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On the Problem of Silica Solubility at High pH

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Preface

In the framework of its Waste Management Programme the Paul Scherrer Institute is performing work to increase the understanding of repository near field behaviour. These investigations are performed in close cooperation with, and with the financial support of NAGRA. The present report is therefore issued simultaneously as a PSI report and as a NAGRA NTB.

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Abstract

The aqueous system $\text{Na}_2\text{O}-\text{H}_2\text{O}-\text{SiO}_2$ is considered to play an important rôle when strong alkaline pore waters of a cement based intermediate level radioactive waste repository intrude into the rock formations surrounding the near field. Under such conditions unknown quantities of silica may dissolve. Therefore the pH-dependence of the solubility of amorphous silica and quartz is investigated by a parameter variation study using the geochemical speciation code MINEQL/EIR. Published silica solubility data obtained in sodium hydroxide solutions at 25 and 90°C are compared with the results of four models which use different proposed values of the rather uncertain equilibrium constants. Of main interest is the question of whether, in a high pH region, the silica solubility can be explained with different monomeric species only, or to what extent additional polymeric silica species have to be considered as well. Furthermore, the influence of silica-sodium ion pairing under such extreme conditions is also studied.

The solubility of amorphous silica at 25°C is well understood up to a pH of about 10.5, where it is determined by the solubility product and the first dissociation constant of monomeric silicic acid. In more alkaline media the total solubility increases dramatically. This behaviour is less well understood due to uncertainties of the second deprotonation and polymerisation constants. Despite these uncertainties, it is shown that the most probable cause of the increased solubility of amorphous silica in the region between pH 10.5 and 11.3 is the formation of dimers, trimers and tetramers. Below a total silica concentration of 0.01 M and $\text{pH} \leq 10.0$, however, polymerisation proves to be insignificant.

Besides low temperature studies using amorphous silica, the solubility of quartz has also been measured in NaOH solutions at 90°C. As is the case at lower temperatures, the reported values for the second dissociation constant at 90°C scatter widely. Although it is not possible to extract this value from the few analytical data, it can be shown that in a NaOH medium up to 0.1 M only mononuclear silica species are stable. Therefore it is concluded that the trend of monomers to form polymers decreases strongly with temperature. In addition, there are indications that, in strong NaOH solutions at elevated temperatures, silica-sodium ion pairing gains importance.

Zusammenfassung

Dem wässrigem System $\text{Na}_2\text{O-SiO}_2\text{-H}_2\text{O}$ wird eine grosse Bedeutung beigemessen, wenn stark alkalische Zementporenwässer aus einem mit Zement verfüllten Endlager für schwach radioaktive Abfälle in das umgebende Gestein des Nahfeldes eindringen. Unter solchen extremen Bedingungen lösen sich möglicherweise enorme Mengen an Kieselsäure. Daher werden in einer Modellstudie die Löslichkeiten von amorphen Silikagel und Quarz in Natriumhydroxidlösungen in Abhängigkeit des pH untersucht. Publierte Löslichkeitsdaten gemessen bei 25 und 90 °C werden mit den Resultaten von vier Modellen verglichen, die sich durch Variation verschiedener Gleichgewichtskonstanten zwischen Kieselsäurespezien ergeben. Als Berechnungsgrundlage dient der geochemische Speziationscode MINEQL/EIR. Die zentrale Frage ist, ob sich die SiO_2 -Löslichkeit bei einem hohen pH allein mit monomeren Spezien erklären lässt, oder ob zusätzliche polymere Spezien berücksichtigt werden müssen. Zusätzlich wird auch der Einfluss einer Komplexbildung von Kieselsäure mit Natrium untersucht.

Die Löslichkeit von amorphen Silikagel bei 25°C wird allgemein gut verstanden bis etwa pH 10.5, wobei sie durch das Löslichkeitsprodukt der Festphase und durch die erste Dissoziationskonstante von monomerer Kieselsäure bestimmt wird. Mit zunehmender Natriumhydroxidkonzentration steigt die totale SiO_2 -Löslichkeit jedoch sprunghaft an. Dies Verhalten wird weniger gut verstanden, da es über die zweite Deprotonierungsreaktion und verschiedene Polymerisationsgleichgewichte widersprüchliche Aussagen gibt. Aufgrund der gewonnenen Resultate ist es wahrscheinlich, dass zwischen pH 10.5 und 11.3 vermehrt Polymere in Form von Dimeren, Trimeren und Tetrameren auftreten. Polymerisation ist allerdings bedeutungslos in Lösungen mit totaler SiO_2 -Konzentration unter 0.01 M und im Falle gesättigter Lösungen unterhalb eines pH-Wertes von 10.0.

In der Literatur lassen sich auch einige Werke ausmachen, in denen Löslichkeitsuntersuchungen von Quarz in NaOH-Lösungen bei 90°C beschrieben sind. Auch in diesen Berichten werden wiederum bezüglich der zweiten Deprotonierungskonstanten widersprüchliche Angaben gemacht. Obwohl es mit dem vorhandenen Datenmaterial nicht möglich ist, diese Konstante zu extrahieren, kann gezeigt werden, dass in NaOH-Lösungen bis 0.1 M vornehmlich monomere Silikatspezien auftreten. Dies deutet darauf hin, dass die Polymerisierbarkeit von Kieselsäure mit steigender Temperatur stark abnimmt. Es gibt jedoch Anzeichen dafür, dass in konzentrierten NaOH-Lösungen bei erhöhten Temperaturen zusätzlich mit Bildung von Natriumsilikat-Komplexen gerechnet werden muss.

Résumé

Le système $\text{Na}_2\text{O}-\text{H}_2\text{O}-\text{SiO}_2$ joue un rôle important lorsque les eaux des pores fortement alcalines du ciment utilisé pour le stockage des déchets faiblement radioactifs pénètrent la roche environnante du stockage final. Dans de telles conditions, des quantités inconnues de silice peuvent se dissoudre. Afin d'étudier la solubilité de la silice et du quartz en fonction du pH, la variation d'un paramètre en utilisant le code géochimique (MINEQL/EIR) a été examinée. Les valeurs de la solubilité de la silice dans une solution d'hydroxyde de sodium à 25 et 90°C publiées dans la littérature furent ensuite comparées aux résultats obtenus à partir de quatre modèles en utilisant différentes valeurs de constantes d'équilibre. L'intérêt principal était la question de savoir si la solubilité de la silice dans un environnement de pH élevé peut être expliquée par la présence unique des espèces différentes monomériques ou si des espèces polymériques additionnelles furent considérées. L'influence de la formation de la paire ionique silice-sodium dans ces conditions extrêmes a également été étudiée.

La solubilité de la silice amorphe à 25°C est bien comprise jusqu'à un pH d'environ 10.5. Elle est déterminée par le produit de solubilité et la première constante de dissociation de l'acide silicique monomérique. En milieu plus alcalins, la solubilité totale augmente fortement. Cette propriété est moins bien comprise car les constantes de la seconde déprotonation et de polymérisation sont incertaines. En dépit de ces incertitudes, il a été démontré que la cause la plus probable de l'augmentation de la solubilité des silices amorphes lorsque l'on considère des valeurs pH comprises entre 10.5 et 11.3 est due à la formation de polymères dimériques, trimériques et tétramériques. Cependant, lorsque la concentration de silice totale est inférieure à 0.01 M et le $\text{pH} \leq 10.0$, la polymérisation semble être insignifiante.

La solubilité du quartz n'a pas seulement été étudiée à basse température en utilisant de la silice amorphe mais aussi dans des solutions contenant du NaOH à 90°C. À côté des études de la silice amorphe à basse température, la solubilité du quartz à 90°C dans des solutions contenant du NaOH a été mesurée. Les valeurs de la seconde constante de dissociation à 90°C obtenues sont fortement disparates, comme ce fut le cas pour ces valeurs reportées à basses températures. Quoiqu'il ne fut pas possible d'extraire la valeur de la seconde constante de dissociation à partir de quelques données analytiques, lorsque la concentration de soude caustique n'excède pas 0.1 M, seules les silices monomériques sont stables. Par conséquent, la tendance que des monomères forme de polymères décroît fortement avec la température. Il y a de surcroît que dans les solutions de NaOH concentrées à températures élevées, les complexes de paires ioniques silice-sodium gagnent en importance.

1 Introduction

In the planning of the disposal of low and medium level radioactive waste, it is foreseen that large quantities of cementitious material will be used as a solidification matrix and in repository construction. The pore-water of fresh, unaltered cement is basically a strong alkali hydroxide solution saturated with calcium hydroxide, leading to a very high pH of about 13 (Berner, 1987, 1989). In these reports, Berner also pointed out that, even in more aged cement when all alkali hydroxide is removed from the system, the pH will be maintained at a value of about 12 because of the restricted solubility of calcium-silicate-hydrates. Since it is likely that a high pH plume will intrude into the rocks surrounding the near field, the interaction processes between the cement pore water and the regional geology should be studied. One of the problems in modelling such conditions is the unknown solubility of SiO_2 , one of the major rock forming minerals.

In principle, SiO_2 dissolution and its speciation should be investigated in both strong alkali and calcium hydroxide solutions. Unfortunately, the behavior of SiO_2 dissolution caused by infiltration of strong calcium hydroxide solutions is difficult to predict because it is likely that amorphous calcium-silicate-hydrates (CSH-gels) will be formed (Lunden and Andersson, 1989). The composition of such phases is generally not known precisely, they are metastable and show an incongruent dissolution behavior (Berner, 1989). CSH-gels have been observed in experiments being performed under similar conditions (Roller and Ervin, 1940; Kalousek, 1952; Greenberg and Chang, 1965) and it is possible that such phases will cover the surfaces of the minerals in the host rock and thus may prevent further corrosion of quartz. Modelling studies of the movement of a high pH front into the host rock are in progress at the Paul Scherrer Institute and the University of Bern.

Before being able to calculate silica solubility and speciation in the complex chemical systems of the altered near field, it is necessary to evaluate the different chemical reactions and equilibrium constants in the pure SiO_2 system. For such an investigation it is helpful to consider only experimental data obtained in silica saturated sodium hydroxide solutions because in this system no secondary solid phases will be formed. Therefore in this study analytical silica solubility data obtained in sodium hydroxide solutions were compared with calculated solubilities by the use of different model approaches. Due to a parameter variation study of proposed, but rather uncertain equilibrium constants, a final model is presented which most reliably predicts the silica solubility and speciation in a high pH regime.

