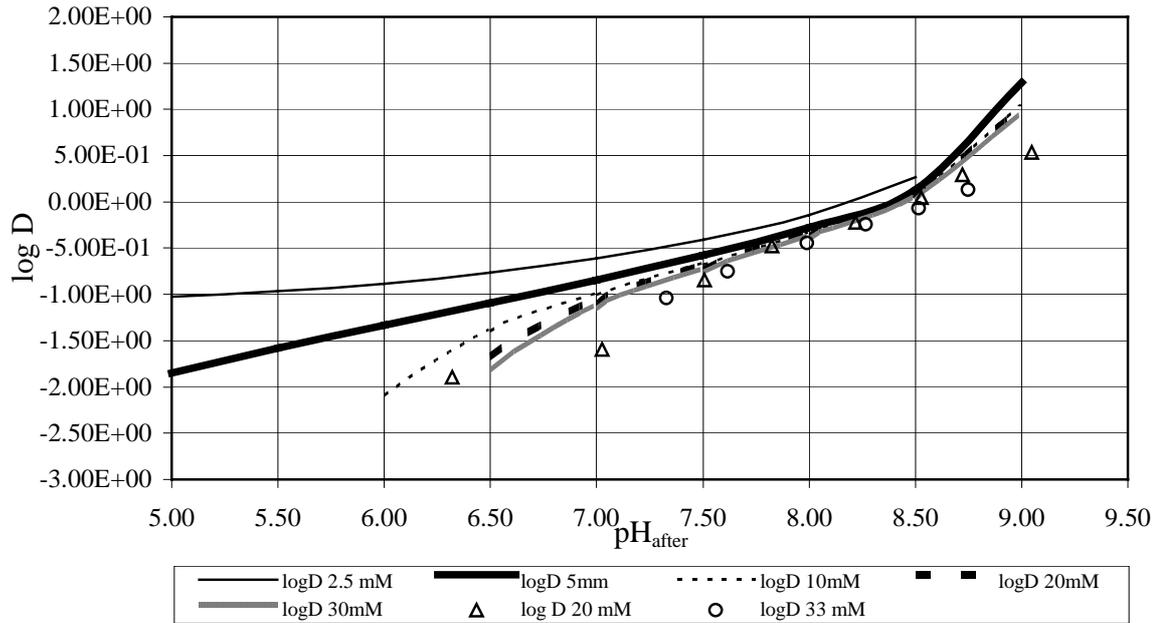


Figure 7.2.1. log D as derived from Equation 22 at different initial Ca^{2+} concentrations as a function of pH_{after} (lines) and the log D values as calculated from the experimental results.

Figure 7.2.2 shows the log D curve for the adsorption of 20 mM Ca^{2+} ions with associated ions NO_3^- compared with Cl^- . Probably even if NO_3^- gives a higher conversion the Ca^{2+} ions are not able to form complexes with the stoichiometric amount of hydroxyl groups, due to steric hindrance.

Figure 7.2.3 shows the log D curve for the adsorption of 20 mM Ca^{2+} ions at an elevated temperature, 37°C. The higher slope for the reaction at elevated temperature can be expected since the higher mobility of the Ca^{2+} ions makes stoichiometric reaction with the hydroxyl groups at the surface more probable.

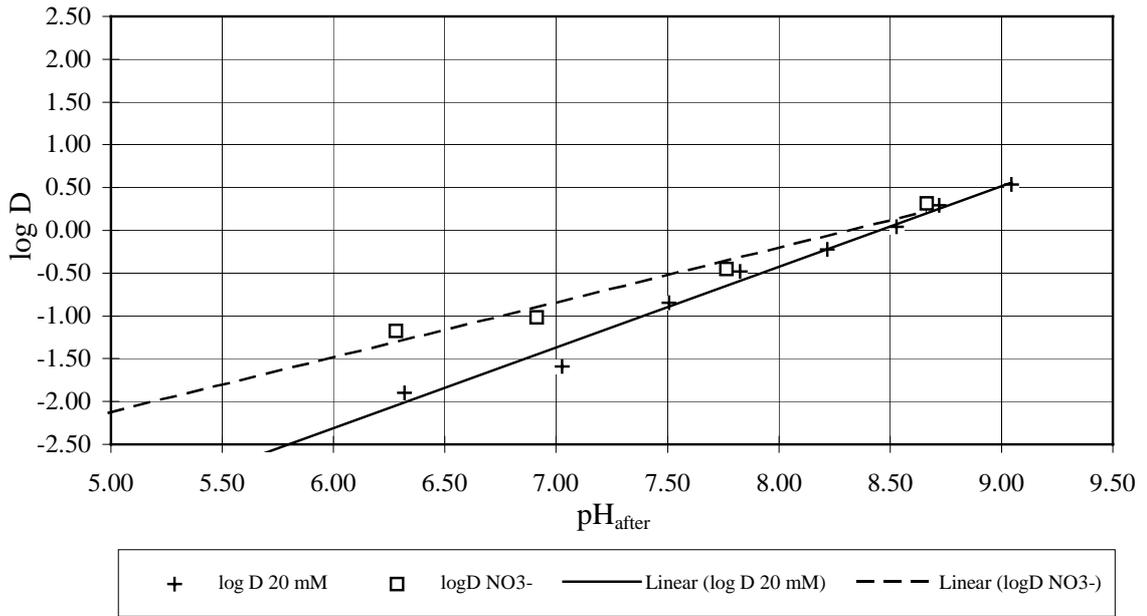


Figure 7.2.2. Log D as calculated for adsorption of 20 mM Ca²⁺ ions with different associated anions

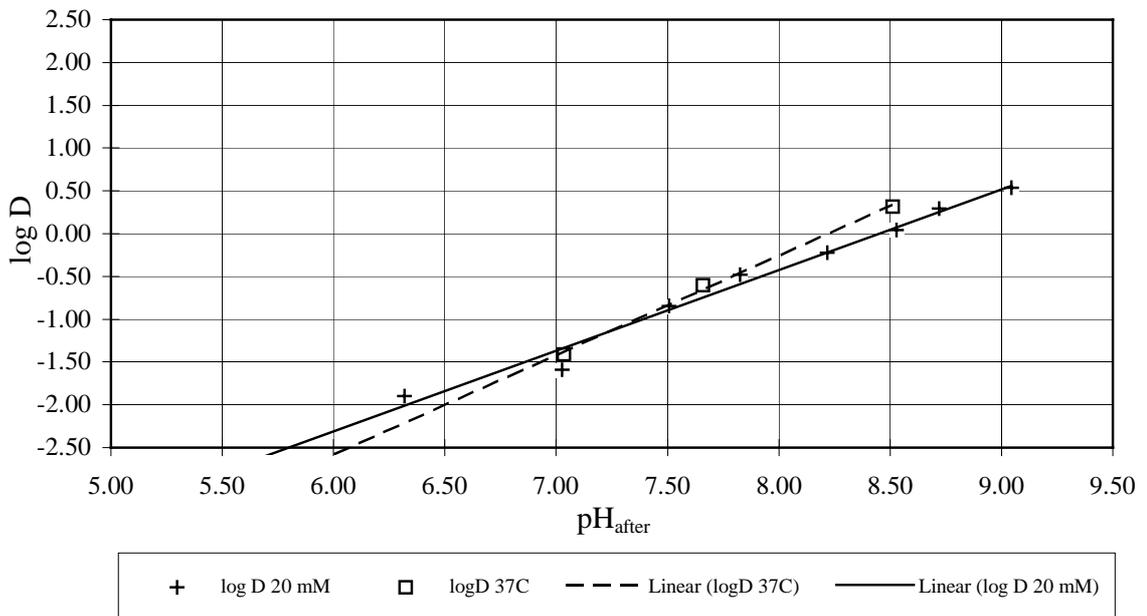


Figure 7.2.3. Log D as calculated for adsorption of 20 mM Ca²⁺ ions at 20°C and 37°C

Determination of the apparent equilibrium constant

From Figure 7.2.1 a mean equilibrium constant could be calculated using Equation 16 by using $n=1$ and assuming that the activity of the solution equals the concentration:

$$\log D = \log(K \cdot [SiOH]) + pH \quad (23)$$

However the equilibrium constant can also directly be calculated from the modelled values and experimental values for the adsorption of 2.5 mM, 20 mM and 33 mM.

The results of these calculations are shown in Figure 7.3.1.

Figure 7.3.1. also shows that the equilibrium constant is not constant in the pH range studied. For the adsorption of 20 mM Ca^{2+} ions, the pK value for a $=SiOCa^+$ complex ranges from 7.1 to 7.4. Schindler (1994) gives a rough estimation of the intrinsic equilibrium constant of $-\log K_{=SiOCa^+} \approx 8.6$.

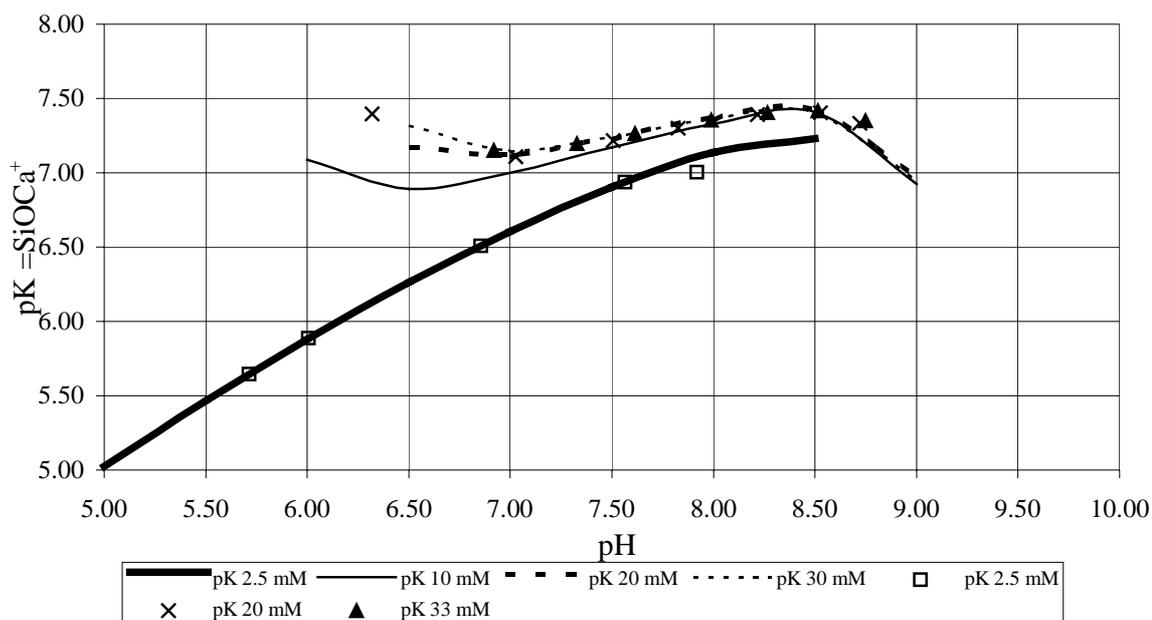


Figure 7.3.1. Calculated $pK_{=SiOCa^+}$ for the adsorption of Ca^{2+} ions on the silica gel at 20°C as a function of pH

The apparent equilibrium constant can also be used in the model for ion exchange reactions on silica as derived by Allen *et al.* (1971). Using Allen's *et al.* (1971) approach as described in Section 6.3, instead of one type of hydroxyl group more types have to be taken into account. It is also assumed that the difference between the free energies of H^+ and Ca^{2+} ions at the surface increases linearly with the quantity x defined similar to Equation 17:

$$\log x = \log \frac{[\equiv SiO_I Ca^+] + [\equiv SiO_{II} Ca^+]}{[\equiv SiO_I H]_0 + [\equiv SiO_{II} H]_0} \quad (24)$$

Where the indices I and II indicate type I and type II hydroxyl groups, respectively. Then the free-energy change in the exchange process may be described by:

$$\Delta G = -RT \ln K_0 / Q + Ax \quad (18)$$

in which Q is a concentration quotient and A is a constant of proportionality.

Using two types of hydroxyl groups, from which one reacts more rapidly three equations can be written similar to those derived by Allen *et al.* (1971), within which x_i describes the fraction of groups on which protons have been replaced by Ca^{2+} ions and ϕ describes the fraction of type I sites.

$$\log \frac{x_I}{1 - x_I} + \frac{A_I x_I}{2.303RT} = pH + \log K_{I,0} + \log[Ca^{2+}] \quad (25)$$

$$\log \frac{x_{II}}{1 - x_{II}} + \frac{A_{II} x_{II}}{2.303RT} = pH + \log K_{II,0} + \log[Ca^{2+}] \quad (26)$$

$$x = x_I \phi + x_{II} (1 - \phi) \quad (21)$$

Figure 7.3.2. shows $\log x$ as a function of pH for the adsorption of 20 mM Ca^{2+} ions as calculated. For this gel ϕ is assumed to be 0.46 as determined in Section 6.3. of this thesis. $pK_{I,0}=7.1$ and $pK_{II,0}=7.4$. These pK-values are taken from Figure 7.3.1. They represent those values in a pH range around 6.9 and around 8.4, where the pK remains more or less constant, indicating formation of surface complexes with two types of hydroxyl groups.

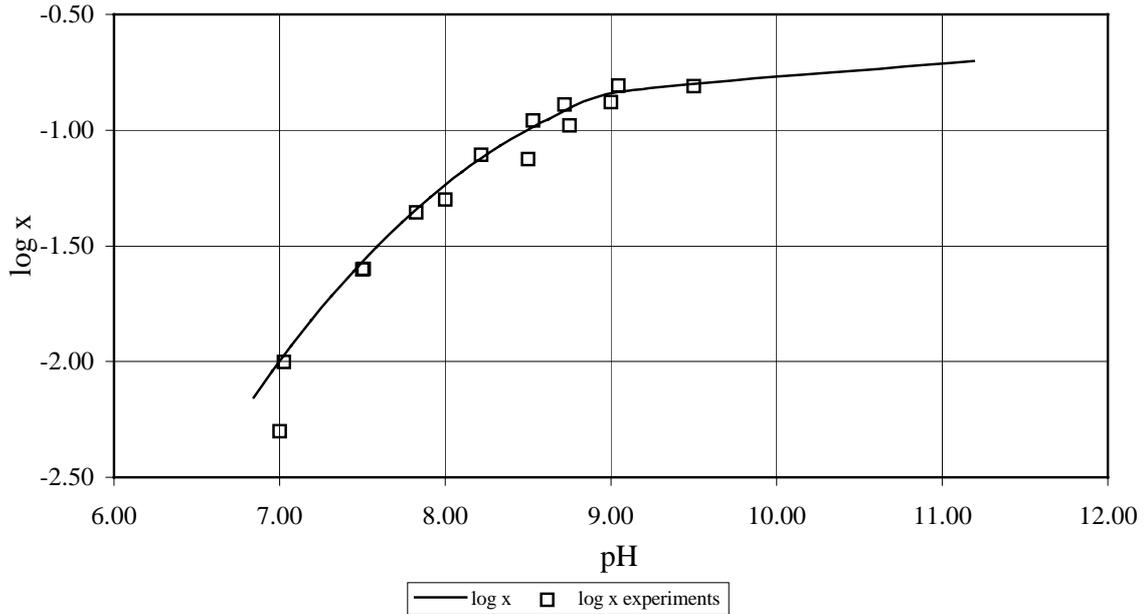


Figure 7.3.2. Log x for adsorption of 20 mM Ca²⁺ ions as a function of pH the drawn line represents the curve as calculated with Allen's method having $\hat{u} = 0.46$ and a pK_{-SiOCa^+} of 7.1 and 7.4, respectively

The mean deviation in log x is 0.08. Figure 7.3.2. shows the good agreement between measurements and model. Thus the approach for adsorption of Na⁺ ions on hydroxyl groups as defined by Allen *et al.* (1971) seems to be useful for the adsorption of Ca²⁺ ions on silica gel in presence of Na⁺ ions as well.

Comparison of SOLGASWATER simulations with experimental results

It is noted that the constants as derived in the previous paragraph are only apparent constants and should be recalculated to intrinsic constants before they can be used in the SOLGASWATER^S input files. For this purpose the Stefan-Boltzmann equation (Section 4.1) can be used:

$$\beta_n = \exp\left(\frac{(z-n)F\phi}{RT}\right) \frac{[H^+]^n \{(\equiv SiO)_n M^{(z-n)}\}}{\{\equiv SiOH\}^n [M^{z+}]} \quad \text{where } n \text{ is } 1 \dots z \quad (2)$$

However, if it is assumed that the potential difference between complex and bulk solution, \hat{u} , can be neglected the apparent equilibrium constant can be used as an intrinsic constant and used in the SOLGASWATER^S simulations.

The simulation was carried out using the equilibrium constants for the $=\text{SiONa}$ complex as derived in Section 6.3 of this thesis, *i.e.* $\dot{\nu}=0.46$, $\text{p}K_{\text{I},0,=\text{SiONa}}=6.4$ and $\text{p}K_{\text{II},0,=\text{SiONa}}=9.6$. The constants for the $=\text{SiOCa}^+$ complexes were as derived in the former paragraph, *i.e.* $\text{p}K_{\text{I},0,=\text{SiOCa}^+}=7.1$ and $\text{p}K_{\text{II},0,=\text{SiOCa}^+}=7.4$. figure 7.4.1 shows the results from the simulation for adsorption of 20 mM Ca^{2+} ions.

It is shown that the simulation describes the experiments very well.

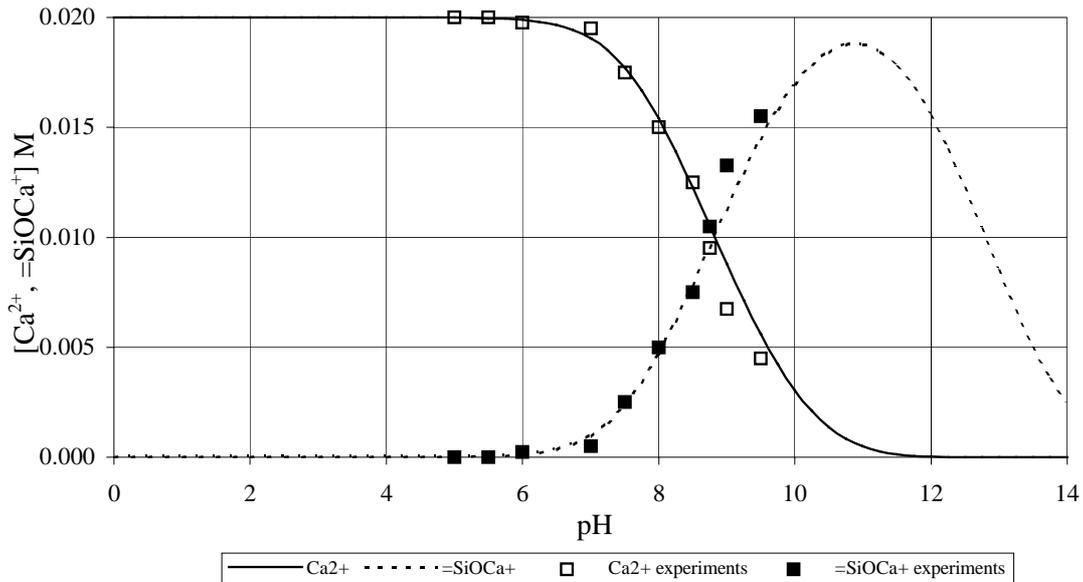


Figure 7.4.1 Simulation of the complexation of 20 mM Ca^{2+} ions on the silica gel using two types of reactive groups, *i.e.* $\dot{\nu}=0.46$,

Conclusions $=\text{SiO}-\text{Ca}^{2+}-\text{Na}^+$ system

1. Adsorption of Ca^{2+} ions on the silica gel leads to formation of complexes of the type $=\text{SiOCa}^+$.
2. The adsorption can be described assuming that the surface has two different active groups with differing reactivity.
3. The two apparent equilibrium constants, $\text{p}K$, for formation of $=\text{SiOCa}^+$ complexes are 7.1 and 7.4, respectively.
4. The model to describe the complexation as derived by Allen *et al.* (1971) can be used to describe the complexation of Ca^{2+} ions on the silica gel.
5. SOLGASWATER^S simulations show good agreement with the experiments in the pH range considered, *i.e.* 5..9.5.

THE =SIOH-MG²⁺-NA⁺ SYSTEM

The ion exchange of Mg²⁺ ions on Aldrich's 28,863-2 gel

Experimental procedure

The ion exchange of Mg²⁺ ions on silica gel has been investigated by titration of the gel as described in Section 7.1.

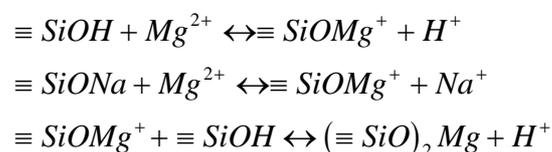
Since Ca²⁺ and Mg²⁺ are much alike, the ion exchange is supposed to be comparable. Therefore the same experimental procedure has been followed for the complexation of Mg²⁺ ions on the silica gel with the difference that 1.5 mM Mg²⁺ ions are adsorbed instead of 2.5 mM. This is because adsorption of 1.5 mM Mg²⁺ ions might be of interest since this concentration is present in the Simulated Body Fluid as used by Kokubo *et al.* (1992). Thus the ion exchange is studied ranging from 0.02 meq H⁺/g gel to 0.47 meq OH⁻/g gel, *i.e.* in a pH range 5 to 9.5.

The ratio between the volume, V, and the amount of gel, m, was V/m = 0.01 l/g. All chemicals were of the highest chemical purity grade available. The water used was deionised and distilled.

Experiments have been carried out at initial Mg²⁺ concentrations of 1.5 mM, 20 mM and 33 mM. In all but one case the associated ion was Cl⁻, in one series the associated ion was NO₃⁻. Furthermore, one series was carried out at 37°C.

Experiments were planned in the concentration range 0..33 mM using a computer program (code name FPLAN) modified by Ahlbeck (1996).

After 24h reaction time equilibrium was supposed to be reached and part of the Mg²⁺ was supposed to exchange H⁺ ions of the silica gel in a similar way as Ca²⁺, *i.e.*:



The Mg²⁺ concentration after reaction is determined by EDTA titration of the decanted solution.

Data analysis was carried out with a linear regression method using backwards elimination with a computer program (code names REGMAT and MULTREG)(Ahlbeck 1996).

Experimental results of adsorption of $MgCl_2$ on the silica gel at 20°C

Experiments and experimental results are summarised and shown in Table 8.1.1 and 8.1.2 and Figures 8.1.1...8.1.3.

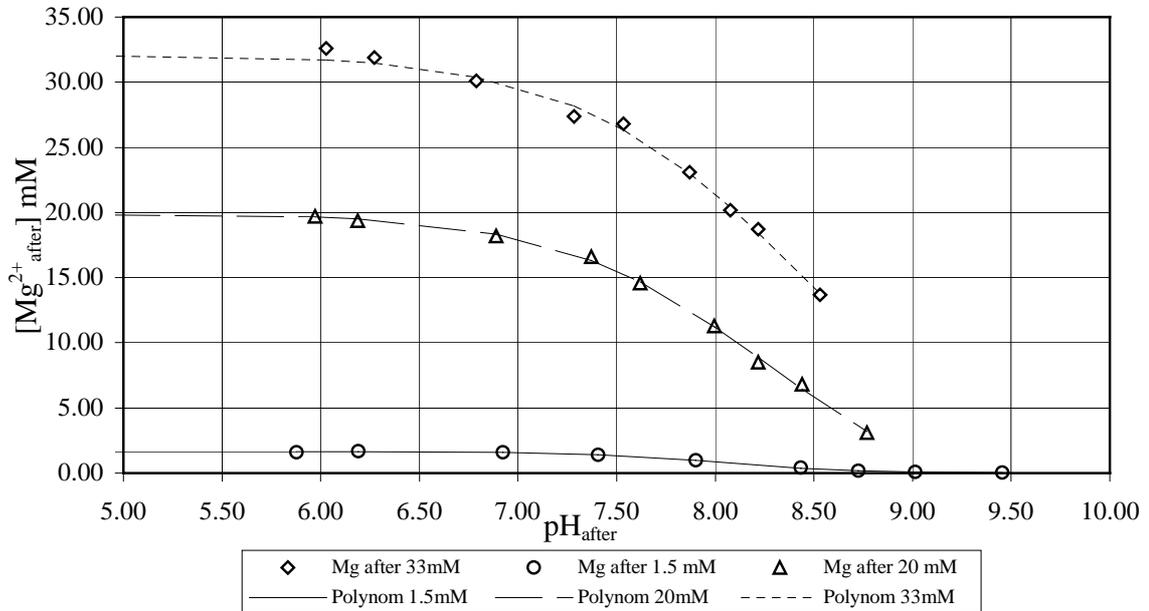


Figure 8.1.1. Measured concentration of Mg^{2+} ions, Mg_{after} , as a function of pH_{after} . The drawn lines represent a calculated sigmoidal using a least sum of squares curve fitting procedure.

Figure 8.1.2 and Table 8.1.2. show the experimental results from the experiments carried out following the experimental plan as described above. The drawn lines in Figure 8.1.2 represent the model derived by the linear regression model.

Linear regression showed that the experiments can be described using the polynomial:

$$Mg_{after}^{2+} = -0.123319 + 1.00968 * Mg_{initial}^{2+} - 0.117521 * 10^{-3} * Mg_{initial}^{2+} \exp pH_{after} \quad (27)$$

$$R^2 = 96.81$$

Figure 8.1.3. gives an indication of the validity of the used model.

Table 8.1.1. Results of the adsorption of Mg^{2+} ions on the silica gel: Initial Mg^{2+} concentrations of 1.5 mM, 20 mM and 33 mM, respectively.