It is well known that the solubility of silica in sodium hydroxide solutions increases strongly with pH (Alexander et al., 1954; Greenberg and Price, 1957) and concentrated NaOH solutions will dissolve increasingly large amounts of silica gels (Greenberg and Sinclair, 1955; Greenberg, 1957; Iler, 1979) until, in about a 5 molar NaOH medium at 25°C, gelatinous water glasses of the general formula $\text{Na}_2\text{SiO}_3 \cdot x\text{H}_2\text{O}$ are formed (Gmelin, 1964). Unfortunately, in strong alkaline solutions the amount of total dissolved silica as function of pH is not known and predicted solubilities at high pH differ by orders of magnitude. Up to a pH of about 10.5, the processes controlling the solubility of amorphous silica are fairly well understood but, due to the lack of reliable solubility data at high pH as well as to different interpretation of stable silica species and their equilibrium constants, a large scatter of predicted total silica solubilities at very high pH is found in the literature. One of the major problems is the uncertainty of the value of the second dissociation constant of aqueous monomeric silicic acid but also less work has been done to determine association constants between poly- and mononuclear silica species. As will be shown in this study, all reported analytical data obtained at high pH require either a low pK for the second dissociation reaction or the presence of additional polymeric species. The stability of polymers in both dilute and strong sodium hydroxide solutions has been discussed intensively and some of the conclusions will be briefly presented here:

In aqueous solutions which are supersaturated with respect to amorphous silica, polymerisation proceeds until colloidal solutions are produced and silica gel begins to precipitate. As many reactions involving polysilicates are very slow, establishment of chemical equilibrium often requires several months. Therefore, extraction of equilibrium constants from experimental measurements of different polynuclear silica species has to be done with some care. Note that it is also extremely difficult to detect the structure of the different polymeric species by means of common analytical techniques. Nevertheless, with modern potentiometric methods certain polysilicate equilibria have been reported (Lagerström, 1959; Ingry, 1959; Sjöberg et al., 1985). In contrast to silica supersaturated solutions, Bilinsky and Ingry (1967) could show that, in both dilute and strong electrolyte solutions at 25°C, only mononuclear silica species will be formed at least up to a total concentration of dissolved silica of 0.001 M. Similar observations have been made by Greenberg (1957), who studied polymerisation kinetics of silica in sodium hydroxide solutions. He observed a decrease of low molecular weight polynuclear silica species with increasing pH and proposed that these species are destroyed by peptisation. He, therefore, concluded that a considerable number of his experiments could be interpreted without postulating the existence of polymeric silica particles. In

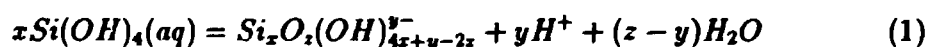
contrast to these authors, Alvarez and Sparks (1985), using laser Raman spectroscopy, gave evidence that dilute aqueous sodium silicate solutions contain polymers and not just monomers. Similar conclusions have been given by Cary (1982) in a NMR study and Applin (1987), who studied the diffusion of dissolved silicic acid in neutral water.

It should be mentioned, in addition, that in high alkaline media silica ion pairing may also become important (Seward, 1974). The question is, therefore, to evaluate to what extent polynuclear silicic and silica sodium complexes are present in silica saturated, strong sodium hydroxide solutions. Besides the modelling work presented in section 4 in this study, additional information is presented concerning a) the chemistry of the different silica species which will be considered and b) the different analytical techniques generally being used to determine dissolved silica and thermodynamic data. Note, that reading of these sections (2 and 3) is not a prerequisite for the modelling section, but the information given there is intended to give the reader some basic background knowledge of the chemistry of silica in alkaline medium. Furthermore, explanations are given as to why the solubility of silica and its speciation at high pH is poorly understood.

2 The Different Silica Species

2.1 Notation of the equilibrium constants

Before presenting the different silica species and equilibria, the notation of the equilibrium constants will be briefly explained. The chemical equilibrium between different silica species involving simple dissociation and polymerisation can be generally written in terms of hydrolysis of the neutral dissolved silica species $\text{Si}(\text{OH})_4(\text{aq})$:



where x refers to the numbers of Si bound per molecule and y to the charge of the species. Thus, for any given values of x , y and z , it can be distinguished between the different species. Application of the law of mass action yields the equilibrium constants between the silica species, and $\log K$ -values are used to describe the equilibrium between two directly related species. To conform with standard literature data, all reactions given in the text are related to the basic aquatic silica species $\text{Si}(\text{OH})_4(\text{aq})$ and all equilibrium constants of species which are not directly related, are denoted by $\log \beta_{x,y}$.

2.2 The solid phases

Among the major naturally occurring solid SiO_2 -phases, three modifications have to be distinguished, each with different physical and chemical properties. SiO_2 occurs mainly as a) amorphous, uncrystallized and optical opaque silica gel or opal, as b) microcrystalline chalcedony and as c) well crystallized, optically anisotropic quartz. In nature, amorphous silica is often precipitated from hot alkaline spring waters due to a decrease in temperature and/or pH. Silica gels may also precipitate in shallow marine or fluvial environments by biologic activity. If such sediments are exposed to slightly higher temperatures and pressures, diagenetic processes will occur leading to formation of chalcedony. This phase can, however, also be formed directly by organic production from marine algae (mainly spongiae) or from silica supersaturated hydrothermal solutions into shallow crustal environments. The most common SiO_2 -mineral of the earth's crust is quartz. This rock forming mineral is formed during crystallization of intermediate and acidic magmatic melts and during most of the metamorphic processes in the earth's crust.

2.3 Monomeric species

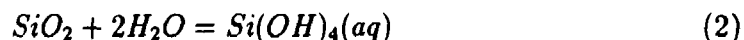
The solubility of solid SiO_2 has been measured in neutral and dilute alkaline aqueous solutions at 25 °C and 1 bar and the results for quartz and amorphous silica are presented in table 1. ¹ This table also includes the method used to obtain the data. The following methods have been used: a) experimental techniques (colorimetric silicomolybdate, potentiometric and conductivity measurements), b) calculations (fitting of published thermodynamic data) and c) recommendations (from critical review). Note that the most common experimental techniques will be explained in section 3.1.

¹Since the pH dependency of chalcedony has not been investigated, no thermodynamic data of this mineral are considered in this report. Note that all measured chalcedony solubilities are between quartz and amorphous silica. This is plausible because its crystallinity is intermediate between these phases.

Table 1: Compilation of reported $\log K_s$ -values for amorphous silica and quartz at 25°C.

amorphous silica	quartz	method	reference
-2.70		silico-molybdate	Alexander et al. (1954)
-2.55		silico-molybdate	Goto et al. (1955)
-2.74		silico-molybdate	Greenberg and Price (1957)
	-3.74	calculated	van Lier et al. (1960)
	-4.00	silico-molybdate	Morey et al. (1962)
	-3.97	calculated	Morey et al. (1962)
	-4.00	silico-molybdate	Keller et al. (1963)
-2.89		potentiometry	Jørgensen (1968)
	-4.00	calculated	Henderson et al. (1970)
-2.70		silico-molybdate	Marsh et al. (1975)
	-4.00	calculated	Baes and Mesmer (1976)
-3.02	-3.98	recommended	Smith and Martell (1976)
-2.60	-4.00	recommended	Iler (1979)
-2.70	-3.97	calculated	Rimstidt and Barnes (1980)
	-3.98	calculated	Fournier and Potter (1982)

Due to the low solubility of SiO_2 in pure water, the structure of the dissolved neutral species has not yet been clearly determined by common spectral methods. Nevertheless, the dissolution of SiO_2 in water is generally believed to be the result of the acceptance of two water molecules per SiO_2 . Thereby a molecule, with Si in the center surrounded by four OH-groups in tetrahedral coordination, is formed (Iler, 1979). This means that the dissolution of silica in neutral water is limited by the solubility of SiO_2 as an undissociated acid, that is, by the chemical equilibrium:



Application of the law of mass action yields the solubility product, K_s , which equals the activity of dissolved hydrous silica in equilibrium with solid SiO_2 :

$$K_s = \{\text{Si}(\text{OH})_4(\text{aq})\} \quad (3)$$

Whereas reported $\log K_s$ -values in table 1 agree fairly well for quartz, those for amorphous silica are scattered between 2.5 and 3.0. Reasons for this scatter of data are given in section 3.2. In any case, quartz is about 1 order of magnitude less soluble than amorphous silica. Dissolution experiments with quartz indicated, however, that the surface

of dissolving grains were covered by a thin layer of amorphous silica (Baumann, 1955; Stöber, 1956). Therefore these authors concluded that the solid SiO_2 -phase in a quartz saturated aqueous solution is silica gel, which means that the dissolution of quartz in water must be an irreversible process. There is, however, no further evidence found in the literature supporting this hypothesis.

In order to obtain a better understanding of important chemical processes in the earth's crust and mantle, the solubility of silica has also been studied in high pressure and temperature experiments (Crerar and Anderson, 1971; Walther and Helgeson, 1977; Rimstidt and Barnes, 1980; Rignatsdottir and Walther, 1983; Fournier, 1980; Fournier and Potter, 1982; Kaiser, 1984). Crerar and Anderson (1971) calculated a temperature function for the approximation of quartz solubility in the range of 123 - 350°C by least square polynomial fits of their measured data, and obtained the following relation,

$$\log K_s^{\text{quartz}} = -1.468 + 252.9/T - 3.217 \cdot 10^5/T^2 \quad (4)$$

where T is the absolute temperature in K.

Rimstidt and Barnes (1980) calculated the temperature dependence of amorphous silica and quartz solubility in the range of 0 - 300°C based on stoichiometry and activity of the reactants in equation 1. They proposed the following relations:

$$\log K_s^{\text{quartz}} = 1.888 - 2.028 \cdot 10^{-3}/T - 1560/T \quad (5)$$

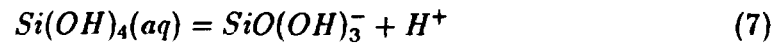
$$\log K_s^{\text{am.silica}} = -0.338 - 7.890 \cdot 10^{-4}/T - 840/T \quad (6)$$

Table 2 summarizes published $\log K_s$ data for quartz at 90 °C because, in the modelling section, the pH dependence of quartz was also studied at this temperature.

Table 2: Compilation of reported logK_s-values for amorphous silica and quartz at 90°C.

amorphous silica	quartz	method	reference
-2.12		silico-molybdate	Goto (1955)
	-3.05	silico-molybdate	van Lier et al. (1960)
	-3.05	calculated	van Lier et al. (1960)
	-3.20	calculated	Crerar and Anderson (1971)
	-3.16	calculated	Walther and Helgeson (1977)
	-3.16	calculated	Fournier (1980)
-2.26	-3.14	calculated	Rimstidt and Barnes (1980)

Although there is some evidence for a neutral dimeric silica species besides Si(OH)₄(aq) (Applin, 1987), formation of polymers in neutral or slight alkaline solutions is negligible (Alexander et al., 1954; Fleming and Crerar, 1971; Bilinski and Ingry, 1967; Iler, 1979; Schwarzenhuber et al., 1987). In strong alkaline solutions, however, a dramatic increase of the silica solubility has been observed (Alexander et al., 1954; Goto, 1955; Greenberg and Price, 1957; Greenberg, 1957; Van Lier et al., 1960; Marsh et al., 1975; Iler, 1979; Schwarzenhuber et al., 1987). This trend is generally interpreted by the dissociation of the neutral, monomeric silicic acid in more alkaline media:



Application of the law of mass action yields the equilibrium constant, K_{1,1}, of the first dissociation reaction:

$$K_{1,1} = \frac{\{SiO(OH)_3^-\}\{H^+\}}{\{Si(OH)_4(aq)\}} \quad (8)$$

As presented in table 3, fairly similar results were obtained for logK_{1,1} at 25 °C, although three different techniques have been used. The high pK of about 10 for this reaction indicates that Si(OH)₄(aq) is a weak acid. This means that the total silica solubility will not change significantly below a pH of 10.

Table 3: Compilation of reported values of the first and second dissociation constant of silicic acid at low temperatures. Those results which are marked with an asterisk have not been corrected for ionic strength.