No	Mg^{2+} initial mM	pH _{initial}	meq OH ⁻ /g [*]	pH _{after}	Mg^{2+} after mM ^{**}
1	1.5	5	-0.02	3.79	1.6
2	1.5	5.5	0	5.88	1.6
3	1.5	6	0.01	6.19	1.7
4	1.5	7	0.05	6.92	1.6
5	1.5	7.5	0.1	7.41	1.4
6	1.5	8	0.15	7.90	1
7	1.5	8.5	0.23	8.44	0.4
8	1.5	8.75	0.3	8.73	0.2
9	1.5	9	0.35	9.01	0.1
10	1.5	9.5	0.47	9.45	0.05
11	20	5	-0.02	4.01	20
12	20	5.5	0	5.97	19.7
13	20	6	0.01	6.19	19.4
14	20	7	0.05	6.89	18.2
15	20	7.5	0.1	7.37	16.6
16	20	8	0.15	7.62	14.6
17	20	8.5	0.23	7.99	11.3
18	20	8.75	0.3	8.22	8.5
19	20	9	0.35	8.44	6.8
20	20	9.5	0.47	8.78	3.1
21	33	5	-0.02	4.03	31.5
22	33	5.5	0	6.03	32.6
23	33	6	0.01	6.27	31.9
24	33	7	0.05	6.79	30.1
25	33	7.5	0.1	7.28	27.4
26	33	8	0.15	7.54	26.8
27	33	8.5	0.23	7.87	23.1
28	33	8.75	0.3	8.08	20.2
29	33	9	0.35	8.22	18.7
30	33	9.5	0.47	8.53	13.7

* Negative values represent addition of H^+ ions

** At pH values above 8.5 a white precipitate was seen in some samples, indicating the formation of $Mg(OH)_2$.

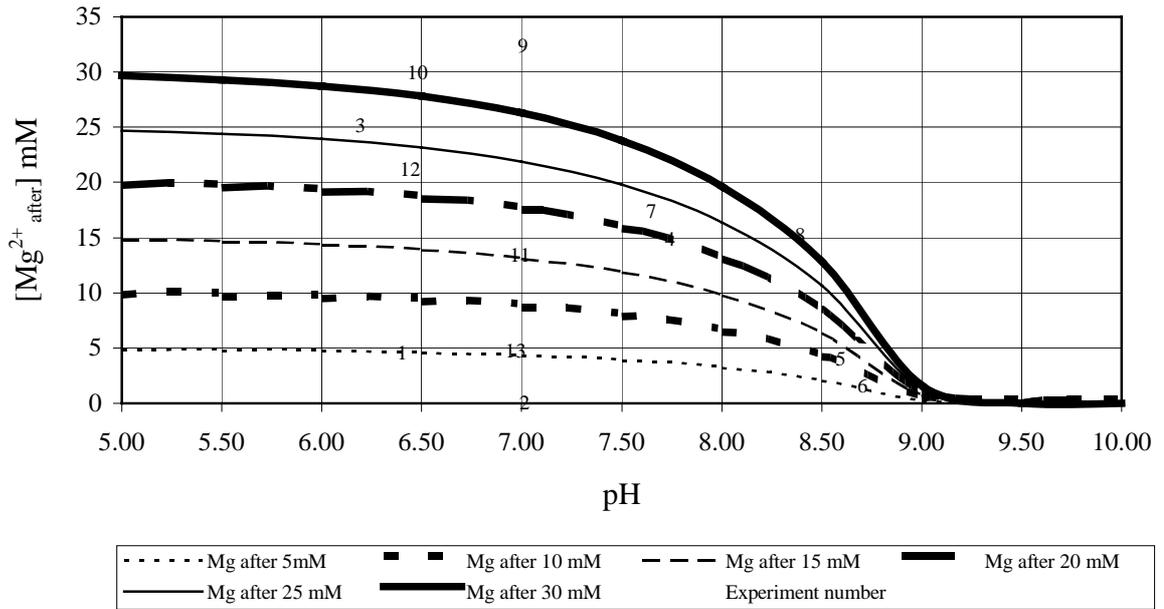


Figure 8.1.2. Experimental results and model lines as derived with the above described linear regression method. Mg^{2+}_{after} is plotted as a function of pH_{after} .

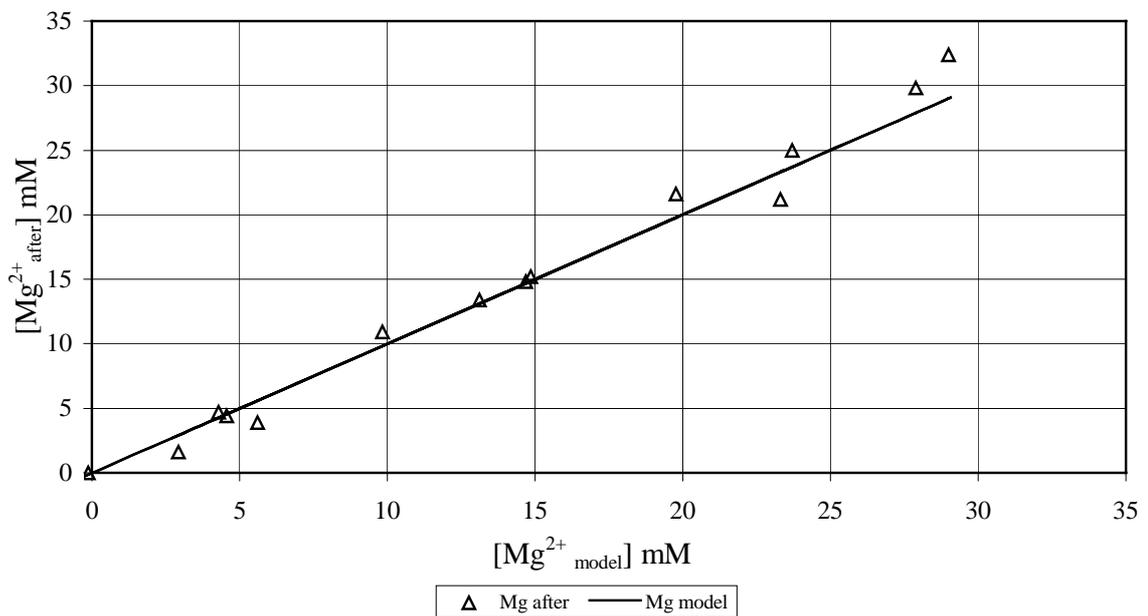


Figure 8.1.3. Measured Mg^{2+} concentration, Mg^{2+}_{after} , as a function of the calculated concentration of Mg^{2+} ions after adsorption, Mg^{2+}_{model} .

Table 8.1.2. Results of the adsorption of Mg^{2+} ions on the silica gel at different initial concentrations and pH values as planned.

No	Mg^{2+} initial mM	pH _{initial}	meq OH ⁻ /g [*]	pH _{after}	Mg^{2+} after mM ^{**}
1	0	7	0.01	6.41	4.4
2	5	6	0.05	7.06	0
3	5	8	-0.02	6.18	25.0
4	10	9	0.15	7.74	14.8
5	10	5	0.35	8.58	3.9
6	15	9	0.35	8.70	1.6
7	15	7	0.15	7.65	17.4
8	20	8	0.35	8.38	15.2
9	20	6	0.05	6.99	32.4
10	20	5	0.01	6.47	29.8
11	25	5	0.05	6.98	13.4
12	30	9	0.01	6.42	21.2
13	30	6	0.15	6.97	4.7
14	33	8	-0.02	4.82	21.6
15	33	7	-0.02	4.78	10.9

* Negative values represent addition of H⁺ ions.

** At pH values above 8.5 a white precipitate was seen in some samples, indicating the formation of Mg(OH)₂.

Influence of the associated ion on the adsorption on Mg^{2+} ions on the silica gel

Figure 8.1.4. and Table 8.1.3. show the results from adsorption of 20 mM Mg^{2+} with NO_3^- as the associated ion.

Whereas the adsorption of Ca^{2+} showed a slight difference in the adsorption when NO_3^- was present instead of Cl^- , this difference is not noted in case Mg^{2+} is adsorbed to the gel. Maybe Mg^{2+} shows less metal-solution-anion interactions than Ca^{2+} due to its smaller size and higher mobility.

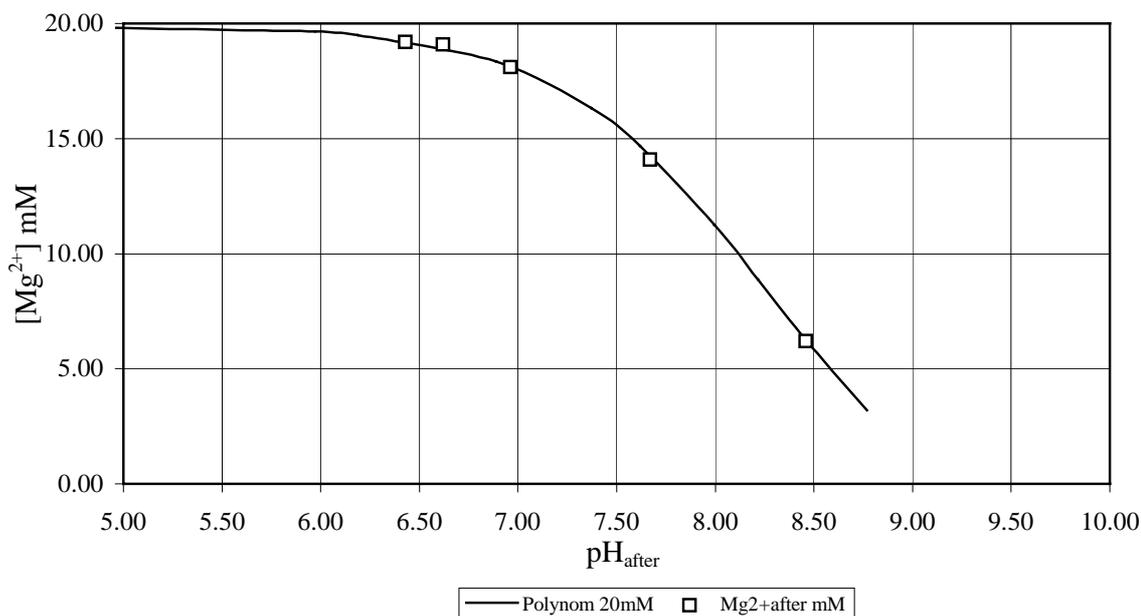


Figure 8.1.4. Comparison of different associated anions in adsorption of 20 mM Mg^{2+} ions on the silica gel. Mg^{2+} after is plotted as a function of pH_{after} .

Table 8.1.3. Adsorption of 20 mM Mg^{2+} ions on the silica gel: The associated ion is NO_3^- .

No	Mg^{2+} initial mM	$pH_{initial}$	meq OH^- /g*	pH_{after}	Mg^{2+} after mM
1	20	5	-0.02	6.43	19.2
2	20	6	0.01	6.62	19.1
3	20	7	0.05	6.96	18.1
4	20	8	0.15	7.67	14.1
5	20	9	0.35	8.46	6.2

* Negative values represent addition of H^+ ions

The influence of temperature on the adsorption of Mg^{2+} ions on the silica gel

Figure 8.1.5 shows the temperature dependency of the adsorption of Mg^{2+} ions. It shows that at a higher temperature more ions become adsorbed. However, the difference in adsorption behaviour is less profound than when Ca^{2+} ions are adsorbed. This might be due to the fact that Mg^{2+} already has a higher mobility at lower temperatures than Ca^{2+} ions or on experimental errors is unclear.

Table 8.1.4. Adsorption of 20 mM Mg²⁺ ions on the silica gel at 37°C.

No	Mg ²⁺ _{initial} mM	pH _{initial}	meq OH ⁻ /g*	pH _{after}	Mg ²⁺ _{after} mM
1	20	5	-0.2	6.39	20.4
2	20	6	0.01	6.57	19.9
3	20	7	0.05	6.94	19.0
4	20	8	0.15	7.64	15.1
5	20	9	0.35	8.38	6.2

* Negative values represent addition of H⁺ ions.

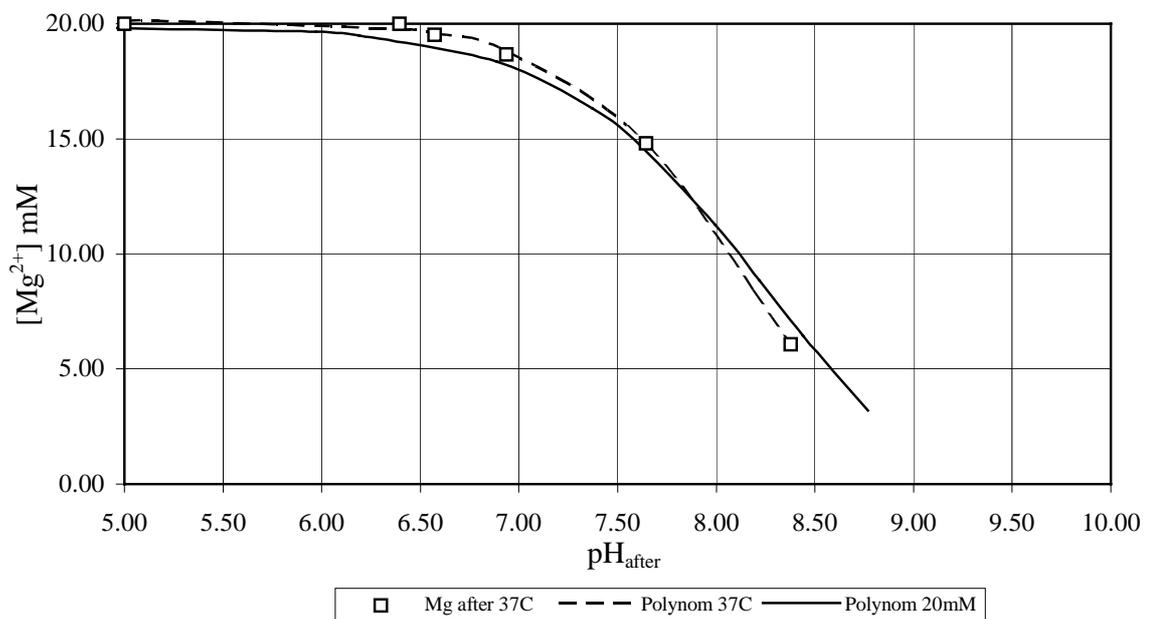


Figure 8.1.5. Comparison of the adsorption of Mg²⁺ ions on the silica gel on 20°C and 37°C respectively.

Determination of the type of complex involved in the adsorption of Mg^{2+} ions

The method as derived by Ahrlund *et al.* (1960) and applied for the adsorption of Ca^{2+} ions, as described in Section 7.2 of this thesis can also be used for the adsorption of Mg^{2+} ions.

Using Equations 14 and 16, the number of hydroxyl groups, n , can be estimated from a $\log D$ vs. pH plot giving a straight line with slope n .

$$D = \frac{\{(\equiv SiO)_n M\}}{[M^{z+}]} \quad (14)$$

$$\log D = -n \log[H^+] + Cst \quad (16)$$

Figure 8.2.1 shows the $\log D$ curve as derived from the model lines as shown in Figure 8.1.2 and described by Equation 27 (lines) and the $\log D$ for the adsorption of 1.5 mM, 20 mM and 33 mM Mg^{2+} ions on the silica gel (points) at 20°C.

Above a pH value of 6, where the adsorption becomes relevant the slope, n , as calculated from the experimental values varies between 0.75 and 1.3. This makes the formation of a $=SiOMg^+$ complex most probable. The formation of this type of complex already was expected since Ca^{2+} ions and Mg^{2+} ions are quite similar.

Since no substantial difference was found in adsorption of Mg^{2+} ions when NO_3^- was present instead of Cl^- ions, it is assumed that the same type of complex is formed with only one hydroxyl group as described above.

Figure 8.2.2 shows the $\log D$ curve for the adsorption of 20 mM Mg^{2+} ions at an elevated temperature, 37°C.

The slope, n , at 20°C was 0.86 whereas the slope at 37°C is slightly higher, *i.e.* 1.08. Probably the higher mobility of the ions makes it possible that a stoichiometric amount of hydroxyl groups become involved in the ion exchange reaction.

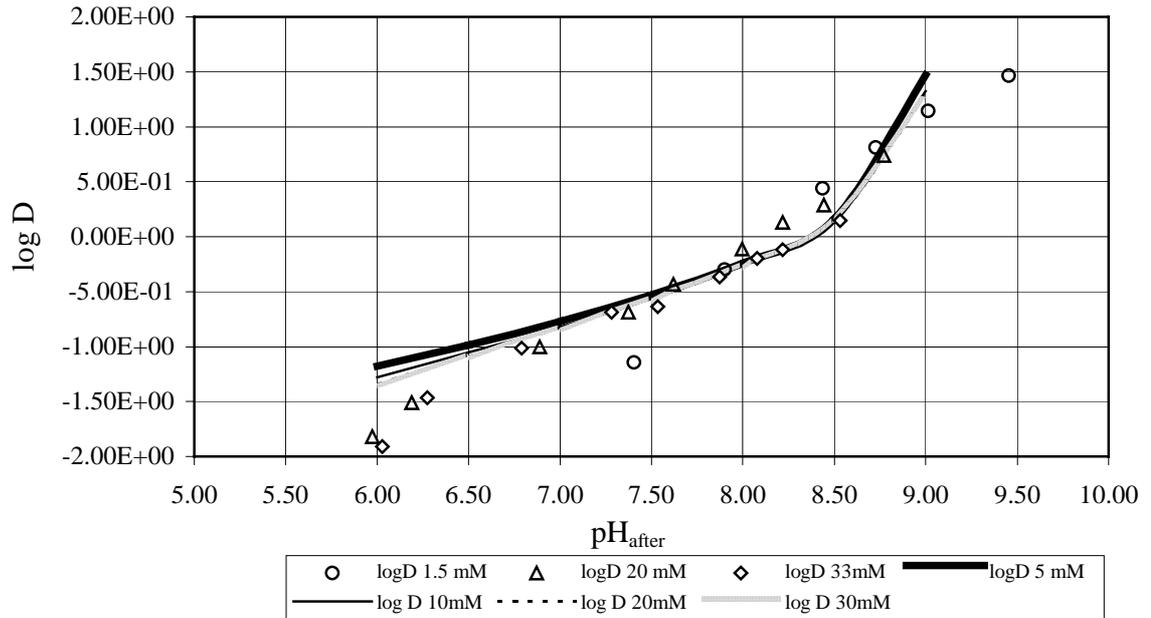


Figure 8.2.1. $\log D$ as derived from Equation 27 (lines) and as calculated from experimental values (points) as a function of the measured pH_{after}

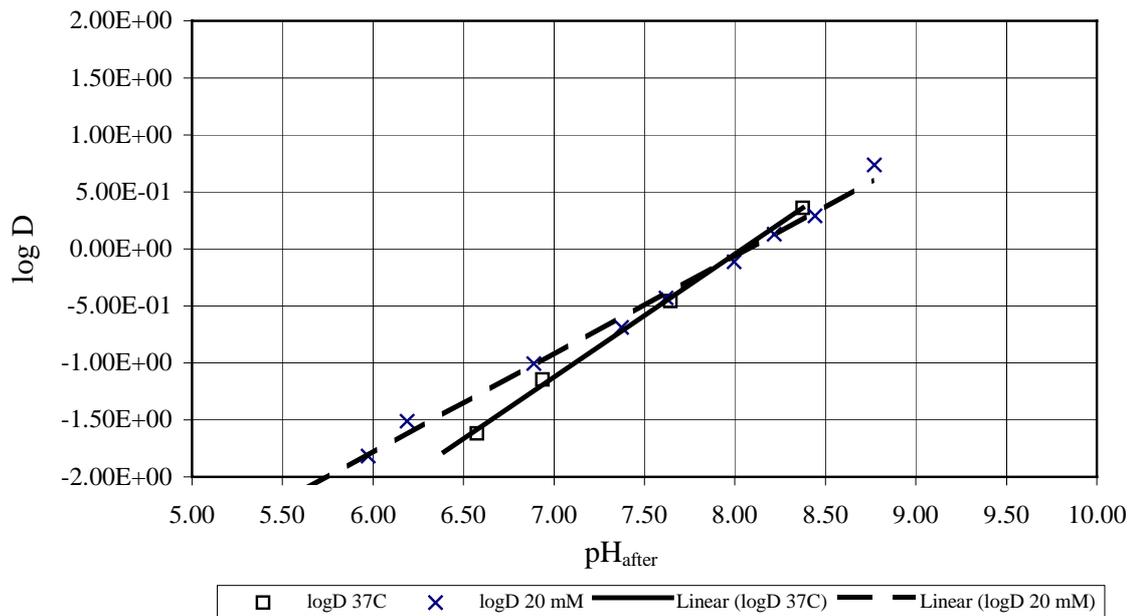


Figure 8.2.2. $\log D$ as calculated for adsorption of 20 mM Mg^{2+} ions at 20°C and 37°C

Determination of the apparent equilibrium constant

The apparent equilibrium constant for the formation of a $=\text{SiOMg}^+$ complex can be calculated from the modelled and experimental values as shown in Figure 8.3.1.

As found with the adsorption of Ca^{2+} ions the apparent equilibrium constant for the complexation of Mg^{2+} is changing with pH.

The pK ranges from 6.3 to 7.4 in the pH range 6...8.5 where adsorption becomes relevant. Schindler (1994) gives an estimation for the intrinsic equilibrium constant of $-\log K = 7.8$ at an ionic strength of 0.1N.

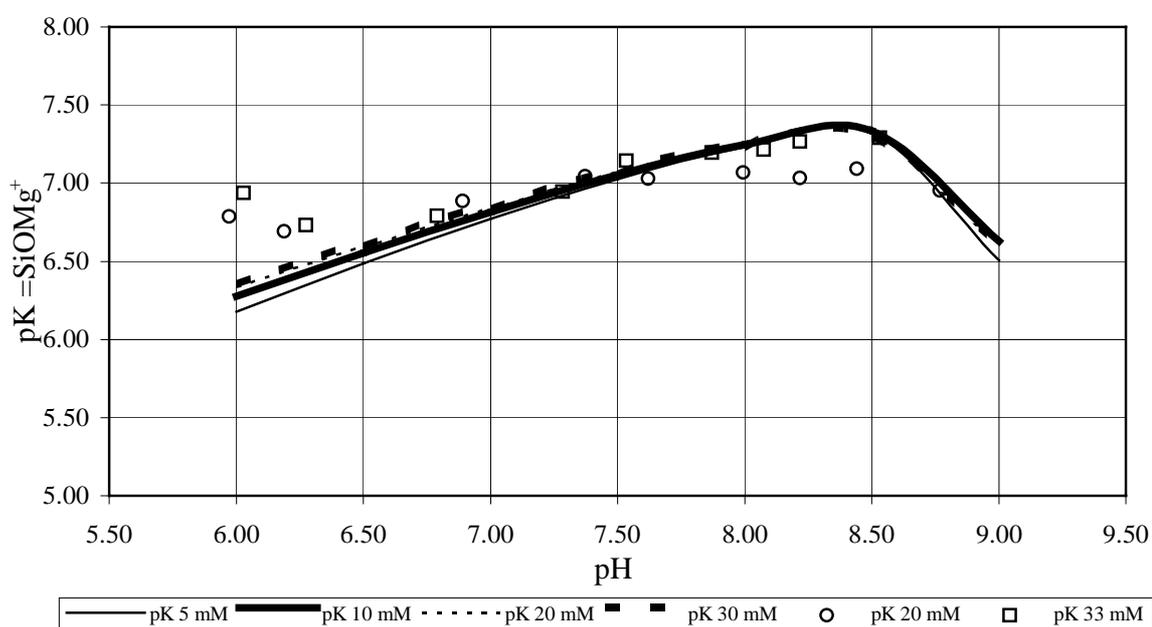


Figure 8.3.1. Calculated $pK_{=\text{SiOMg}^+}$ for the adsorption of Mg^{2+} ions on the silica gel at 20°C as a function of pH.

Using Allen's *et al.* (1971) approach as described in Sections 6.3 and 7.3 two different types of hydroxyl groups can be taken into account.

Using the same procedure as for the adsorption of Ca^{2+} ions Equation 17 becomes:

$$\log x = \log \frac{[\equiv \text{SiO}_I \text{Mg}^+] + [\equiv \text{SiO}_{II} \text{Mg}^+]}{[\equiv \text{SiO}_I \text{H}]_0 + [\equiv \text{SiO}_{II} \text{H}]_0} \quad (28)$$

Where the indices I and II indicate type I and type II hydroxyl groups, respectively.
and

$$\log \frac{x_I}{1-x_I} + \frac{A_I x_I}{2.303RT} = pH + \log K_{I,0} + \log[Mg^{2+}] \quad (29)$$

$$\log \frac{x_{II}}{1-x_{II}} + \frac{A_{II} x_{II}}{2.303RT} = pH + \log K_{II,0} + \log[Mg^{2+}] \quad (30)$$

$$x = x_I \varphi + x_{II} (1 - \varphi) \quad (21)$$

Figure 8.3.2 shows $\log x$ as a function of pH for the adsorption of 20 mM Mg^{2+} ions as calculated from the above-described procedure. For this gel φ is assumed to be 0.46 as determined in Section 6.3 of this thesis. $pK_{I,0}=6.5$ and $pK_{II,0}=7.4$. In this figure, the experimental points were taken from the polynomial described by Equation 27. The pK -values are taken from Figure 8.3.1. They represent those values around a pH of 6.3 and 7.4..8.6 where the pK remains more or less constant indicating the formation of surface complexes with two different types of hydroxyl groups.

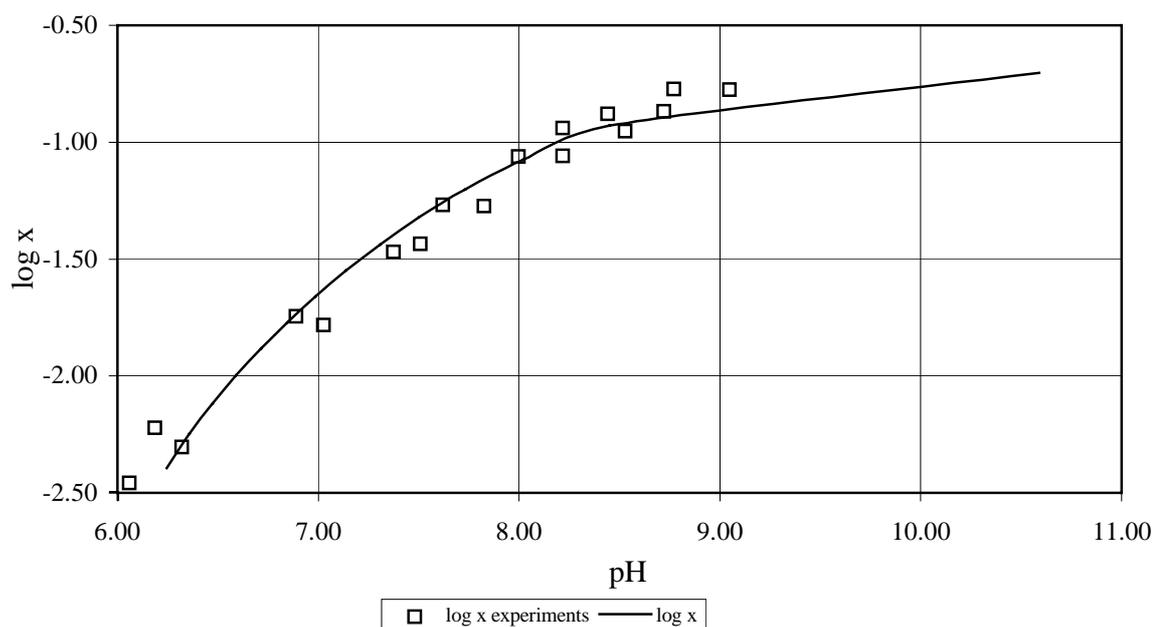


Figure 8.3.2. Log x for adsorption of 20 mM Mg^{2+} ions as a function of pH the drawn line represents the curve as calculated with Allen's method having $\varphi = 0.46$ and two pK_{-SiOMg^+} values of 6.5 and 7.4.

Figure 8.3.2. shows the good agreement between experiments and model. The mean deviation in $\log x$ is only 0.08. Thus it seems that Allen's *et al.* (1971) approach is useful for describing the adsorption of Mg^{2+} ions on a silica gel.

Comparison of SOLGASWATER simulations with experimental results

If it is assumed that the potential difference between complex and bulk solution, \hat{u} , can be neglected, the apparent equilibrium constant can be used as an intrinsic constant and used in the SOLGASWATER^S simulations.

The simulation was carried out using the equilibrium constants for the $=SiONa$ complex as derived in Section 6.3 of this thesis, *i.e.* $\hat{u}=0.46$, $pK_{I,0,=SiONa}=6.4$ and $pK_{II,0,=SiONa}=9.6$. The constants for the $=SiOMg^+$ complexes were as derived in the former paragraph, *i.e.* $pK_{I,0,=SiOMg^+}=6.5$ and $pK_{II,0,=SiOMg^+}=7.4$, respectively.