$\log K_{1,1}$	$\log \beta_{1,2}$	T[°C]	method	reference
-9.80	-21.96	30	conductivity	Roller and Ervin (1940)
-9.80		25	silico-molybdate	Alexander et al. (1954)
-9.77		25	silico-molybdate	Greenberg and Price (1957)
-9.85	-21.65	25	conductivity	Greenberg (1958)
-9.60		25	conductivity	Schwartz and Müller (1958)
-9.46 *	-22.02 *	25	potentiometry	Lagerström (1959)
-9.43 *	-22.14 *	25	potentiometry	Lagerström (1959)
-9.51 *	-22.02 *	25	potentiometry	Ingri (1959)
-9.46 *		25	potentiometry	Bilinski and Ingry (1967)
-9.80	-21.61	25	conductivity	Ryzhenko (1967)
-9.90	-21.60	25	calculated	Ryzhenko (1967)
-9.80	-22.20	25	LRS	Freud (1973)
-9.80		25	silico-molybdate	Marsh et al. (1975)
-9.86	-22.92	25	calculated	Baes and Mesmer (1976)
-9.82		25	calculated	Busey and Mesmer (1977)
-9.83	-23.10	25	potentiometry	Sjöberg et al. (1981)
-9.84	-23.27	25	calculated	Sjöberg et al. (1985)
-9.81	-23.14	25	calculated	NEA-TDB (1989)

The first dissociation constant of silicic acid is strongly dependent on temperature. Fleming and Crerar (1982)² summarized literature data from 0 - 350°C and calculated an empirical function for the temperature dependence of $K_{1,1}$:

$$\text{Log} K_{1,1} = 1479/T - 0.6496 - \text{Log} K_w(T) \quad (9)$$

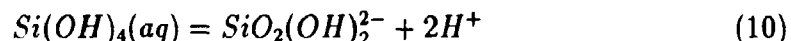
where T is the absolute temperature in K and K_w is the dissociation constant of water at the given temperature. Measured and calculated $\log K_{1,1}$ -values at higher temperatures are given in table 4. This table shows that as for 90°C, as for 25°C, agreeing $\log K_{1,1}$ -values have been published.

²These authors calculated, in addition, the solubility of quartz and amorphous silica up to 300°C and pH 12. Note, however, that in their model only the monomeric silica species $\text{Si}(\text{OH})_4(\text{aq})$ and $\text{SiO}(\text{OH})_3^-$ are considered.

Table 4: Compilation of reported values for the first and second dissociation constant of silica at higher temperatures. Those results which are marked with an asterisk have not been corrected for ionic strength.

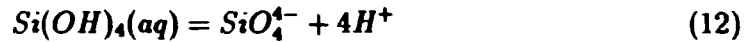
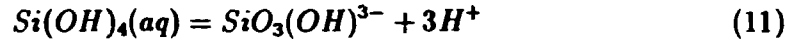
$\log K_{1,1}$	$\log \beta_{1,2}$	T[°C]	method employed	reference
-9.20		90	silico-molybdate	van Lier et al. (1960)
-9.20	-18.44	100	conductivity	Ryzhenko (1967)
-9.24	-18.39	90	calculated	Ryzhenko (1967)
-9.65 *	-22.25 *	60	potentiometry	Busey and Mesmer (1977)
-9.20		90	calculated	Busey and Mesmer (1977)
-9.20		90	calculated	Crerar and Anderson (1970)
-9.17	-19.87	90	silico-molybdate	Schwarzenhuber et al. (1987)

Harman (1928) was the first to propose the existence of a doubly negative charged silica monomer, formed by hydrolysis of the metasilicate Na_2SiO_3 in dilute aqueous solutions. According to Roller and Ervin (1940), Greenberg (1958), Ryzhenko (1959), Ingry (1959), Lagerström, (1959), Freud (1973) and Sjöberg et al. (1981, 1983), such a species is only important in strong hydroxide solutions. Evidence for the existence of this species in a mixture of sodium metasilicate and sodium hydroxide has been given by Early (1959) and Freud (1973) by the use of Raman spectroscopy and it is generally believed that the chemical formula of this species is $\text{SiO}_2(\text{OH})_2^{2-}$. In analogy to equation (7), the second deprotonation reaction for monomeric hydrous silica is then given by the following reaction:



A compilation of published $\log \beta_{1,2}$ -values is also given in table 3. In contrast to the well known first dissociation constant, $\log \beta_{1,2}$ -values vary from 21.6 (Greenberg, 1958, Ryzhenko, 1967) to values about 23.3 (Baes and Mesmer, 1976; Sjöberg et al., 1981, 1983; NEA-TDB, 1989). The reliability of the early results from Greenberg and Ryzhenko has been criticised by several authors (Baes and Mesmer, 1976; Busey and Mesmer, 1977; Sjöberg et al., 1981, 1983). By extrapolation of selected analytical data to zero ionic strength, the NEA recently calculated a value of 23.14 (NEA-TDB, 1989). This would mean that $\text{SiO}_2(\text{OH})_2^{2-}$ would be less important below a pH of about 13. This also explains the scatter of reported $\log \beta_{1,2}$ -values. Since $\text{SiO}(\text{OH})_3^-$ is a weak acid, changes in measured hydroxide concentrations produced by further silica hydrolysis are small and difficult to measure accurately at the high OH-concentrations.

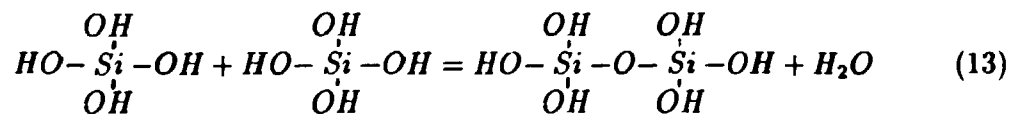
A further stepwise dissociation of silicic acid has been reported by Freud (1973). By interpreting Raman laser spectra he detected stable $\text{SiO}_3(\text{OH})^{3-}$ as well as $\text{SiO}(\text{OH})_2^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$, in different sodium silicate solutions and proposed the following equilibria:



Freud did not succeed in detecting the species SiO_4^{4-} and explained this by an extreme high $\text{pK}_{1,4}$ -value of about 18. In addition, he also proposed an extreme high value of about 15 for $\text{pK}_{1,3}$. Because no further evidence for the existence of these species in aqueous solutions has been mentioned in literature, they are likely to be meaningless in silica saturated solutions, even at extremely high OH-concentrations. Therefore these species are not considered in the present modelling study.

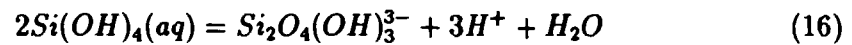
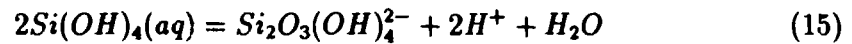
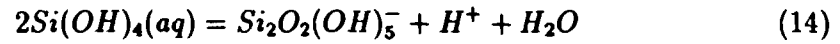
2.4 Polymeric species

Polymerisation is a general name for any process by which large molecules are produced by small ones joining together. The polymerisation of silicic acid has been referred to frequently as a condensation reaction (Greenberg and Sinclair, 1955; Iler, 1979; Applin, 1987). According to Bishop and Baer (1972), who studied polymerisation kinetics of silicic acid in dilute aqueous solutions, the most simple condensation reaction to form a neutral dimer is likely to proceed in this way:



Silica polymorphs are formed in silica supersaturated solutions prior to precipitation of a silica gel (Iler, 1979). It has been shown that, during coagulation of silica particles to form a pure silica gel, several bound OH-groups per molecule will disappear by the formation of strong O-bonding. Therefore it is likely that the influence of a strong base will cause peptisation of the particles, which results in a reformation of OH-groups by hydration and formation of dissolved silica species (Gmelin, 1959). The stability of silica polymorphs in alkaline media has also been discussed by Iler (1979). He pointed out that condensation of highly concentrated sodium silicate solutions leads to formation of silica water glasses. These water glasses will decompose to form firstly colloidal

particles and then polymers in more dilute aqueous solutions. In increasingly dilute solutions of sodium silicate below 0.1 M, polymerisation will decrease drastically until, in more dilute media, only monomeric species become stable. The existence of distinct polymers in concentrated solutions of Na- and Ca-silicates was first suggested by Roller and Ervin (1940) by using a potentiometric titration technique. These authors suggested the existence of three negatively charged silica dimers, formed by the hydrolysis of calcium silicate. They proposed the following equilibria:



From their data, Roller and Ervin (1940) also calculated formation constants for these polymer equilibria. These results are presented in table 5. There is some doubt whether Roller and Ervin interpreted their data correctly, because of the unknown contribution of silica calcium ion pairs to total dissolved silicate (Iler, 1979). Note that such complexes are likely to occur in strong calcium hydroxide solutions (Santschi and Schindler, 1974).

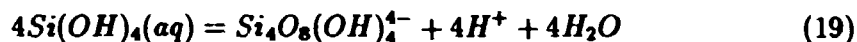
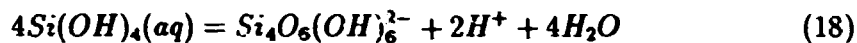
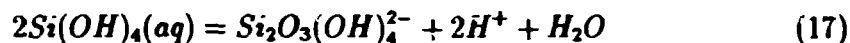
Table 5: Compilation of reported log-values of the equilibrium constants between silica polymers and $\text{Si}(\text{OH})_4(\text{aq})$. The references are the following: (1) Roller and Ervin (194), (2) Lagerström (1959), (3) Ingry (1959), (4) Baes and Mesmer (1976), (5) Sjöberg et al. (1985), (6) Applin (1987), (7) NEA-TDB (1989). The values marked with an asterisk are not corrected to $I = 0$.

X,Y	(1)	(2)	(3)	(4)	(5)	(6)	(7)
2,0						+2.52	
2,1	-6.46				-7.75 *		-8.1
2,2	-16.26	-18.12 *			-18.00 *		-19.0
2,3	-29.06						
3,3(cyclic)					-26.43 *		-28.6
3,3(linear)					-25.40 *		-27.5
4,2		-12.57 *	-12.37 *	-13.44			
4,3					-23.42 *		-25.5
4,4		-32.48 *		-35.80	-32.81 *		-34.9
5,5					≤ -41.5 *		

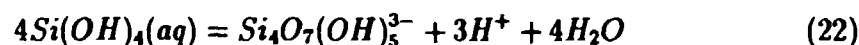
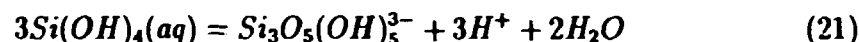
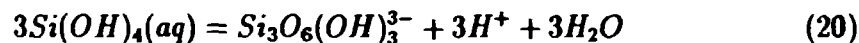
A few years later, Alexander et al. (1954) proposed the presence of polynuclear species in silica saturated NaOH solutions, at least above pH 11. They measured a total silica solubility which was a factor of two higher than could be explained by the use of the equilibria given in equations 2 and 7. In their study, dissolved silica was detected colorimetrically using the silico-molybdate method (see section 3). At pH 11, half of the dissolved silica reacted with molybdic acid in less than two minutes to form a coloured silico-molybdic complex. The other part of the silica reacted much more slowly, and formation of the silico-molybdic complex was completed is not less than 40 minutes. One year previously, however, Alexander (1953) observed that monomeric silica species react with molybdic acid very rapidly, while polysilicate acids react more slowly because they first have to decompose before they undergo reaction with molybdic acid.

Lagerström (1959) was the first to use modern potentiometric methods to investigate polysilicate equilibria being formed by hydrolysis of amorphous silica in alkaline solutions. He carried out conductivity measurements in a 0.5 M NaClO_4 medium at 25°C and proposed stability constants of the tetrameric species $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$, besides $\text{Si}(\text{OH})_4(\text{aq})$, $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$. In a more concentrated 3 M NaClO_4 medium, he calculated the presence of additional dimeric $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ and tetrameric $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$ and

proposed, in summary, the following equilibria:



The polymerisation constants of these and the following polymer equilibria are also given in table 5. By application of the extended Debye-Hückel theory, Baes and Messmer (1976) extrapolated the tetramer formation constants from Lagerström to zero ionic strength. In a further potentiometric study using a 0.5 M NaCl electrolyte medium and dilute sodium silicate solutions, Ingry (1959) confirmed the presence of an tetramer of the composition $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$. In addition, he obtained similar thermodynamic data for this species as proposed by Lagerström (1959). Sjöberg et al. (1985) made a combined potentiometric and Si-NMR study of polysilicates in a pH range between 11.0 and 12.2 using a 0.6 M NaCl medium. They pointed out that further polysilicate species should also be considered as well. In particular, the additional following sets of equilibria were proposed:

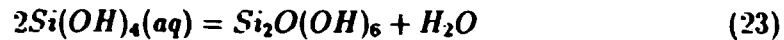


Two of the polymeric species were determined to be cyclic, a trimer of the form $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$, as well as a tetramer of the form $\text{Si}_4\text{O}_7(\text{OH})_5^{3-}$. The other trimeric species, $\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$, was proposed to have a linear structure. Besides a stable dimer of the form $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$, which was also found by Lagerström (1959) their experimental data indicated the existence of the deprotonated form of this species (see equation 13). Evidence for this species has been given much earlier by Roller and Ervin (1940). Note that Sjöberg et al. (1985) also proposed the presence of a 5-fold negatively charged pentamer. For this species, however, no chemical formula was presented.