Figure 8.4.1 shows the results from the simulation for adsorption of 20 mM Mg^{2+} ions.

This figure shows that the SOLGASWATER^S simulations fit the experimental data. The two experimental points at a pH value above 8.5 deviate from the simulation due to an error in the experimental procedure.

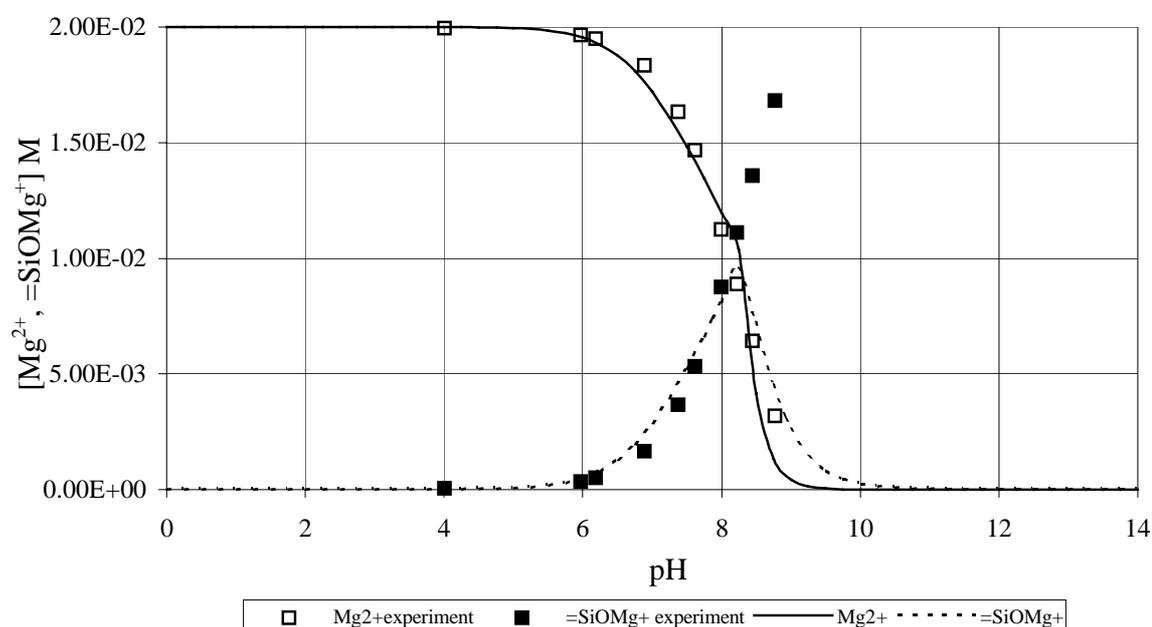


Figure 8.4.1 Simulation of the complexation of 20 mM Mg^{2+} ions on the silica gel using two types of reactive groups, *i.e.* $\hat{u}= 0.46$, $pK_{I,0,=SiOMg^+}=6.5$, $pK_{II,0,=SiOMg^+}=7.4$

Conclusions =SiO-Mg²⁺-Na⁺ system

1. Adsorption of Mg²⁺ ions on the silica gel leads to formation of complexes of the type =SiOMg⁺.
2. The adsorption can be described assuming that the surface has two different active groups with differing reactivity.
3. The apparent equilibrium constant, pK, for formation of the surface complexes equals 6.5 and 7.4 for the adsorption of 20 mM Mg²⁺ ions.
4. The model to describe the complexation as derived by Allen *et al.* (1971) can also be used to describe the complexation of Mg²⁺ ions on the silica gel.
5. SOLGASWATER^S simulations show good agreement with the experiments in the pH range considered.

THE COMPLEXATION OF CA²⁺ AND MG²⁺ IONS

The ion exchange of Ca²⁺ and Mg²⁺ ions on Aldrich's 28,863-2 gel

Experimental procedure

The simultaneous ion exchange of Ca²⁺ and Mg²⁺ on silica gel has been investigated by titration of the gel as described in Sections 6.1, 7.1 and 8.1 of this thesis.

Apart from Na⁺, OH⁻ or H⁺ ions, Ca²⁺ ions with an initial concentration of 2.5 mM and Mg²⁺ ions with an initial concentration of 1.5 mM were added to the suspension. The associated ion was Cl⁻. The ionic strength of the solution was adjusted to 0.1N by addition of NaCl. These concentrations were chosen since they are the same as in Kokubo's Simulated Body Fluid (SBF), which is used in many bioactive glass corrosion experiments (Kokubo *et al.* 1992).

The ion exchange was studied ranging from 0.02 meq H⁺/g gel to 0.47 meq OH⁻/g gel, *i.e.* in a pH range 5 to 9.

The ratio between the volume V, and the amount of gel, m, was as before V/m=0.01 l/g. All chemicals were of the highest chemical purity grade available. Water was deionised and distilled.

Experimental results

The experiments and experimental results are summarised in Table 9.1.1 and Figure 9.1.1.

Figure 9.1.1. shows that the simultaneous adsorption of Ca²⁺ and Mg²⁺ ions at these concentrations involves two non-interfering adsorption processes on the gel. This was expected since the ion concentrations were low in comparison with the ion exchange capacity of the gel. Thus enough hydroxyl groups are available for both the Ca²⁺ and Mg²⁺ ions.

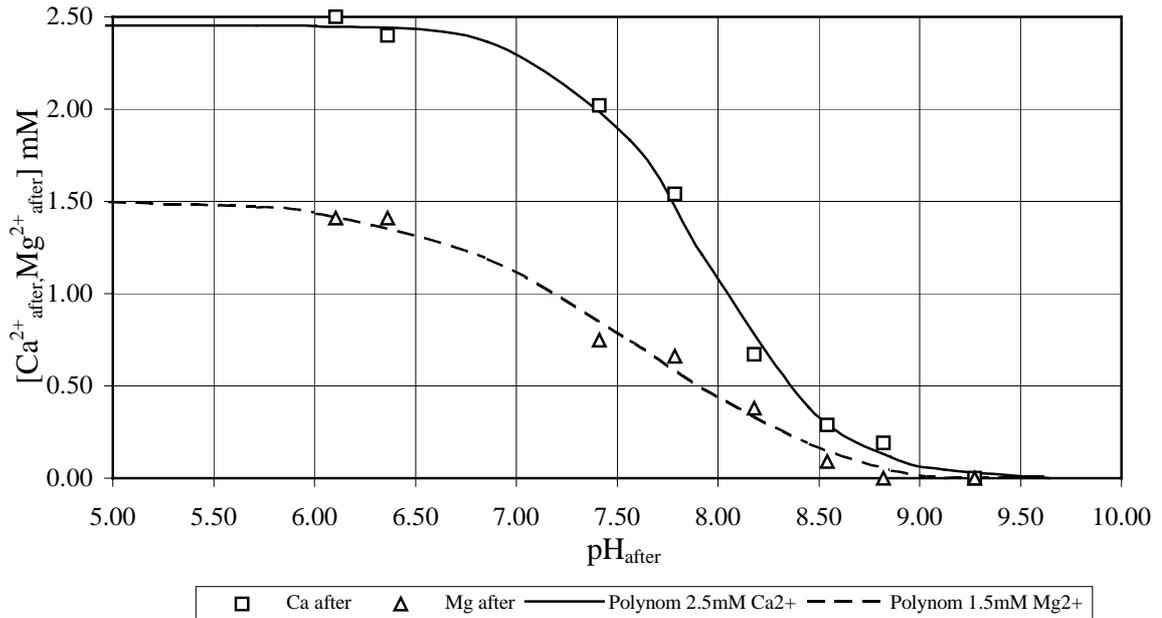


Figure 9.1.1. Measured concentration of Ca^{2+} and Mg^{2+} ions as a function of measured pH. The drawn lines represent a calculated sigmoidal using a least sum of squares curve fitting procedure.

Table 9.1.1. Results of the simultaneous adsorption of Ca^{2+} and Mg^{2+} ions on the silica gel.

No	Ca^{2+} initial mM	Mg^{2+} initial mM	$\text{pH}_{\text{initial}}$	meq OH^- /g*	pH_{after}	Ca^{2+} after mM	Mg^{2+} after mM
1	2.5	1.5	5	-0.02	4.205	2.5	1.5
2	2.5	1.5	5.5	0	6.104	2.5	1.41
3	2.5	1.5	6	0.01	6.363	2.4	1.41
4	2.5	1.5	7	0.05	6.941	-	-
5	2.5	1.5	7.5	0.1	7.411	2.02	0.75
6	2.5	1.5	8	0.15	7.787	1.54	0.66
7	2.5	1.5	8.5	0.23	8.181	0.67	0.38
8	2.5	1.5	8.75	0.3	8.543	0.29	0.09
9	2.5	1.5	9	0.35	8.819	0.20	0
10	2.5	1.5	9.5	0.47	9.272	0	0

* Negative values represent addition of H^+ ions.

SOLGASWATER[§] simulation of the simultaneous adsorption of Ca²⁺ and Mg²⁺ ions

From Sections 7.3 and 8.3 respectively it can be read that the apparent equilibrium constant, pK, for the adsorption of 2.5 mM Ca²⁺ ions ranges from 6.4 to 7.1 and for the adsorption of 1.5 mM Mg²⁺ ions ranges from 6.3 to 6.7. In Section 6.3 it was estimated that the silica gel consists of at least two types of hydroxyl groups with a fraction of the most active group, \hat{u} , which equals 0.46.

Assuming that the potential difference between the surface complexes and the bulk solution, \hat{u} , can be neglected, a simple SOLGASWATER[§] simulation could be carried out. Since the ion concentrations of Ca²⁺ and Mg²⁺ are low in comparison with the amount of hydroxyl groups available, it is assumed that all these ions adsorb on the most reactive groups. Thus the adsorption of Ca²⁺ and Mg²⁺ ions takes place as if only one type of hydroxyl group was available, whereas the Na⁺ ions present might occupy both types of hydroxyl groups.

Using the pK values for Na- complexes of 6.4 and 9.6, respectively, 6.7 for the Ca-complex and 6.5 for the Mg-complex, the simulation gives a result as shown in Figure 9.2.1. This figure shows that the SOLGASWATER[§] simulations can also be used in simultaneous complexation of different cations. It should be noted, however, that the results of the simulations heavily depend on the values used in the input files. Therefore a clear *a priori* understanding of the chemical processes involved is necessary.

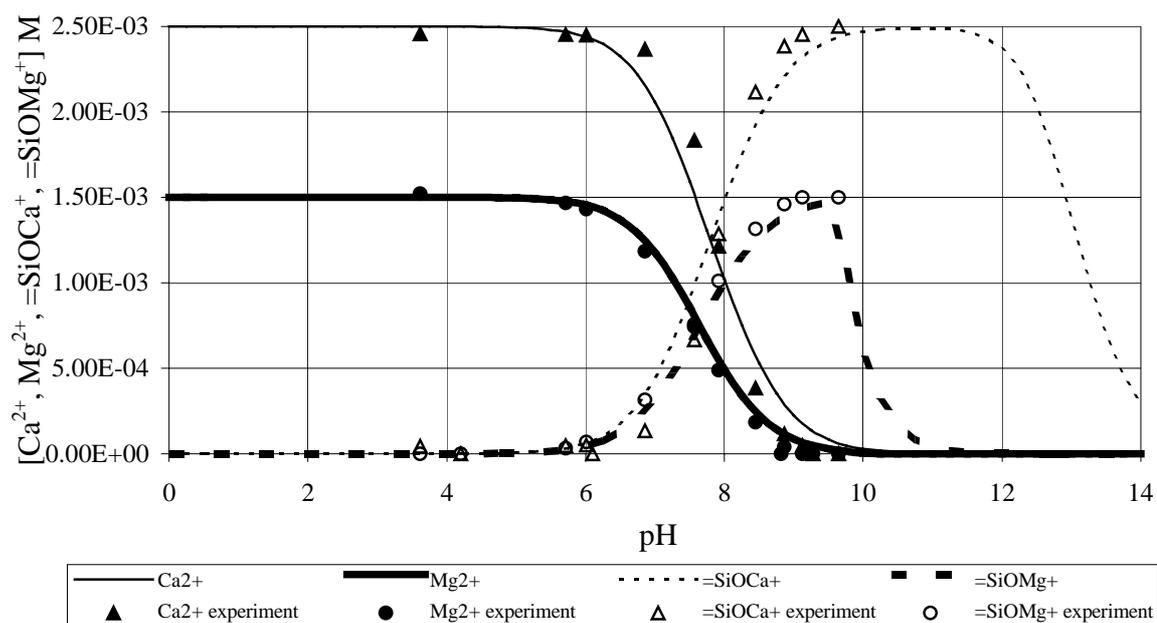


Figure 9.2.1. Results of the SOLGASWATER[§] simulation of the simultaneous complexation of 2.5 mM Ca²⁺ and 1.5 mM Mg²⁺ ions. The points show experimental values.

Conclusions =SiO-Ca²⁺-Mg²⁺-Na⁺ system

1. Simultaneous adsorption of low concentrations of Ca²⁺ and Mg²⁺ ions occurs as two non-interfering adsorption processes.
2. The adsorption of very low concentrations of cations occurs as if only one type of hydroxyl groups is present.
3. SOLGASWATER[§] simulations can be used to simulate simultaneous adsorption of cations as well.

THE =SIOH-AL³⁺-NA⁺ SYSTEM

The ion exchange of Al³⁺ on Aldrich's 28,863-2 gel

Experimental procedure

The ion exchange of Al³⁺ ions on silica gel has been investigated by titration of the gel as described in Section 6.1 of this thesis.