Under the assumption of similarity of the ion interaction coefficients between phosphoric and silica species, the NEA recently extrapolated the equilibrium constants from Sjöberg et al. (1985) to zero ionic strength (NEA-TDB, draft, 1989).

In a more recent study, the presence of a stable uncharged dimer of the form $\text{Si}_2\text{O}(\text{OH})_6$ was reported by Applin (1987), who studied the diffusion of dissolved silicic acid in neutral water. Diffusion coefficients were obtained by measuring the dissolved silica

content of the distilled water after a given length of time. As the measured diffusion coefficients decreased as function of increasing silica concentration he proposed the following equilibrium:



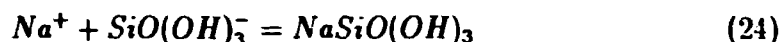
Evidence for this dimer species has been given before by Cary et al. (1982) in a NMR study performed in neutral aqueous solutions containing 1.6 mM dissolved silica. He estimated about 6 per cent of the dissolved silica species being present as $\text{Si}_2\text{O}(\text{OH})_6$. If the equilibrium constant for equation (23) from Applin (1987) is used (see table 5), it is concluded that, for the 1.6 mM solution, about half of the dissolved silica would be converted to this dimeric species. Therefore the validity of this equilibrium constant may be in doubt. The species $\text{Si}_2\text{O}(\text{OH})_6$ is not considered in the present modelling work.

2.5 Silica-sodium complexes

The possibility of complex formation or ion pairing of neutral and deprotonated silicic acid with metal ions such as Na^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} and Fe^{3+} is an important question often raised by geochemists. Unfortunately, there is little information concerning the ligand properties of deprotonated $\text{Si}(\text{OH})_4(\text{aq})$. Therefore the association properties of silicic acid and positively charged ions cannot be predicted theoretically. About 20 years ago, the occurrence of silica ion pairing in natural aqueous systems was first reported by Weber and Stumm (1965). They determined a silica iron complex of the form $\text{FeSiO}(\text{OH})_3^{2+}$. In laboratory experiments, complex formation of silicic acid with Ca^{2+} and Mg^{2+} has been studied by Santschi and Schindler (1974). Preliminary model calculations of the stability of silicate minerals in a high pH environment of a cement based nuclear waste repository showed that the complexes $\text{Ca}(\text{SiO}(\text{OH})_3)_2$ and $\text{CaSiO}_2(\text{OH})_2$ might contribute significantly to the silicate speciation in the pore waters of the altered near field (Eikenberg, 1990). For the current modelling study, it is, however, only of interest to investigate silica ion pairing in sodium hydroxide solutions.

Association between the sodium ion and silicic acid has been discussed by Crerar and Anderson (1971), Baes and Mesmer (1976), Sjöberg et al., (1983) and Applin (1987). These authors pointed out that, in dilute neutral or slightly alkaline solutions, silica-sodium complexes will not be formed in significant amounts. The question is, however, to what extent these complexes are stable in more alkaline media. It has been suggested

that complexation of dissociated silica with Na^+ proceeds in the following manner (Seward, 1974):



Seward investigated this association reaction over a temperature range of 135 - 301°C and determined $\log K_{\text{ass}}$ -values between 1.2 and 1.4 for this reaction. Unfortunately in this study no information is given about the enthalpy change with temperature. Assuming the $\log K_{\text{ass}}$ -values to be similar at lower temperatures, silica sodium ion pairing will contribute significantly to the silica solubility above 0.1 NaOH molarity (see section 4). A critical review of the work of Seward (1974) has been made by Busey and Mesmer (1977). They pointed out several technical reasons why the experimental data should be treated with some care. In addition, they observed a very small salt effect on the first silica deprotonation equilibrium in concentrated (1 - 5 molar) NaCl media. Therefore, they concluded that little or no sodium silica complexation will appear, even in strongly alkaline solutions.

Marshall (1980) and Marshall and Warakomski (1980) studied the solubility of amorphous silica in sets of different salt solutions of mainly Na-, K-, Mg-, Ca-chlorides, -sulphates and -nitrates. In their experiments, the salt concentrations were varied from 0 - 6 molar, the pH between 4 and 10 and the temperature between 0 and 300°C. In contrast to what would be expected if complexation of silica with other ions in the solution would have taken place, a decrease of the silica solubility with increasing concentration of salt was observed at low temperatures. Also, no significant change in pH was observed. This "salting-out effect" indicated that no significant complexation of silicic acid with the alkali ions of the salts occurred, because complexation should increase the total silica solubility. The authors further concluded that "salting-out" is also dependent on the hydration number of cations surrounded by water molecules. A high hydration number means that the number of "free" molecules of the solvent (water) will decrease, which causes a lower silica solubility. At elevated temperatures above 100°C, however, an increase of dissolved silica with salt concentration was observed. This effect was now explained with silica salt complexation, which is important only at higher temperatures. Rowe et al. (1968) studied the phase relations in the aqueous system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ at temperatures between 200 and 300°C. According to their data, no sodium silica compounds should be stable at low NaOH concentrations ≤ 0.1 M but complexation was predicted to become important in stronger alkaline media.

2.6 Summary

The solubility of silica and the first dissociation constant of silicic acid are well known over a wide range of temperatures at standard pressure. At 25°C the solubility of silica in SiO₂ saturated solutions is well understood up to a pH of about 10.5. Solubility data obtained at higher pH indicates, however, the presence of additional silica species. One of the species being suggested is the monosilicate SiO₂(OH)₂²⁻, which is found at very high pH.

Potentiometric studies performed in silica rich solutions give evidence for the presence of negatively charged low molecular weight silica polymers, such as dimers, trimers and tetramers. At standard temperature, such species might increase the total silica solubility dramatically at high pH, but most probably polymerisation decreases rapidly with increasing temperature.

By analogy to polymerisation, complex formation of silicic acid with the sodium ion has been reported to be insignificant in dilute NaOH solutions. Experiments performed in strong electrolyte solutions indicated, in addition, that silica sodium ion pairing is also insignificant in strongly alkaline media, but is likely to gain importance at elevated temperatures.

3 Evaluation of Literature Data

3.1 Analytical techniques employed

Silica hydrolysis has been studied by application of different analytical techniques: potentiometric titration techniques in a hydrogen electrode or glass electrode concentration cell (emf-method), conductivity measurement, atomic adsorption spectroscopy (AAS), laser Raman spectroscopy (LRS), nuclear magnetic resonance methods (NMR), light scattering or colorimetric methods such as spectrophotometry of silico-molybdic complexes (silico-molybdate blue or yellow method). The most widely used technique, potentiometry by hydrogen electrode, allows accurate measurements of the hydrogen ion concentration as a function of the solution composition and temperature. With the determination of the H⁺-concentration (and therefore OH⁻) and a knowledge of the composition of a given solution, it is possible to calculate the number Z of OH⁻ bound per Si. This corresponds to the average negative charge per Si. By varying the Si-

concentration of the solution, Z will also vary and due to this variation, equilibrium constants may be obtained very accurately. Since the emf-method allows only the determination of number of Si-atoms per molecule and the charge of the silica species, the H_2O -content of the species has to be assumed. In some experiments, it was attempted to determine the water contents by additional nuclear magnetic resonance methods or spectroscopic studies. The complete formula of the polymers presented in equations 17–19 is, for instance, assumed from what is known of the structural chemistry of silicates (Lagerström, 1959). The chemical formula of the polymers in equations 14–15 and 19–22 was obtained by a Si-NMR study (Sjöberg et al., 1985). For the determination of polysilicate equilibria, the essential advantage of the emf-method is that chemical equilibria are rapidly obtained because solutions with Si-concentrations far below saturation can be investigated at high pH.

Colorimetric methods, i.e. mainly spectrophotometry of a silico-molybdic complex, have been applied to those experiments in which the total silica solubility as function of pH has been measured. Such experiments are performed in a temperature controlled cell and the optical density of the silico-molybdic complex at a distinct wavelength is measured with a spectrophotometer.

All other spectroscopic or photometric methods such as Raman spectroscopy or light scattering, are commonly used to determine the structure and formula of a dissolved species. They are, however, often not sensitive enough to distinguish unambiguously between the different silica species, but they are helpful for a better interpretation of potentiometrically derived results.

3.2 Quality of analytical data

A wide range of data have been reported on the solubility of quartz and amorphous silica as function of temperature. Unfortunately, less data are available as function of pH. In the following, some reasons will be presented which should help to understand the disagreement between published thermodynamic data.

1. Grinding of quartz particles is a common procedure to obtain a large surface area, because chemical equilibrium is then more rapidly attained. Grinding might, however, produce a disturbed surface layer, which leads to solubility properties intermediate between crystallized quartz and amorphous silica (Henderson et al.,

1970). These authors pointed out that the removal of the disturbed surface layer is essential before the solubility of quartz can be determined accurately. This factor has not been considered in the older literature.

2. Different solubility data for amorphous silica resulted from the use of different analytical techniques and forms of amorphous silica being studied. Such forms are wet silica gel, colloidal particles in the form of a sol or finely ground powder. Solubility has been studied mainly by dissolution, but also by precipitation of silica sols by removal of Na^+ from sodium silicate solutions.
3. Due to slow silica dissolution at low temperatures, chemical equilibria between silica species and solid SiO_2 are reached after a long period of time (several months) only. Some of the solubility experiments from van Lier et al. (1960) and Henderson et al. (1970) at 25 °C were performed, however, in less than 14 days, a time at which in similar experiments (Alexander et al., 1954; Mash et al., 1975) equilibrium was not reached.
4. The reaction rate of silica dissolution is strongly dependent on temperature and pH. Schwarzenhuber et al. (1987) and Knaus and Wolery (1987) demonstrated that the dissolution rate of quartz strongly increases with pH. Greenberg and Sinclair (1955), however, showed by a light scattering study that the reaction rate of polymers is still low in high pH solutions and attainment of polymer equilibria has not reached completion within weeks. This means that the time scale of polymer equilibria is still unknown and extraction of formation constants has to be done with some care. Since the reaction rates are much faster at higher temperatures, the dissolution of quartz in NaOH solutions has also been studied at 90°C (van Lier et al., 1960; Schwarzenhuber et al., 1987). Extrapolation of their data to 25°C is, however, not possible as the temperature dependence of the equilibrium constants between silica reactions involving polymers and silica sodium complexes is not known.
5. In order to be able to evaluate the quality of silica equilibrium constants measured, solubility data at high pH would be helpful. Unfortunately, such data are rarely found in literature. One of the reasons is that pH measurements at high hydroxide concentration do not give accurate results due to the alkali error of the electrodes and the reaction of the electrode material with the solution.
6. The investigation of polymer equilibria by potentiometric methods are performed in high molar salt solutions. Therefore correction of thermodynamic data for ionic

strength is not that trivial. It is also possible that reactions involving different, but still not observed polymeric species have to be considered as well. In addition, complex formation of the polymer ligands with the ions of the electrolyte might have occurred in some conductivity experiments.

7. Unfortunately, at 25 °C, association constants for the equilibrium of the sodium ion and silicic acid are not known. A link between reported association constants for Ca^{2+} - and Mg^{2+} - silica complexes and dissociated silicic acid at 25°C (Santschi and Schindler, 1974) and single charged Na^{+} - is very doubtful and hence has not been investigated in this work.

3.3 Summary

Silica solubility data and equilibrium constants are mainly determined by potentiometric measurements and the colorimetric silico–molybdate method. The latter yields the most reliable results of the total silica solubility as well as the concentration of the monomeric species in solution. Unfortunately, pH measurements in very strong NaOH solutions have not been performed because of problems due to reaction of the electrode material with the solution.

In contrast to the silico–molybdate method, potentiometric studies allow determination of the equilibrium constants between polymeric species. Those measurements are generally performed, however, in strong electrolyte solutions, because of the much better accuracy of the data. Therefore a reliable correction for ionic strength could be a great problem. Also, possible complex formation of polymeric species with the cations of the electrolyte has never been discussed.

Correct preparation of the solutions is a prerequisite for accurate results. Due to the different analytical procedures being used, different solubility data might have resulted. The most important rôle, however, is played by the reaction rates for the different species. The rates are strongly dependent on temperature, pH and the solution composition. It is doubtful if, in all experiments, chemical equilibrium has been reached.

4 Modelling Work

This section is based mainly on a comparison study of reported silica solubility data as a function of pH with different model curves. Only analytical data obtained in sodium hydroxide solutions were considered. These data are given in tables 8 and 9 in appendix A. The core of the modelling work is a parameter variation of rather uncertain equilibrium constants for silica poly- and monomers. It was attempted to develop a model which describes most reliably the silica speciation and its solubility, even in strong hydroxide solutions. First of all, it is of prime importance whether polymeric species have to be considered besides monomers in a higher pH region, or if analytical data can be explained with monomeric species only by simple variation of the uncertain value of $\log \beta_{1,2}$. In addition, a sensitivity analysis was performed in order to investigate the influence of silica-sodium pairing at a high pH. This has been done by a parameter variation study of the proposed association equilibrium between Na^+ and dissociated silicic acid. The silica solubility was studied at 25°C and 90°C, since most of the analytical data refer to these temperatures. All speciation calculations were performed by the use of the geochemical equilibrium code MINEQL/EIR (Schweingruber, 1980, 1981, 1982). Since this computer code uses the Davies-approximation for calculation of the ionic strength, all model calculations have been performed only up to $I = 0.5$ M (explanations are given in appendix B). This study focusses on the following topics in detail:

1. Value of the solubility product of amorphous silica.
2. Evaluation of the second deprotonation constant of aqueous silica.
3. Discussion of the presence of charged silica polymer species besides monomers and evaluation of their thermodynamic properties.
4. Discussion of the influence of sodium silicate complexes in highly alkaline environments.

4.1 Silica solubility in sodium hydroxide solutions at 25°C

The modelling work was started first by the use of the most recently recommended and updated silica equilibrium constants. Solubility constants for quartz and amorphous silica were taken from Rimstidt and Barnes (1980) and all deprotonation constants

from the NEA-TDB draft (1989). The values used are summarized in table 6 and the application of these constants to calculate the silica solubility will be denoted as model 1A. Before presenting the other three models in this table, let us first compare model 1A with the measured solubility data for amorphous silica (table 8, Appendix A). These data are plotted in a solubility versus pH diagram as shown in figure 1.

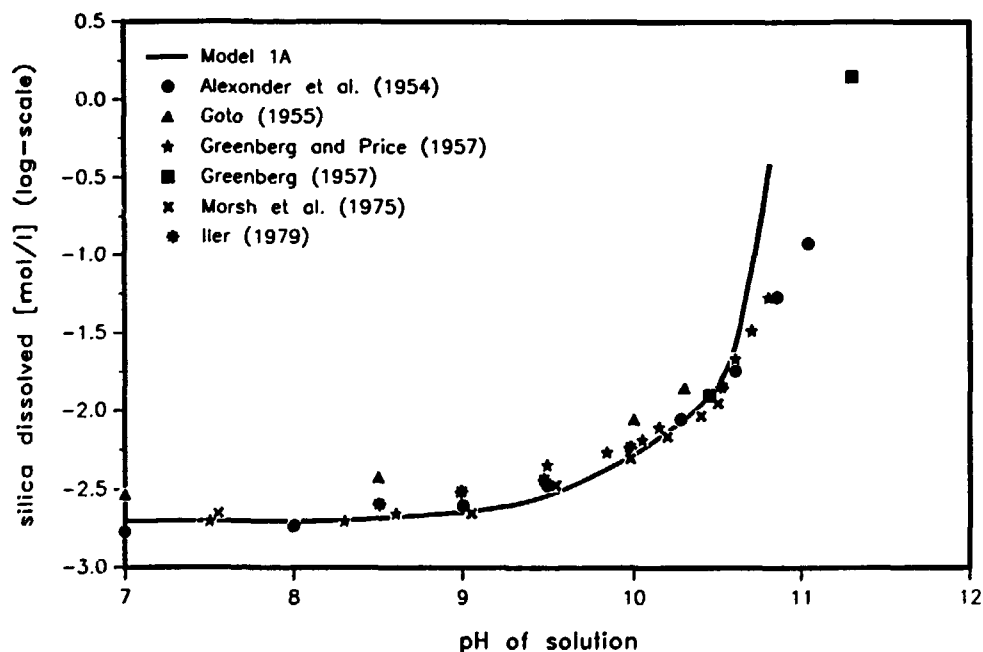


Figure 1: Solubility of amorphous silica in sodium hydroxide solutions as a function of pH at 25°C. Besides the analytical data, the calculated solubility according to model 1A is plotted.

In this figure, the calculated solubilities according to model 1A have also been drawn. It is obvious that this curve does fit quite well the measured solubility the data up to a pH of about 10.5. Therefore, the use of the $\log K_s$ -value of -2.70 from Rimstidt and Barnes (1980) is recommended. From pH 9 to pH 10.5, the increasing solubility by pH is best explained with additional dissociation of $\text{Si(OH)}_4(\text{aq})$, by using of the generally accepted value of -9.81 for $\text{Log}K_{1,1}$ (NEA-TDB, 1989).

Above pH 10.5, however, the calculated solubility is significantly higher than the analytical data indicate. Therefore it is obvious that the further set of equilibrium constants used here cannot be directly applied to calculate the solubility of amorphous silica above this pH. In order to estimate the silica solubility at high pH more realistically, three additional models have been introduced for the following reasons:

1. From the literature review study (section 2 and 3), it remains uncertain whether the analytical data can be explained with pure monomeric species or with additional polymers. Therefore a rough distinction will be made between model 1 (considering polymers) and 2 (excluding polymers).
2. As has been shown model 1A does not fit well to the analytical results above a pH of 10.5. Therefore, in the case of considering polymer formation at high pH, an additional model 1B will be introduced, where $\log\beta_{3,3}$ and $\log\beta_{4,4}$ of the equilibrium involving the "linear" trimeric $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$ and tetrameric $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$ will be varied, because these species are calculated to be mainly responsible for the steep, unrealistic increase of the solubility above pH 10.5.
3. If the silica solubility is modeled by exclusion of all polymers, then $\log\beta_{1,2}$ has to be increased about three orders of magnitude in order to obtain agreement between model calculations and analytical data. Therefore, in addition to a model 2A in a further model, 2B, the still uncertain second dissociation constant was varied.

In particular, the following models were considered and the equilibrium constants used are given in table 6:

1. Model 1A: use of the most recently recommended equilibrium constants for all equilibria between monomeric and polymeric silica species (see table 6).
2. Model 1B: as Model 1A, but with variation of $\log\beta_{3,3}$ and $\log\beta_{4,4}$
3. Model 2A: as Model 1A, but with exclusion of all polymeric species
4. Model 2B: as Model 2A, i.e. exclusion of polymers, but with variation of $\text{Log}\beta_{1,2}$

Table 6: Compilation of the equilibrium constants being used in the four models 1A, 1B, 2A and 2B. (1) equilibrium not considered, (2) value used in extended model 2A (all explanations in text).

	25°C			
	1A	1B	2A	2B
$\log K_2^{am.silica}$	-2.70	-2.70	-2.70	-2.70
$\log K_3^{quartz}$	-3.97	-3.97	-3.97	-3.97
$\log K_{1,1}$	-9.81	-9.81	-9.81	-9.81
$\log\beta_{1,2}$	-23.14	-23.14	-23.14	-20.50
$\log\beta_{2,1}$	-8.1	-8.1	(1)	(1)
$\log\beta_{2,2}$	-19.0	-19.0	(1)	(1)
$\log\beta_{3,3}(\text{cyclic})$	-28.6	-28.6	(1)	(1)
$\log\beta_{3,3}(\text{linear})$	-27.5	-30.0	(1)	(1)
$\log\beta_{4,3}$	-25.5	-25.5	(1)	(1)
$\log\beta_{4,4}$	-34.9	-38.0	(1)	(1)
	90°			
$\log K_2^{quartz}$	(1)	(1)	-3.14	-3.14
$\log K_{1,1}$	(1)	(1)	-9.17	-9.17
$\log\beta_{1,2}$	(1)	(1)	-19.87	-18.41
$\log K_{ass}$	(1)	(1)	+1.2 (2)	(1)

The four model curves and the analytical data are shown in figures 2 and 3. Figure 2 represents a magnification of figure 1 in the pH-range between 10 and 11.5. This figure illustrates convincingly that the extreme cases are represented by models 1A and 2A. Compared to the analytical data, model 1A predicts a much to a high solubility above pH 10.5. According to model 2A, however, above this pH more dissolved silica has been measured than the model predicts. Thus, the reality is somewhere between models 1A and 2A. Let us now assume that polymerisation is unimportant up to a pH of 11. In this case, $\log\beta_{1,2}$ has to be increased to a value of -20.5 in order to yield agreement between model 2B and the measured solubility data. This extreme value for $\log\beta_{1,2}$ is certainly not correct for several reasons:

1. For those experiments performed at the highest pH values (10.8 and 11.0), Alexander et al., (1954) proposed the existence of polymeric species besides monomers. The analysed concentration of silica monomers (open circles in figure 2) in these experiments do not distinguish between the species $\text{Si}(\text{OH})_4(\text{aq})$, $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$ because all monomeric species reacted with molybdic acid within a short time (2 minutes). The rest of dissolved silica, however, needed more than half a hour to form a silico-molybdic complex. This slow reaction rate indicates the presence of polymers (Alexander (1953)). The data of the monomeric fraction agree well with the calculated solubility according to model 2A. This gives clear evidence for a minor contribution of $\text{SiO}_2(\text{OH})_2^{2-}$ to the two other monomeric species, at least up to a pH of 11.
2. In analogy to Alexander et al. (1954), van Lier et al (1960) determined the total monomer concentration in equilibrium with quartz. Again, as figure 3 indicates, even at a measured pH of 12.3 the measured solubility of monomers plots on the model 2A curve. This gives clear evidence that $\text{p}K_{1,2}$ must be ≥ 12.3 or $\log\beta_{1,2} \leq -22.1$.
3. An extreme value of $\log\beta_{1,2}$ of -20.5, as used in model 2B, would completely disagree with modern literature data (NEA-TDB, 1989). In addition, a value in the range around -20.5 would have been determined with much more accuracy, because the hydroxide concentration would be much lower than that needed for the potentiometric measurements (Busey and Mesmer, 1977).