Apart from Na⁺, OH⁻ or H⁺ ions, Al³⁺ ions with an initial concentration of 10 mM were added to the suspension. Avoiding possible health risks the associated anion was NO₃⁻ instead of Cl⁻ as used in the adsorption of Ca²⁺ and Mg²⁺ ions. The ionic strength of the solution was adjusted to 0.1N by addition of NaNO₃.

The ion exchange was studied in a pH range ranging from 0 to 13.

The ratio between the volume, V, and the amount of gel, m, was as before V/m=0.01 l/g. All chemicals were of the highest chemical purity grade available. The water was deionised and distilled.

Samples were analysed using a standard backward titration method using EDTA and a ZnCl₂ solution.

Experimental results

In the pH range studied all types of hydroxides can be expected to be present *i.e.* AlOH²⁺, Al(OH)₂⁺, Al(OH)₃, and Al(OH)₄⁻.

The experimental results are summarised in Table 10.1.1 and Figure 10.1.1. Figure 10.1.1 shows that the adsorption of Al³⁺ ions starts at a pH value above 1.5. All Al³⁺ ions seem to be disappeared at a pH value of 4. The small concentration of metal ions detected at higher pH was most probably due to an experimental error.

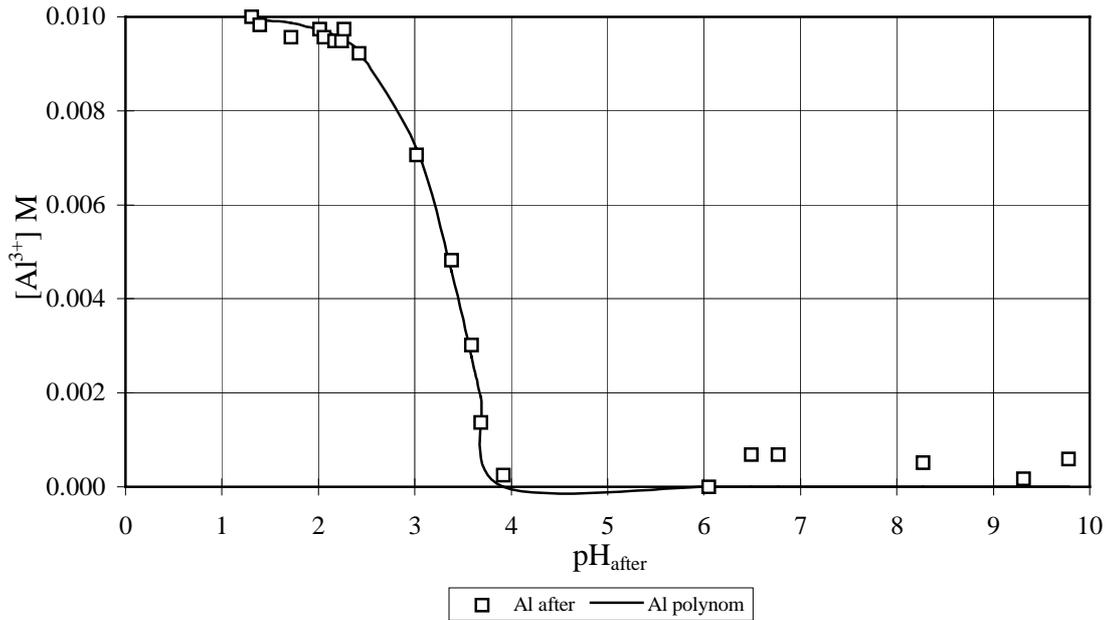


Figure 10.1.1. Measured concentration of Al^{3+} ions as a function of measured pH. The drawn line represents a calculated sigmoidal using a least sum of squares curve fitting procedure.

Table 10.1.1. Results of the adsorption of Al^{3+} ions on the silica gel.

No	Al^{3+} initial mM	$\text{pH}_{\text{initial}}$	meq OH^- /g *	pH_{after}	Al^{3+} after mM
1	10	1.35	-1	1.31	10
2	10	1.42	-0.8	1.39	9.8
3	10	1.50	-0.6	1.49	10.3
4	10	1.69	-0.4	1.72	9.6
5	10	1.96	-0.2	2.02	9.7
6	10	2.01	-0.18	2.06	9.6
7	10	2.09	-0.16	2.17	9.5
8	10	2.15	-0.14	2.24	9.5
9	10	2.21	-0.12	2.27	9.7
10	10	2.3	-0.1	2.42	9.2
11	10	4.00	0	3.02	7.1
12	10	4.40	0.1	3.38	4.9
13	10	4.62	0.2	3.59	3.0
14	10	4.83	0.25	3.69	1.4
15	10	4.99	0.3	3.92	2.5

* Negative values represent positive additions of H^+ ions

Table 10.1.1. Continued

No	Al ³⁺ _{initial} mM	pH _{initial}	meq OH ⁻ /g *	pH _{after}	Al ³⁺ _{after} mM
16	10	8.54	0.35	6.05	0
17	10	9.30	0.38	6.49	0.6
18	10	9.61	0.4	6.77	0.7
19	10	11.90	0.6	8.27	0.5
20	10	12.48	0.8	9.32	0.2
21	10	12.70	1	9.78	0.6

* Negative values represent positive additions of H⁺ ions

Determination of the type of complex involved in the adsorption of Al³⁺ ions

The method as derived by Ahrland *et al.* (1960) and used for adsorption of Ca²⁺ and Mg²⁺ ions, as described in Sections 7.2 and 8.2 of this thesis, can also be used for the adsorption of Al³⁺ ions.

Using Equations 14 and 16, the number of hydroxyl groups, n, can be estimated from a log D vs. pH plot giving a straight line with slope n.

$$D = \frac{\{(\equiv SiO)_n M\}}{[M^{z+}]} \quad (14)$$

$$\log D = -n \log[H^+] + Cst \quad (16)$$

Figure 10.2.1. shows the log D curve as calculated from the experiments.

The slope n equals 1.2 thus making a complex involving one hydroxyl group most probable. In the pH range 1.5...6 where the adsorption seems to be most interesting two types of complexes, both involving only one hydroxyl group can be expected, *i.e.* =SiOAlOH⁺ and =SiOAl(OH)₂.

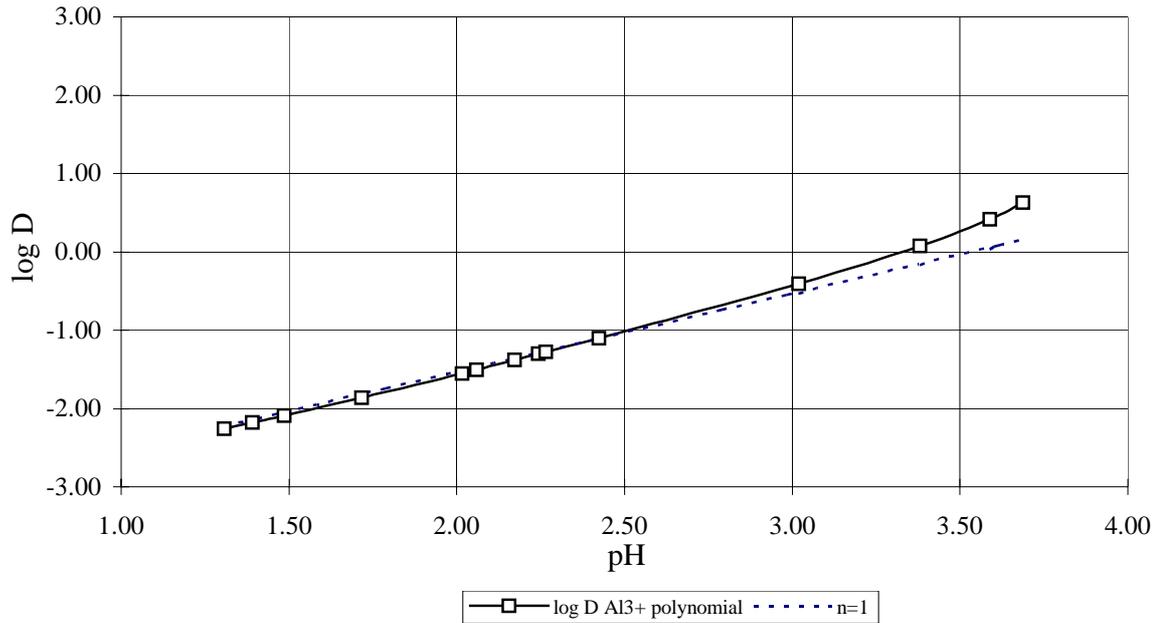


Figure 10.2.1. Log D as calculated from experimental values (points) as a function of the measured pH_{after}

Determination of the apparent equilibrium constant

The apparent equilibrium constant for the formation of a $=\text{SiOAlOH}^+$ or a $=\text{SiOAl}(\text{OH})_2$ complex can be calculated from the experimental values as shown in Figures 10.3.1 and 10.3.2.

As found with the adsorption of Ca^{2+} and Mg^{2+} ions, the apparent equilibrium constant for the complexation of Al^{3+} is changing with pH.

As seen in the adsorption of Ca^{2+} and Mg^{2+} ions at low concentration, there seems to be a single value for the apparent equilibrium constant, pK , which remains constant in a very short pH range. The values are $\text{pK} = 5.8$ for the $=\text{SiOAlOH}^+$ and 9.6 for the $=\text{SiOAl}(\text{OH})_2$ complex, respectively.

Figures 10.3.1 and 10.3.2 also indicate that only one type of hydroxyl group is involved in the complexation. Probably the concentration of Al^{3+} ions is low compared to the amount of hydroxyl groups with a relative high reactivity. Therefore it is not necessary to use Allen's *et al.* (1971) approach as used for the adsorption of higher concentrations of Ca^{2+} and Mg^{2+} ions as described in Sections 7.3 and 8.3 of this thesis, in order to describe the complexation of the Al^{3+} ions.

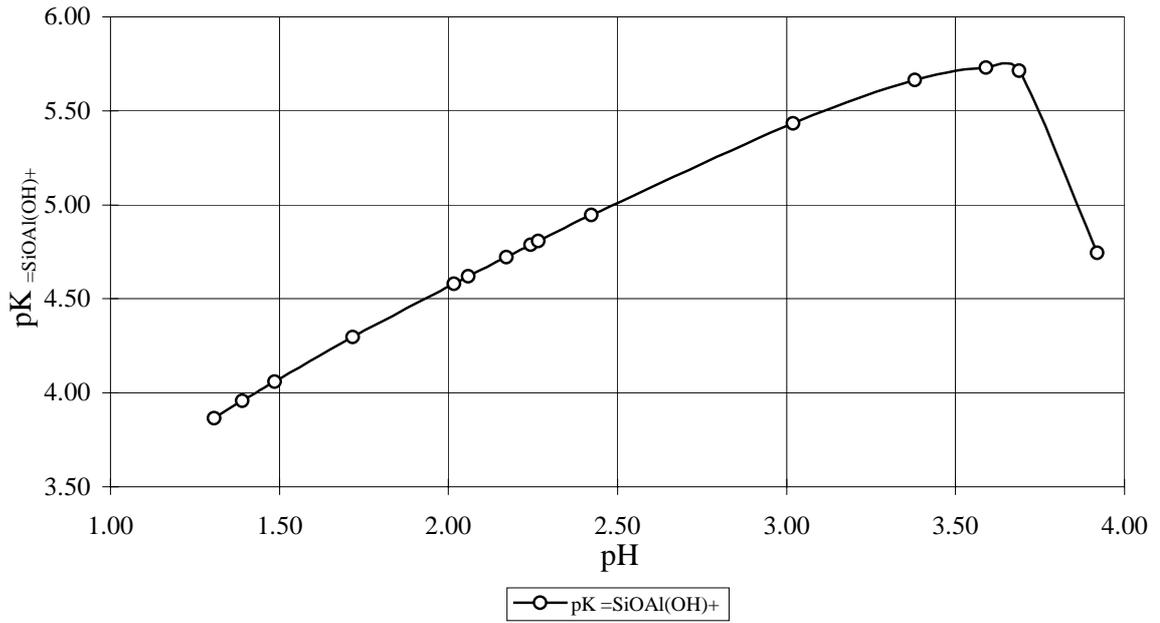


Figure 10.3.1. Calculated $pK_{=SiOAl(OH)+}$ for the adsorption of Al^{3+} ions on the silica gel at 20°C as a function of pH.

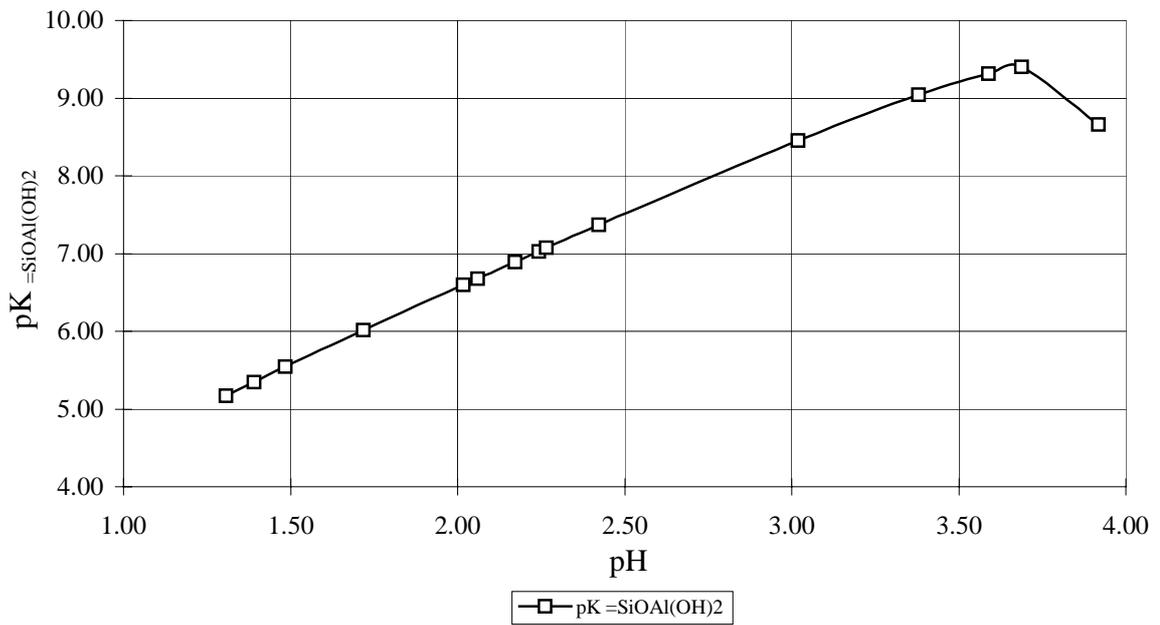


Figure 10.3.2. Calculated $pK_{=SiOAl(OH)2}$ for the adsorption of Al^{3+} ions on the silica gel at 20°C as a function of pH.