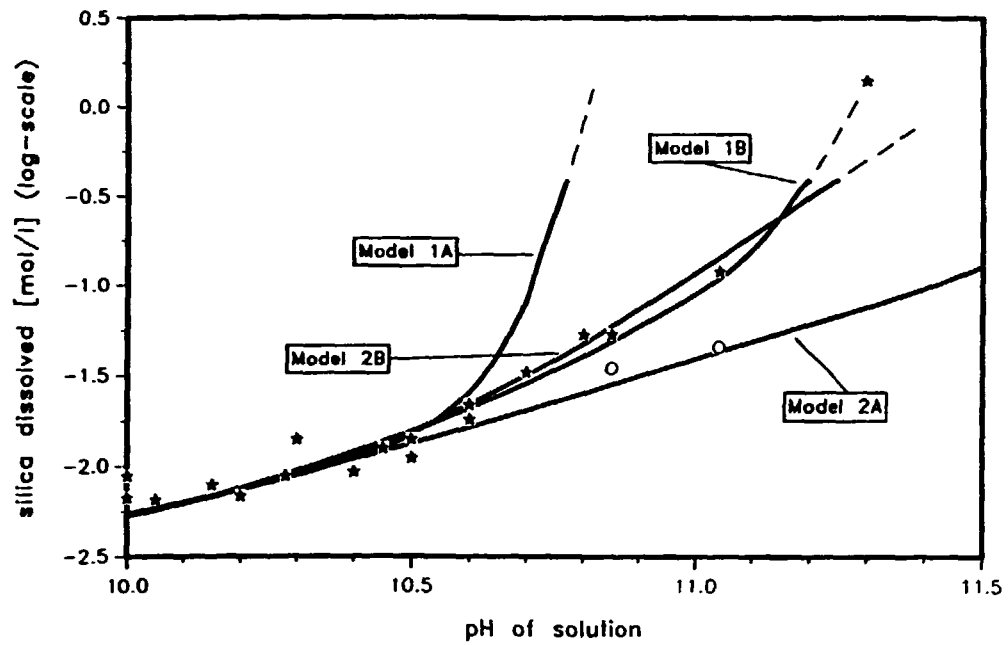


Figure 2: Magnification of figure 1 in the pH-range between 10.0 and 11.5. The open circles represent the concentrations of monomeric silica species determined by Alexander et al. (1954)

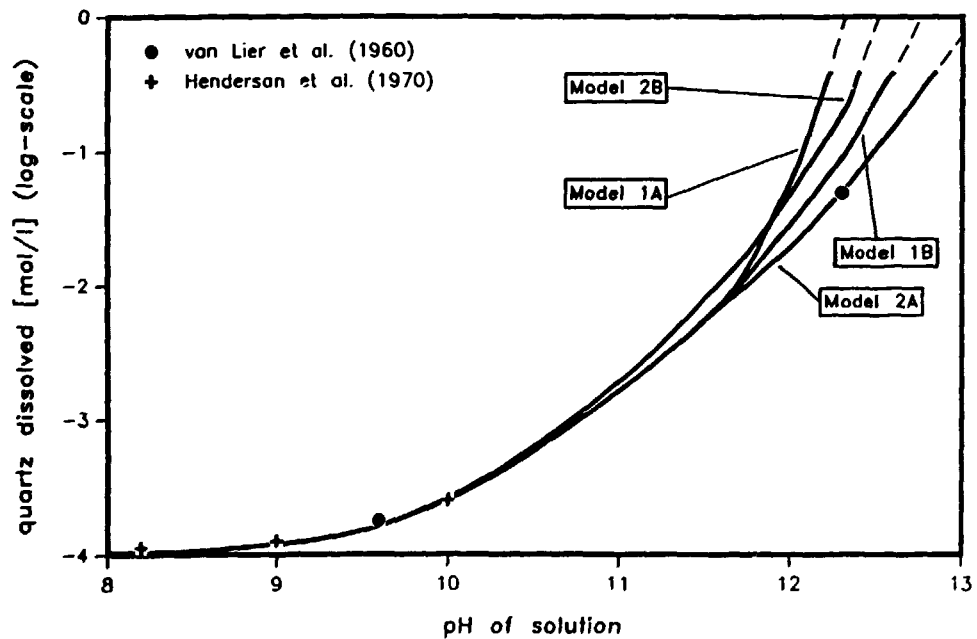


Figure 3: Solubility of quartz in NaOH solutions versus pH at 25°C. The model 2A curve fits well to the monomeric silica species determined by von Lier et al. (1960) even at a high pH of 12.3. This indicates that pK_2 must be higher than this value.

For these reasons model 2B can be rejected and it is therefore likely that the measured elevated solubility between pH 10.5 and 11.3 does not result from the second deprotonation but from polymer formation. Let us therefore now discuss the models which include polymeric species. According to model 1A, a dramatic increase of the silica solubility of about two orders of magnitude in the small pH range between 10.6 and 11.1 is calculated (see figure 2).³ This extreme increase of the model 1A solubility curve results mainly from the equilibrium $4\text{Si}(\text{OH})_4(\text{aq}) = \text{Si}_4\text{O}_8(\text{OH})_4^{4-} + 4\text{H}^+$, which means that only slight variation of the equilibrium constant $\log\beta_{4,4}$ for this reaction will significantly influence the shape of the model 1A curve. Figure 2 shows clearly that the calculated silica solubility involving this tetramer is not consistent with the analytical data. Therefore, it is likely that the solubility of amorphous silica is controlled by different polymerisation reactions, at least between pH 10.5 and 11. In order to exclude significant formation of $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$ up to pH 11, $\log\beta_{4,4}$ must be lower than -38. Even then, the calculated solubility at pH 11 is about twice as high as the analytical results, now because of a strong increase in the "linear" trimer (50 per cent of the total speciation). It was calculated that, with increasing pH, the amount of this species would remain above 50 per cent of the total silica species. Note, however, that Sjöberg et al. (1985) observed this species in only minor amounts between pH 11 and 12 and therefore, in this study, $\log\beta_{3,3}(\text{linear})$ was varied up to a value of -30, where it was found that this species would remain negligible. By the use of $\log\beta_{3,3}$ of -30 and $\log\beta_{4,4}$ of -38 in model 1B, the resulting solubility agrees much better with the analytical data. It was calculated that the contributing polymeric species are a dimer, a "cyclic" trimer and a "cyclic" tetramer of the forms $\text{Si}_2\text{O}_3(\text{OH})_2^{2-}$, $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$ and $\text{Si}_4\text{O}_7(\text{OH})_5^{3-}$, respectively. Note, however, that with model 1B, only a minimum value for the concentration of dissolved silica at pH above 11 can be predicted. This is because additional, higher molecular polymers may then gain importance.

An indication of additional higher polynuclear species may be obtained from the extremely high solubility of amorphous silica of 1.5 mol/l determined by Greenberg (1957) in a conductivity study. In different experiments, he determined $\log K_{1,1}$ and $\log\beta_{1,2}$ by the use of various silica and sodium hydroxide solutions. In two experiments, the solutions remained supersaturated because the amorphous silica gel added to the strong NaOH solution did not dissolve totally with time. In a 1 M NaOH solution, the pH dropped with time to stay constant at a relative low value of 11.3. With $\log\beta_{3,3}$ (linear trimer) = -30 and $\log\beta_{4,4}$ = -38, the extrapolated model 1B solubility curve fits well to

³Note that for NaOH solutions saturated with quartz, the steep increase of the solubility occurs about 1 pH unit later (see figure 3). This is due to the lower solubility product of quartz.

the measured solubility at pH = 11.3. The reliability of the measured silica solubility is supported by the two other measured parameters: NaOH-concentration and pH-value. Whereas, according to model 2A and 2B, between 0.1 and 0.2 M NaOH solution are calculated to yield a pH of 11.3, model 1B predicts a high 1 M NaOH concentration. It is evident that this strong buffering effect on pH must have resulted mainly from a strong increase of polymeric species. It is, however, also possible that in highly alkaline media, silica sodium ion pairs become more stable and therefore the values of $\log \beta_{3,3}$ (linear trimer) and $\log \beta_{4,4}$ should be treated as lower limits. Complex formation of silicic acid with cations will be discussed in more detail in section 4.2.

It has now been shown that the silica solubility is sufficiently explained by model 1B. For completeness, however, the quality of the additional proposed equilibrium constants for the different dimeric species from Roller and Ervin (1940) and for the tetramer species $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$ determined by Lagerström (1959) and Ingry (1959) should be discussed. With the use of the equilibrium constants from Roller and Ervin (1940) for the three dimeric species $\text{Si}_2\text{O}_2(\text{OH})_5^-$, $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ and $\text{Si}_2\text{O}_4(\text{OH})_3^{3-}$, a ten times higher solubility at pH = $\text{pK}_{1,1} = 9.8$ is calculated, mainly due to the generation of the single and double charged dimeric species. Such a high solubility at this pH is not compatible with the analytical data and therefore these values for $\log \beta_{2,1}$ and $\log \beta_{2,2}$ can be ruled out. The third dimer was calculated to be insignificant. The quality of $\log \beta_{4,2}$, found by an extrapolation to zero ionic strength (Baes and Mesmer, 1976), is more difficult to estimate. If the species $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$ is included into model 1B, then it will contribute with maximal 20% to the total solubility between pH 10.7 and 11.3. Although Sjöberg et al. (1985) have not detected this species with NMR spectroscopy, it cannot be decided in this study whether this species should be considered or not, because the change in the solubility curve is not sensitive enough for the few published data.

The next consideration focuses on the strength of polymerisation in dilute solutions in terms of total dissolved silica. It has been shown that in dilute solutions of sodium silicate, with high $\text{SiO}_2:\text{Na}_2\text{O}$ mole ratios up to 3:1 and pH value about 10.5, a considerable number of experimental data can be explained without postulating the existence of polymeric particles or aggregates of monosilicic acid (Greenberg, 1957, 1958). Decrease of polymerisation in strongly alkaline but silica undersaturated solutions has also been reported by Lagerström (1959) and Sjöberg et al. (1985). Therefore it was interesting to calculate at which concentration levels of total dissolved silica, polymerisation is likely to be unimportant. In figure 4 the dependence on pH is shown for three different

ferent concentrations of total dissolved silica: 1×10^{-2} , 5×10^{-2} and 1×10^{-1} M. The calculations performed with model 1B showed that, below 1×10^{-2} M, silica polymers are negligible at any given pH and even in concentrated NaOH solution, the trend to form polymers decreases with pH. This is because, in strong hydroxide solutions, the activity coefficients of the polymeric species are decreasing more rapidly than those of the monomers. This causes a more rapid decrease in the polymer formation constants compared to those of the monomers. Note, in strong hydroxide solution polymerisation constants need to be corrected because some polymers will associate with the hydroxide ion, which results in a decomposition of these molecules by hydrolysis (Greenberg, 1957).

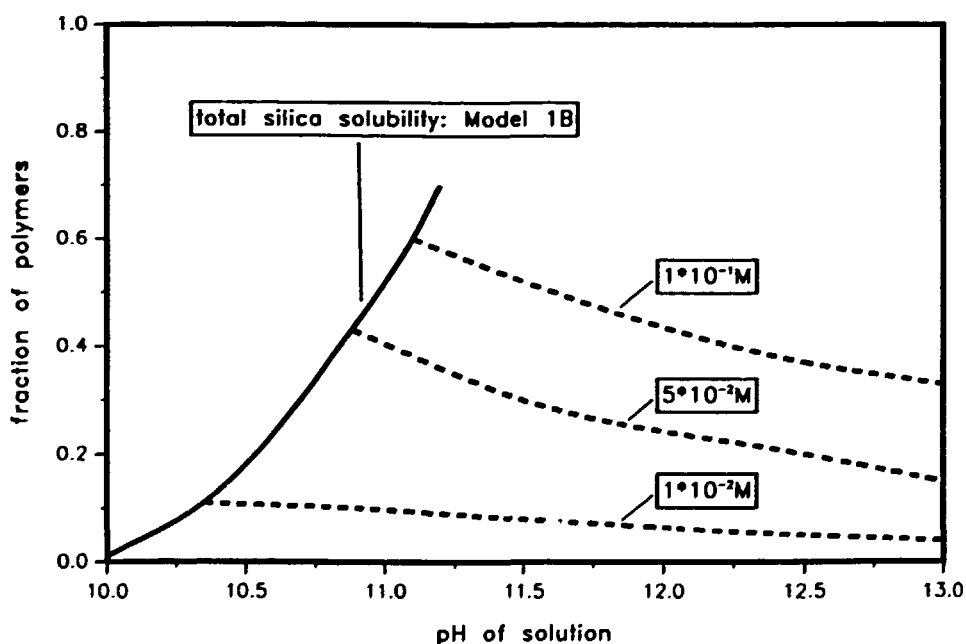


Figure 4: The dependence on pH of the fraction of polymers to the total silica speciation for a) amorphous silica saturated (solid line) and b) three undersaturated solutions (dashed lines).

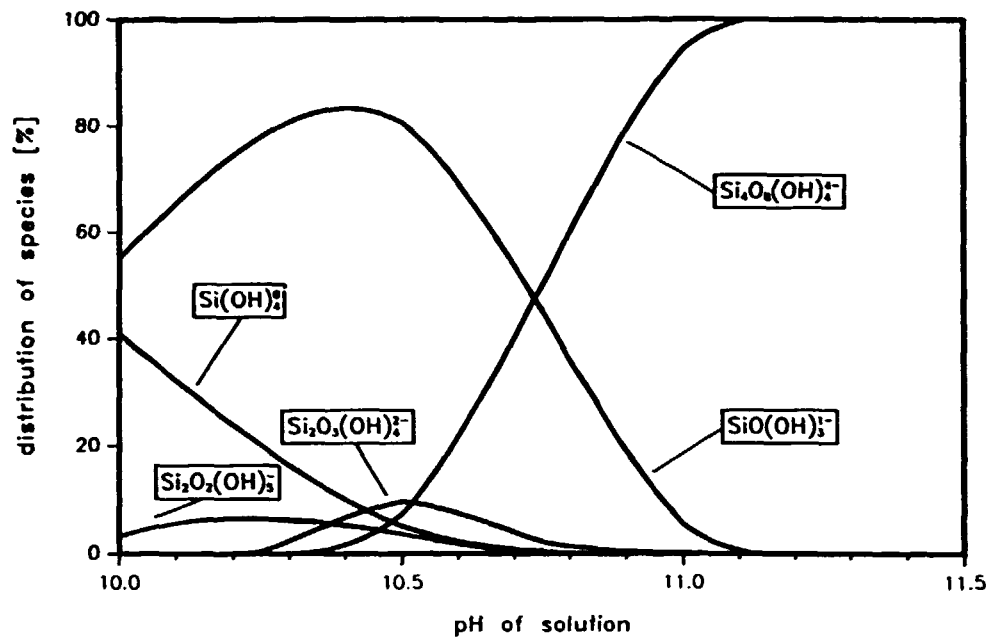


Figure 5: pH dependent distribution of the silica species at 25°C in amorphous silica saturated NaOH solutions, according to model 1A.

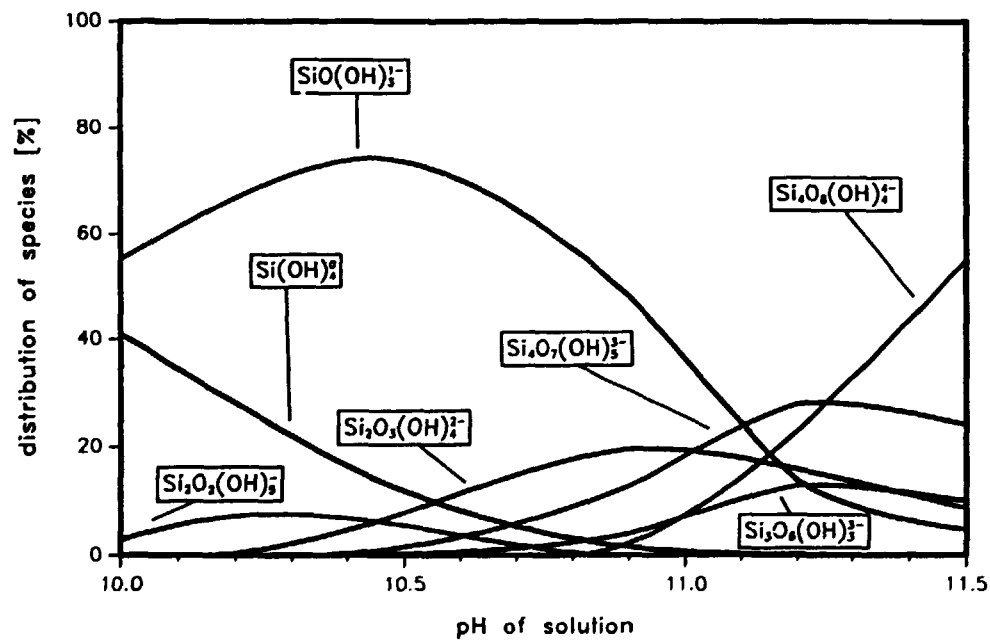


Figure 6: pH dependent distribution of the silica species at 25°C in amorphous silica saturated NaOH solutions, according to model 1B.

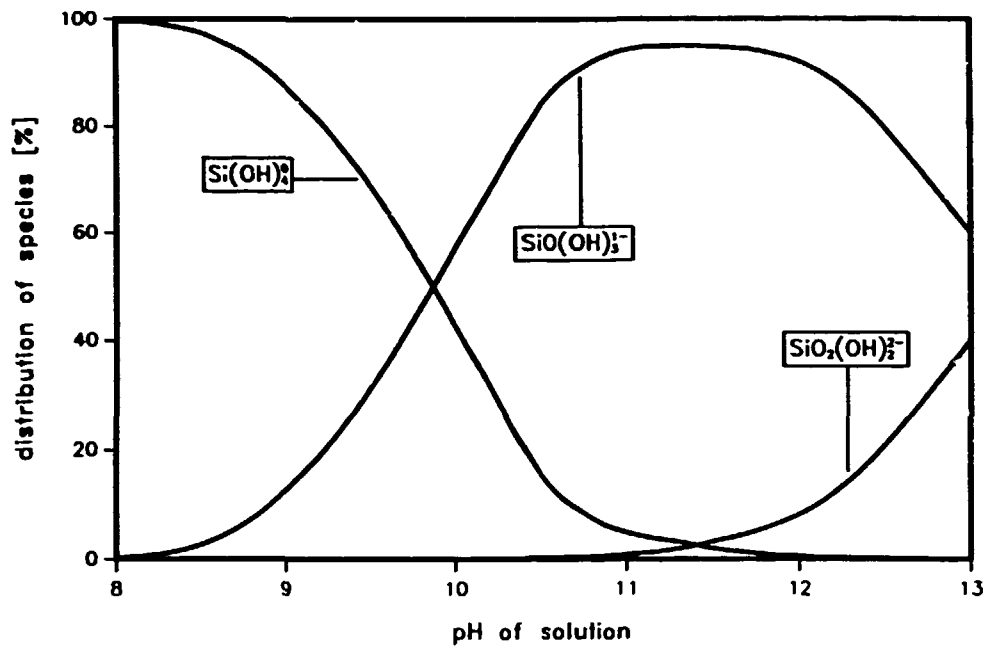


Figure 7: pH dependent distribution of the silica species at 25°C in amorphous silica saturated NaOH solutions, according to model 2A.

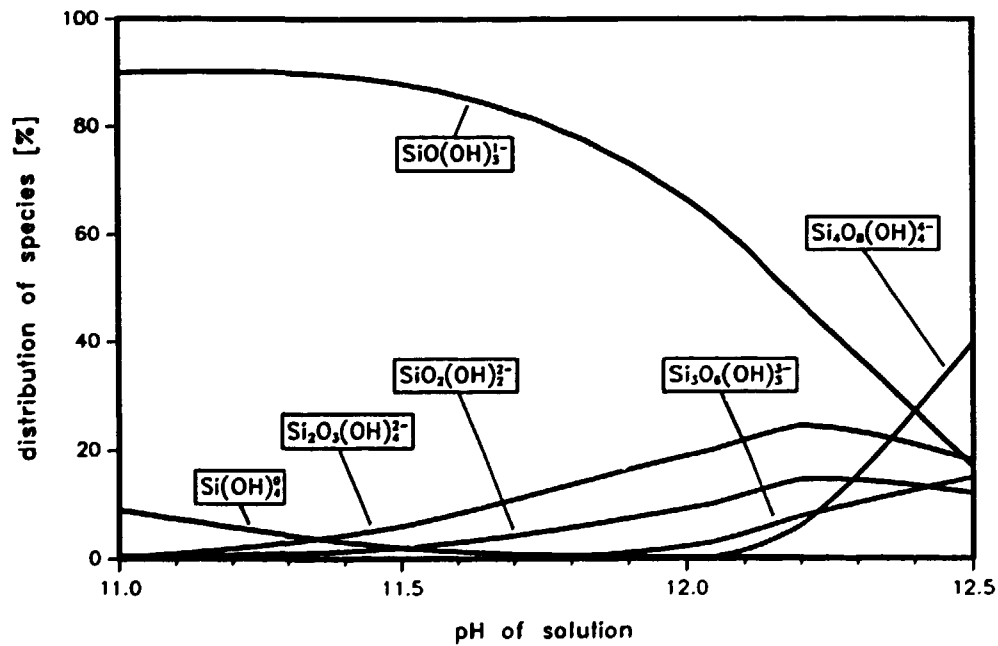


Figure 8: pH dependent distribution of the silica species at 25°C in quartz saturated NaOH solutions, according to model 1B.

The calculated distribution of silica species with pH in aqueous solution in equilibrium with amorphous silica is shown in figures 5 – 7. These figures show that, up to a pH of 9.8 the species $\text{Si}(\text{OH})_4(\text{aq})$ dominates. At higher pH, the models predict a different speciation. According to model 1A (figure 5) between pH 10 and 10.6, the species $\text{SiO}(\text{OH})_3^-$ is predominant; at higher pH the polymer species $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$. Due to the steep ingrowth of this species, other possible polymers are totally suppressed. In figure 6, the distribution of silica species is shown according to the model 1B results. It is indicated that, at pH above 11 a couple of low molecular silica polyforms become stable. Figure 7 illustrates the silica speciation resulting from model 2A. In this case no polymers will be formed and the silica speciation is determined by the three monomeric species only. Such a situation holds for sodium hydroxide solution with total dissolved silica below 0.01 M. Note that, in this case, below a pH of 13, the monomeric species $\text{SiO}_2(\text{OH})_2^{2-}$ is unimportant. For comparison, in figure 8 the speciation in quartz saturated NaOH solutions is plotted according to the model 1B calculations.

4.2 Silica solubility in sodium hydroxide solutions at 90°C

Besides silica solubility experiments performed at 25 °C and 1 bar, the solubility of quartz has been measured in sodium hydroxide solutions at 90°C (van Lier, 1960; Schwarzenhuber et al., 1987). This has been done in order to reach chemical equilibrium within a relative short time. In principle, these 90°C data, extrapolated to 25°C, may be useful to distinguish between the different silica species in solution. Therefore, as a first step, it was necessary to evaluate the quality of the reported equilibrium constants at 90°C. Tables 2 and 4 illustrate that, at this elevated temperature the situation is analogous to 25°C: well defined values for $\log K_1^{\text{quartz}}$ and $\log K_{1,1}$ with less data and differing values for $\log \beta_{1,2}$. Unfortunately, most of the solubility data have been obtained only in weak sodium hydroxide solutions (see table 9). This is because strong and hot sodium hydroxide solutions will cause extensive corrosion of the pH glass electrodes.