SOLGASWATER[§] simulations of the adsorption of Al³⁺ ions

Assuming that the potential difference, \hat{u} , between the surface complex and the bulk solution can be neglected, a simple SOLGASWATER[§] simulation could be carried out. Al³⁺ ions are assumed only to occupy the most reactive hydroxyl groups present, whereas the Na⁺ ions are supposed to occupy two different types of hydroxyl groups as described in Section 6.3 of this thesis.

Using the apparent equilibrium constants as calculated from Figures 10.3.1 and 10.3.2 and as determined in Section 6.3, gives simulation results as shown in Figure 10.4.1.

The SOLGASWATER[§] input file is shown in Appendix 13.2.10.

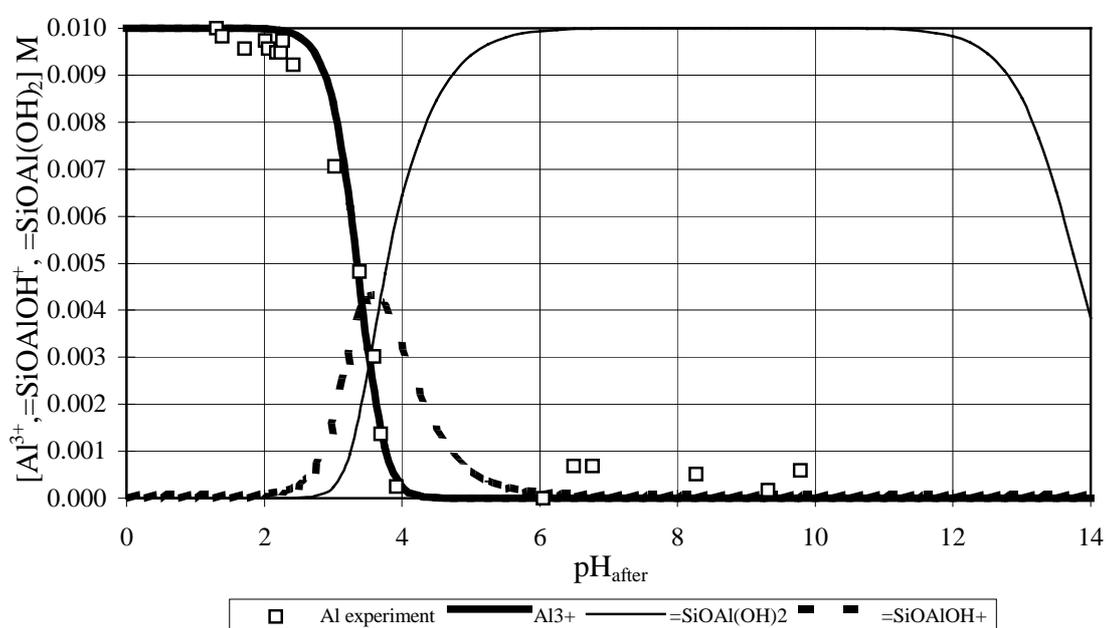


Figure 10.4.1. Results of the SOLGASWATER[§] simulation of the adsorption of 10 mM Al³⁺ ions on the silica gel. The points show experimental values.

Figure 10.4.1 shows that most probable a complex of the type =SiOAl(OH)₂ is formed in a pH range 3...12, thus indirectly indicating the possible inhibitory effect on the complexation of Ca²⁺ ions when present in sufficient amounts.

Conclusions $=\text{SiO}^-$ - Al^{3+} - Na^+ system

1. Adsorption of low concentrations of Al^{3+} ions occurs only at one type of hydroxyl groups, most probably the most reactive type present at the gel surface.
2. Two different types of complexes are found to be formed, both involving only a single surface hydroxyl group, *i.e.* $=\text{SiOAlOH}^+$ and $=\text{SiOAl}(\text{OH})_2$.
3. SOLGASWATER[§] simulations can be used to simulate the adsorption of Al^{3+} ions as well.

GENERAL DISCUSSION AND CONCLUSIONS

Gel characterisation

In order to study the complexation of different cations on a silica it is very important to know more about the surface structure. Here, Aldrich's 28,8632-2 gel is used.

The BET surface area determined by N₂ adsorption using the extended BET equation was 411 m²/g, the specific pore volume equalled 0.74 cm³/g and the reported particle diameter was between 63 and 212 Åm.

In Section 6.2, the adsorption of a simple cation, Na⁺, is used to determine the ion exchange capacity of the gel. This capacity was 100 mM in a sample containing 0.01 l fluid/g gel. The gel is only partly hydroxylated containing 1.5 =SiOH/nm².

Using Allen's *et al.* (1971) approach in order to describe the complexation of Na⁺ ions of a silica gel, it was found that the adsorption as carried out with the simple shaking experiments could be described using a surface containing two types of hydroxyl groups. The fraction, α , of the most reactive group is found to be 0.46 for the adsorption of Na⁺.

In principle a silica gel surface contains three types of active groups, *i.e.* in order of increasing reactivity =SiOH, =Si(OH)₂, and -Si(OH)₃. Which two of these groups Allen took into account is unclear. However it is unlikely that the first one, which might be present in abundance on a glass, was taken into account by Allen *et al.* (1971) due to its low flexibility and reactivity in comparison with the two others.

Furthermore it should be noted that Allen did not take the surface charge into account but only dealt with the decrease in surface reactivity as an increase in surface complexes formed.

Determination of the type of complexes formed in the experiments

The type of complexes formed in the adsorption experiments as described in Sections 7.2, 8.2 and 10.2 could be determined graphically by simply rewriting the equation for the equilibrium constant. It shows that most probably $=\text{SiOCa}^+$ is formed in case of adsorption of Ca^{2+} ions, that $=\text{SiOMg}^+$ is formed in case of adsorption of Mg^{2+} ions and $=\text{SiOAlOH}^+$ and $=\text{SiOAl}(\text{OH})_2$ are formed in case of adsorption of Al^{3+} ions.

The involvement of only one hydroxyl group in the adsorption of Ca^{2+} and Mg^{2+} ions might be because the gel was found to be only partly hydroxylated, *i.e.* does not contain the maximum possible amount of hydroxyl groups necessary to form complexes involving more than one hydroxyl group. If it is further assumed that the hydroxyl groups are of different types with a different reactivity, it becomes evident that the amount of hydroxyl groups such as $-\text{Si}(\text{OH})_3$ might be very low, thus making the formation of these types of complexes unlikely. Two types of hydroxyl groups have been taken into account. The fraction, \bar{u} , of the most reactive group equalled 0.46 for the gel considered.

Determination of equilibrium constants

Using Allen's *et al.* (1971) approach it was demonstrated in Section 6.3 that the complexation of Na^+ ions on the silica gel could be described with two equilibrium constants. These constants describe either a surface completely in the hydroxide form or a surface completely in the ionic state, *i.e.* $=\text{SiOH}$ groups or $=\text{SiO}^-$ groups. The two equilibrium constants were, *i.e.* $\text{pK}_{\text{I},0,=\text{SiONa}}=6.4$ and $\text{pK}_{\text{II},0,=\text{SiONa}}=9.6$ giving a mean deviation between Allen's model and measurements of 0.03.

For the complexation of Ca^{2+} and Mg^{2+} the apparent equilibrium constant is calculated from the separate experiments carried out and from the model equations (22) and (27) for the adsorption of Ca^{2+} and Mg^{2+} respectively as described in Sections 7.3 and 8.3 and plotted in Figures 7.3.1 and 8.3.1. From these figures it could already be seen that there is a difference in complexation of cations at low concentrations and at high concentrations. At low concentrations there seems to be only one value at which the pK value is more or less constant, whereas at higher concentrations two pK values can be found. Thus at low concentrations cations seem to form complexes with only one type of hydroxyl group, most probably the most reactive one present at the surface, whereas at higher concentrations more than one type of surface complex should be taken into account.

The pK values found for the adsorption of 2.5 mM Ca^{2+} ions are found to be $\text{pK}_{=\text{SiOCa}^+}=6.7$. For the complexation of 1.5 mM Mg^{2+} ions $\text{pK}_{=\text{SiOMg}^+}=6.5$. The pK value for adsorption of Ca^{2+} ions at higher concentrations is found to be in the range between 7.1 and 7.4, whereas the pK value for adsorption of Mg^{2+} ions at higher

concentrations is found to be in the range between 6.3 and 7.4. The pK values for the adsorption of 10 mM Al^{3+} ions equalled 5.75 and 9.55 for the formation of $=\text{SiOAlOH}^+$ and $=\text{SiOAl}(\text{OH})_2$, respectively.

Schindler (1994) gave an estimation for the formation of surface complexes of 8.6 for the $=\text{SiOCa}^+$ and 7.8 for the $=\text{SiOMg}^+$ complexes, respectively.

The differences in the constants as found by Schindler and as described in this work might be explained from the difference in gels and thus in types of hydroxyl groups present and in differences in the experimental procedures. In this work only very simple shaking experiments were carried out. However, also simple experiments can be used to give an estimation of the processes involved.

Considering the possible existence of two different equilibrium constants allows the extension of Allen's *et al.* (1971) model to the adsorption of Ca^{2+} and Mg^{2+} . Using the calculated pK values and a fraction, \bar{u} , of most reactive groups of 0.46 gives a mean deviation between experiments and Allen's extended model of 0.08 for adsorption of Ca^{2+} ions and of 0.08 for the adsorption of Mg^{2+} ions.

SOLGASWATER[§]-simulations

SOLGASWATER[§] simulations of the adsorption of Ca^{2+} , Mg^{2+} and Al^{3+} on an imaginary silica gel, as described in Chapter 5, show that if reliable equilibrium constants are available for the present system, simulation results can be used to predict possible effects of the presence of cations in bioactive glasses used or in the surrounding body fluid of a bioactive glass implant. However, even when SOLGASWATER[§] simulations give realistic results it should be noted that the results heavily depend upon the complexes taken into account and their equilibrium constants.

The simulations show that the concentration of hydroxyl groups is of importance in the complexation reactions studied in this work. Chapter 6 also shows that characterising the surface is necessary, *i.e.* determination of the type and concentration of different hydroxyl groups in order to give simulation results which are in agreement with the experiments carried out.

When a silica gel surface contains enough hydroxyl groups the adsorption of different cations takes place independently as shown in Sections 5.5, 5.6, 5.7 and Section 9.1 of this thesis. However when the concentration of hydroxyl groups on a gel surface is rather low in comparison with the concentration of cations present in the surrounding fluid complexation with the silica gel surface can become inhibited. When more than one type of cations were present the complexation might become

competitive as shown in Sections 5.5, 5.6, and 5.7. In these sections it was shown that Al^{3+} and Mg^{2+} ions can inhibit the formation of Ca^{2+} complexes.

SOLGASWATER[§] simulations show that the type of complex formed depends on the availability of hydroxyl groups. If many groups are available such as on a fully hydroxylated silica, Ca^{2+} and Mg^{2+} ions can form two types of complexes, *i.e.* $=\text{SiOCa}^+$, $(=\text{SiO})_2\text{Ca}=\text{SiOMg}^+$ and $(=\text{SiO})_2\text{Mg}$, respectively.

The SOLGASWATER[§] simulations carried out as described in Sections 6.4, 7.4, 8.4, 9.2 and 10.4 show good agreement with the experiments carried out.

It should be noted, however, that for the formation of Ca-, Mg- and Al-complexes only apparent constants are determined as described in this work, thus it should be assumed that the potential difference between surface complex and bulk solution can be neglected.

This work and the bioactivity of glass

The unknown structure of the Si-rich layer on a bioactive glass in the body environment or in simulated body fluids makes it very difficult to project the results as described in this thesis on the formation of an apatite layer on a bioactive glass. However, this work shows that Al^{3+} and Mg^{2+} can inhibit the complexation of Ca^{2+} ions on/within the Si-rich layer.

Depending on the type and amount of hydroxyl groups in the Si-rich layer this inhibitory effect will be more or less severe. When in the near future more details are available about the structure of the Si-rich layer formed on top of an bioactive glass, simple adsorption experiments as described in this thesis can be used to give a prediction of possible inhibitory effects of ions present either in the glass or in the surrounding body fluid.

In principle also the possibility of bonding an implant material to a glass coating on one hand and bone bonding on the other can be modelled and studied before any unnecessary animal experiments are carried out.

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APPENDICES

Input files as used in the SOLGASWATER® simulations

Simulation of complexation of sodium ions with two different surface active groups present

Nasilicate complexes with two types of surface active groups : I=0.1

```

6 1 17 0 2
'H+      ' 0.000000    1.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0
'Ca      ' 0.000000    0.0  1.0  0.0  0.0  0.0  0.0  0.0  0.0
'Na      ' 0.000000    0.0  0.0  1.0  0.0  0.0  0.0  0.0  0.0
'SiOH4   ' 0.000000    0.0  0.0  0.0  1.0  0.0  0.0  0.0  0.0
'=SiOH1  ' 0.000000    0.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0
'=SiOH2  ' 0.000000    0.0  0.0  0.0  0.0  0.0  1.0  0.0  0.0
'OH-     ' -13.8000   -1.0  0.0  0.0  0.0  0.0  0.0  0.0  0.0
'SiO(OH)3 ' -9.52000   -1.0  0.0  0.0  1.0  0.0  0.0  0.0  0.0
'SiO2(OH)2 ' -22.6200  -2.0  0.0  0.0  1.0  0.0  0.0  0.0  0.0
'Si2O(OH)6 '  1.30000    0.0  0.0  0.0  2.0  0.0  0.0  0.0  0.0
'Si2O2(OH)5 ' -7.81000   -1.0  0.0  0.0  2.0  0.0  0.0  0.0  0.0
'Si2O3(OH)4 ' -18.1400  -2.0  0.0  0.0  2.0  0.0  0.0  0.0  0.0
'Si4O6(OH)6 ' -12.5700  -2.0  0.0  0.0  4.0  0.0  0.0  0.0  0.0
'=SiOH2+1 ' -3.00000    1.0  0.0  0.0  0.0  1.0  0.0  1.0  0.0
'=SiOH2+2 ' -3.00000    1.0  0.0  0.0  0.0  0.0  1.0  0.0  1.0
'=SiONa1  ' -6.40000   -1.0  0.0  1.0  0.0  1.0  0.0  0.0  0.0
'=SiONa2  ' -9.60000   -1.0  0.0  1.0  0.0  0.0  1.0  0.0  0.0
1 2 3 4 5 6
0 0 0 0 0
2
4 2 1 1 3 1 16 1 17
57 0
10 2 2 9 2 2 20 20
0.000000E+00 -.250000
0.000000E+00
0.100000
-2.70000
0.0460000
0.054000
100.000  411.000  0.750000
100.000  411.000  0.750000
10

```

Simulation of complexation of calcium ions with two different surface active groups present

Ca-nasilicate complexes with two types of surface active groups

	6	1	23	1	2									
'H	' 0.0000000	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				
'Ca	' 0.0000000	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				
'Na	' 0.0000000	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0				
'SiOH4	' 0.0000000	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0				
'=SiOH1	' 0.0000000	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0				
'=SiOH2	' 0.0000000	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0				
'OH-	' -13.80000	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				
'SiO(OH)3	' -9.520000	-1.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0				
'SiO2(OH)2	' -22.26000	-2.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0				
'Si2O(OH)6	' 1.300000	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0				
'Si2O2(OH)5	' -7.810000	-1.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0				
'Si2O3(OH)4	' -18.14000	-2.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0				
'Si4O6(OH)6	' -12.57000	-2.0	0.0	0.0	4.0	0.0	0.0	0.0	0.0	0.0				
'=SiOH2+1	' -3.000000	1.0	0.0	0.0	0.0	1.0	0.0	1.0	0.0	0.0				
'=SiOH2+2	' -3.000000	1.0	0.0	0.0	0.0	0.0	1.0	0.0	1.0	0.0				
'=SiONa1	' -6.400000	-1.0	0.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0				
'=SiONa2	' -9.600000	-1.0	0.0	1.0	0.0	0.0	1.0	0.0	0.0	0.0				
'=SiOCa1	' -7.100000	-1.0	1.0	0.0	0.0	1.0	0.0	1.0	0.0	0.0				
'=SiOCa2	' -7.400000	-1.0	1.0	0.0	0.0	0.0	1.0	0.0	1.0	0.0				
'CaOH+	' -12.50000	-1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				
'CaOSi(OH)	' -9.150000	-1.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0				
'CaO2SiOH	' -19.19000	-2.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0				
'Ca(OSiOH)2	' -16.96000	-2.0	1.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0				
'Ca(OH)2	' -21.02000	-2.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				
1	2	3	4	5	6									
0	0	0	0	0	0									
2														
7	2	1	1	2	1	3	1	16	1	17	1	18	1	19
57	0													
10	2	2	9	2	2	20	20							
0.000000E+00														
20.000000E-3														
0.0400000														
-2.70000														
0.0460000														
0.054000														
100.000		411.000				0.750000								
100.000		411.000				0.750000								

Simulation of complexation of magnesium ions with two different surface active groups present

mg-nasilicate complexes with two types of surface active groups

6 1 23 1 2

'H+	0.0000000	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
'Mg	'0.0000000	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
'Na	0.0000000	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0
'SiOH4	'0.0000000	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0
'=SiOH1	'0.0000000	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0
'=SiOH2	'0.0000000	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0
'OH-	-13.80000	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
'SiO(OH)3	'-9.520000	-1.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0
'SiO2(OH)2	'-22.26000	-2.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0
'Si2O(OH)6	'1.300000	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
'Si2O2(OH)5	'-7.810000	-1.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
'Si2O3(OH)4	'-18.14000	-2.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
'Si4O6(OH)6	'-12.57000	-2.0	0.0	0.0	4.0	0.0	0.0	0.0	0.0
'=SiOH2+1	'-3.000000	1.0	0.0	0.0	0.0	1.0	0.0	1.0	0.0
'=SiOH2+2	'-3.000000	1.0	0.0	0.0	0.0	0.0	1.0	0.0	1.0
'=SiONa1	'-6.400000	-1.0	0.0	1.0	0.0	1.0	0.0	0.0	0.0
'=SiONa2	'-9.600000	-1.0	0.0	1.0	0.0	0.0	1.0	0.0	0.0
'=SiOMg1	'-6.500000	-1.0	1.0	0.0	0.0	1.0	0.0	1.0	0.0
'=SiOMg2	'-7.400000	-1.0	1.0	0.0	0.0	0.0	1.0	0.0	1.0
'MgOH+	'-11.21000	-1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
'MgOSi(OH)	'-8.900000	-1.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0
'MgO2SiOH	'-18.11000	-2.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0
'Mg(OSiOH)2	'-15.23000	-2.0	1.0	0.0	2.0	0.0	0.0	0.0	0.0
'Mg(OH)2	'-14.09000	-2.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0

1 2 3 4 5 6

0 0 0 0 0

2

7 2 1 1 2 1 3 1 16 1 17 1 18 1 19

57 0

10 2 2 9 2 2 20 20

0.000000E+00 -.250000

20.000000E-3

0.0400000

-2.70000

0.0460000

0.054000

100.000 411.000 0.750000
 100.000 411.000 0.750000
 10

Simulation of simultaneous complexation of calcium and magnesium ions with two different surface active groups present

calcium-magnesiumsilicate complexes I=0.1

	7	1	30	2	2								
'H+						.000	1.0	.0	.0	.0	.0	.0	
.0													
'Ca++						.000	.0	1.0	.0	.0	.0	.0	
.0													
'Mg++						.000	.0	.0	1.0	.0	.0	.0	
.0													
'Na+						.000	.0	.0	.0	1.0	.0	.0	
.0													
'Si(OH)4						.000	.0	.0	.0	.0	1.0	.0	
.0													
'=SiOH1						.000	.0	.0	.0	.0	.0	1.0	
.0													
'=SiOH2						.000	.0	.0	.0	.0	.0	.0	1.0
.0													
'OH-						-13.800	-1.0	.0	.0	.0	.0	.0	.0
.0													
'SiO(OH)3						-9.117	-1.0	.0	.0	.0	1.0	.0	.0
.0													
'SiO2(OH)2						-21.062	-2.0	.0	.0	.0	1.0	.0	.0
.0													
'Si2O(OH)6						1.300	.0	.0	.0	.0	2.0	.0	.0
.0													
'Si2O2(OH)5						-7.397	-1.0	.0	.0	.0	2.0	.0	.0
.0													
'Si2O3(OH)4						-16.942	-2.0	.0	.0	.0	2.0	.0	.0
.0													
'Si4O6(OH)6						-12.570	-2.0	.0	.0	.0	4.0	.0	.0
.0													
'CaOH+						-13.029	-1.0	1.0	.0	.0	.0	.0	.0
.0													
'MgOH+						-11.765	-1.0	.0	1.0	.0	.0	.0	.0
.0													

'CaOSi(OH) '	- 9.619	-1.0	1.0	.0	.0	1.0	.0	.0	.0
.0									
'MgOSi(OH) '	- 9.369	-1.0	.0	1.0	.0	1.0	.0	.0	.0
.0									
'CaO2Si(OH) '	-19.629	-2.0	1.0	.0	.0	1.0	.0	.0	.0
.0									
'MgO2Si(OH) '	-18.549	-2.0	.0	1.0	.0	1.0	.0	.0	.0
.0									
'Ca(OSiOH)2 '	-16.589	-2.0	1.0	.0	.0	2.0	.0	.0	.0
.0									
'Mg(OSiOH)2 '	-15.659	-2.0	.0	1.0	.0	2.0	.0	.0	.0
.0									
'=SiONa1 '	- 6.400	-1.0	.0	.0	1.0	.0	1.0	.0	.0
.0									
'=SiONa2 '	- 9.600	-1.0	.0	.0	1.0	.0	.0	1.0	.0
.0									
'=SiOH2+1 '	- 3.000	1.0	.0	.0	.0	.0	1.0	.0	1.0
.0									
'=SiOH2+2 '	- 3.000	1.0	.0	.0	.0	.0	.0	1.0	.0
1.0									
'=SiOCa+1 '	- 6.700	-1.0	1.0	.0	.0	.0	1.0	.0	1.0
.0									
'=SiOCa+2 '	- 6.700	-1.0	1.0	.0	.0	.0	.0	1.0	.0
1.0									
'=SiOMg+1 '	- 6.500	-1.0	.0	1.0	.0	.0	1.0	.0	1.0
.0									
'=SiOMg+2 '	- 6.500	-1.0	.0	1.0	.0	.0	.0	1.0	.0
.0									
'Ca(OH)2 '	-21.549	-2.0	1.0	.0	.0	.0	.0	.0	.0
.0									
'Mg(OH)2 '	-14.619	-2.0	.0	1.0	.0	.0	.0	.0	.0
.0									
1	2	3	4	5	6	7			
0	0	0	0	0	0	0			
2									
7	2	1	1	2	1	3	1	27	1
28	1	29	1	30					
57	0								
10	2	2	2	9	2	2	20	20	
0.000000E+00	-0.25								
2.50e-3									
1.50e-3									
0.092									
-2.70000									

0.046

0.054

100.0000 411.000 0.750000

100.0000 411.000 0.750000 10

Simulation of complexation of aluminium ions with two different surface active groups present

aluminium complexes I=0.1

6	1	28	1	2								
'h+	'	.000	1.0	.0	.0	.0	.0	.0	.0	.0		
'al+++	'	.000	.0	1.0	.0	.0	.0	.0	.0	.0		
'na+	'	.000	.0	.0	1.0	.0	.0	.0	.0	.0		
'si(oh)4	'	.000	.0	.0	.0	1.0	.0	.0	.0	.0		
'=sioh	'	.000	.0	.0	.0	.0	1.0	.0	.0	.0		
'=sioh2	'	.000	.0	.0	.0	.0	.0	1.0	.0	.0		
'oh-	'	-13.800	-1.0	.0	.0	.0	.0	.0	.0	.0		
'sio(oh)3	'	-9.117	-1.0	.0	.0	1.0	.0	.0	.0	.0		
'sio2(oh)2	'	-21.062	-2.0	.0	.0	1.0	.0	.0	.0	.0		
'si2o(oh)6	'	1.300	.0	.0	.0	2.0	.0	.0	.0	.0		
'si2o2(oh)	'	-7.397	-1.0	.0	.0	2.0	.0	.0	.0	.0		
'si2o3(oh)	'	-16.942	-2.0	.0	.0	2.0	.0	.0	.0	.0		
'si4o6(oh)	'	-12.570	-2.0	.0	.0	4.0	.0	.0	.0	.0		
'aloh++	'	-6.225	-1.0	1.0	.0	.0	.0	.0	.0	.0		
'aloh2+	'	-11.698	-2.0	1.0	.0	.0	.0	.0	.0	.0		
'aloh4-	'	-24.595	-4.0	1.0	.0	.0	.0	.0	.0	.0		
'al3oh4++++	'	-13.217	-4.0	3.0	.0	.0	.0	.0	.0	.0		
'kaolinite*	'	-73.564	-4.0	2.0	.0	2.0	.0	.0	.0	.0		
'dickite *	'	-74.494	-4.0	2.0	.0	2.0	.0	.0	.0	.0		
'halloysit*	'	-77.144	-4.0	2.0	.0	2.0	.0	.0	.0	.0		
'=siona1	'	- 6.400	-1.0	.0	1.0	.0	1.0	.0	.0	.0		
'=siona2	'	- 9.600	-1.0	.0	1.0	.0	.0	1.0	.0	.0		
'=sioh2+1	'	- 3.000	1.0	.0	.0	.0	1.0	.0	1.0	.0		
'=sioh2+2	'	- 3.000	1.0	.0	.0	.0	.0	1.0	.0	1.0		
'=sial(oh)2	'	- 9.55	-3.0	1.0	.0	.0	1.0	.0	.0	.0		
'=sial(OH)2	'	- 9.55	-3.0	1.0	.0	.0	.0	1.0	.0	.0		
'=sioal(oh)	'	- 5.75	-2.0	1.0	.0	.0	1.0	.0	1.0	.0		
'=sioal(OH)	'	- 5.75	-2.0	1.0	.0	.0	.0	1.0	.0	1.0		
'al(oh)3	'	- 17.221	-3.0	1.0	.0	.0	.0	.0	.0	.0		
1	2	3	4	5	6							
0	0	0	0	0	0							
2												
6	2	1	1	2	1	25	1	26	1	27	1	28
57	0											
10	2	2	9	2	2	20	20					
0.000000E+00												
10e-3												
0.04												

-2.70000
0.04600000
0.054
100.000 411.000 0.750000
100.000 411.000 0.75
10

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