Since there is no information about the enthalpy changes of the equilibrium constants involving polymers, no model calculation regarding these species have been performed for 90°C. Therefore, no model 1 is presented here. The distinction has been made between model 2A, which uses a $\log \beta_{1,2}$ of -19.87 (value from Schwarzenhuber et al., 1987) and model 2B which uses a $\log \beta_{1,2}$ of -18.41 (value from Ryzhenko, 1967). Figure 9 illustrates that the $\log \beta_{1,2}$ value of -18.41 from Ryzhenko (1967) is likely to be too high. According to the analytical data, the pK for the second deprotonation

should be lower than -10. Therefore the $\log\beta_{1,2}$ value of -19.87 (Schwartzentruber et al. 1987) is recommended. In addition, silica sodium ion pairing according to the results from Seward (1974) was considered in model 2A, because it is believed that at higher temperatures such complexation gains more importance (extended model 2A). The few data can, however, not be used to distinguish between model 2A and extended model 2A. In addition, from this figure it can not be decided to what extend polymers have to be considered above a pH of 10.

Note that up to a pH of at least 11 the calculated solubility of quartz is clearly higher at 90 °C compared to 25 °C (compare figures 9 and 13). This is the result of a) increasing $\log K_s$ and $\log K_{1,1}$ values and b) a decreasing dissociation constant of the water ($\log K_w$) with the temperature. While pK_w is equal to 14 at $I = 0$ and 25 °C is equals to 12.5 at $I = 0$ and 90 °C.

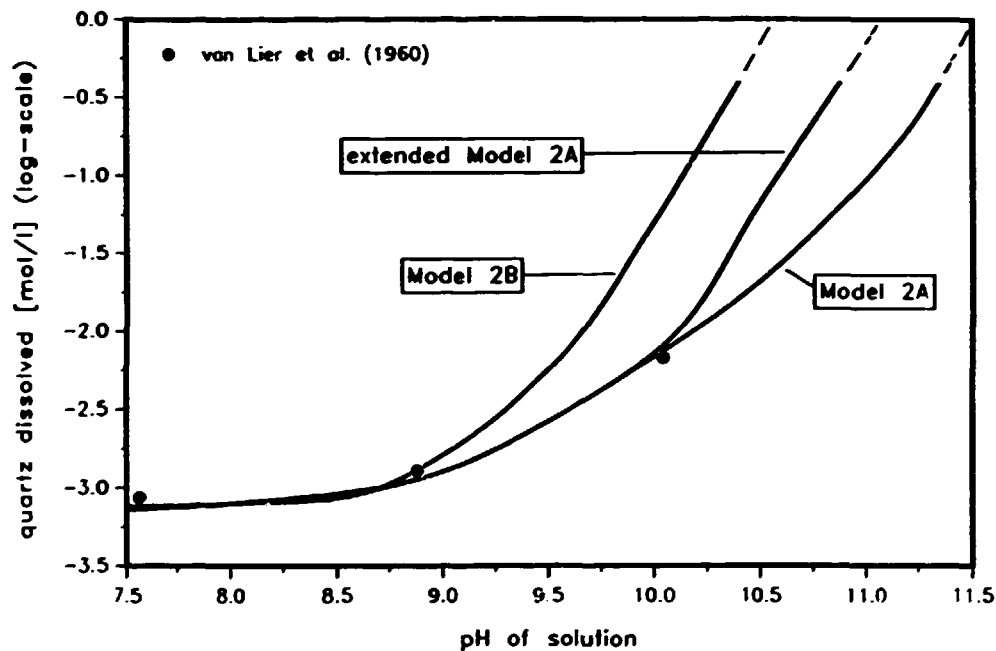


Figure 9: Dependence on pH of the solubility of quartz in NaOH solutions at 90°C. This model 2A curve fits well to the monomeric silica species determined by van Lier et al. (1960), even at pH of 10.0. This indicates that pK_2 must be higher than this value.

Nevertheless, although no pH measurements have been carried out in strong and hot sodium hydroxide solutions, the 90 °C data provide some information. Due to the different reactions between negatively charged silica species and $\text{Si}(\text{OH})_4(\text{aq})$, a different number of protons are generated which will neutralize some hydroxide. For example, according to the reaction $\text{Si}(\text{OH})_4(\text{aq}) = \text{SiO}(\text{OH})_3^- + \text{H}^+$, one hydroxide ion will be neutralized by the dissociated proton. Due to variation of the ratio of hydrogen liberated per silicon (H/S) in the different dissociation reactions, more or less hydroxide will be neutralized at a given concentration of total dissolved silica. In our example, the (H/S) ratio is 1; for the second dissociation reaction (H/S) is 2, but for all polymer species in equilibrium with $\text{Si}(\text{OH})_4$, the ratio (H/S) is less than 1. Therefore, it should be possible to distinguish roughly between the different silica species by plotting the concentration of sodium hydroxide as function of the total dissolved silica concentration.

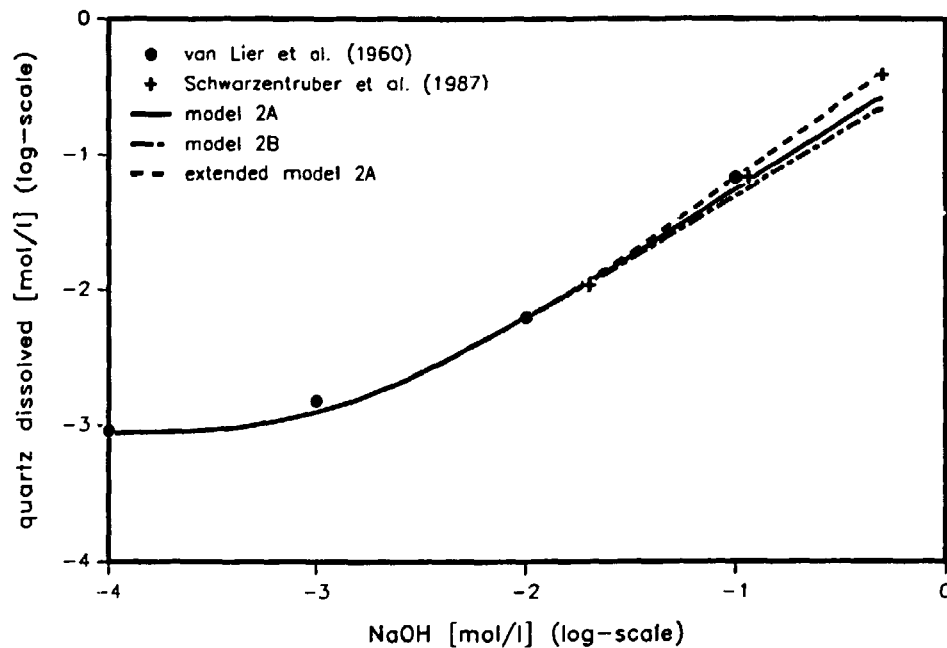


Figure 10: Dependence of the solubility of quartz on sodium hydroxide concentration at 90°C. Note that according to model 2A the calculated pH of a 0.5 M NaOH medium is about 11. All other explanations are given in the text.

This dependency is shown in figure 10. It is conspicuous that there is no clear resolution between model 2A and 2B and hence from this figure extraction of $\log\beta_{1,2}$ is not possible. All data agree with the model 2A or 2B curve, except for the data point measured at the highest 0.5 M NaOH solution (388 ± 8 mM dissolved quartz). Compared to the calculated solubility about twice as much quartz has been dissolved as is predicted from the models. This disagreement can be explained in two ways:

1. There are polynuclear species present in ≥ 0.1 M hydroxide solutions at 90°C . This interpretation is consistent with the explanation of van Lier et al. (1960) and Schwarzenhuber et al. (1987) who studied the dissolution kinetics of quartz at this temperature. They observed that the dissolution rate of quartz is in direct proportion to the hydroxide ion concentration below 0.02 M NaOH medium, but trends to a zero-order relation in a more concentrated solution. This effect was ascribed to the additional generation of slow kinetic polymer reactions. It should be mentioned, in addition, that model calculation using the constants for 25°C yield, for 0.5 M NaOH medium, a predicted silica solubility which is about one order of magnitude higher than the analytical data. It is therefore concluded that the formation constants of polymers must decrease with temperature.
2. The extended model 2A, including silica ion pairing, predicts a similar silica solubility in 0.5 M NaOH solution as the analytical data indicate. In this case the solution would contain the following silica species: $\text{NaSiO}(\text{OH})_3$, $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$.

In summary, it is concluded that, in NaOH solutions ≤ 0.1 M at 90°C , only pure silica monomers are stable. Therefore, the trend towards polymerisation decreases with increasing temperature. In very strong sodium hydroxide solutions, however, silica polymerisation and silica sodium ion pairing has to be considered.

4.3 Influence of silica sodium complexes: a parameter variation study

In this section, a sensitivity analysis has been made to obtain some knowledge about the influences of silica–sodium ion pairing on silica solubility and speciation. Ion pairing, according to the equilibrium $\text{Na}^+ + \text{SiO}(\text{OH})_3^- = \text{NaSiO}(\text{OH})_3$, has been proposed by Seward (1974). He determined $\log K_{a,s}$ values between 1.2 and 1.4 in the temperature range of 130 - 300 °C. For the present study, it is, however, of prime interest to investigate silica–sodium ion pairing at 25°C. Therefore a sensitivity analysis has been performed by a variation of $\log K_{a,s}$ -values and by the use of the amorphous silica solubility data. A maximal $\log K_{a,s}$ value was calculated, allowing a “maximal” proportion of $\text{NaSiO}(\text{OH})_3$ to the silica speciation at pH 10. Up to a pH of 10 the dominant silica species in sodium hydroxide solutions are $\text{Si}(\text{OH})_4(\text{aq})$ and $\text{SiO}(\text{OH})_3^-$. Due to the uncertainty in the analytical data it was decided that the proportion of $\text{NaSiO}(\text{OH})_3$ is total dissolved silica should not exceed 10 – 20 % because then this species would have been detected, or reported $\log K_{1,1}$ values would disagree. On the other hand, a “minimum” value has been calculated under the assumption that, up to pH = 11.3, no silica sodium complexes are stable. Note that complex formation between sodium and $\text{SiO}_2(\text{OH})_2^{2-}$ has not been proposed in the literature. This indicates that the concentration level of $\text{SiO}_2(\text{OH})_2^{2-}$ must be low even in SiO_2 saturated strong sodium hydroxide solutions.

1. **maximal values:** In figure 11, the calculated fraction of $\text{NaSiO}(\text{OH})_3$ is plotted against $\log K_{a,s}$ at a fixed pH of 10. Below $\log K_{a,s} = 1.6$, the fraction of $\text{NaSiO}(\text{OH})_3$ does not exceed 0.15 and thus this value gives approximately the upper limit at the respective temperature and pH. The hypothetical influence of silica sodium complexation using $\log K_{a,s} = 1.6$ is shown in figure 12. It is obvious that model 2A is most sensitive to silica sodium complexation, whereas for model 1A and 1B, the influence is weaker because of competition of additional polymers.
2. **minimum values:** Under the assumption that, at pH 11.3, no silica sodium pairs have been formed and the silica solubility is sufficiently explained by model 1B, then at this pH $\log K_{a,s}$ is not allowed to exceed a value of approximately 1.1 (see figure 11). Therefore, for the range of the analytical data at 25°C, this value gives a lower limit where silica sodium ion pairing does not contribute to the silica speciation in the aqueous phase.

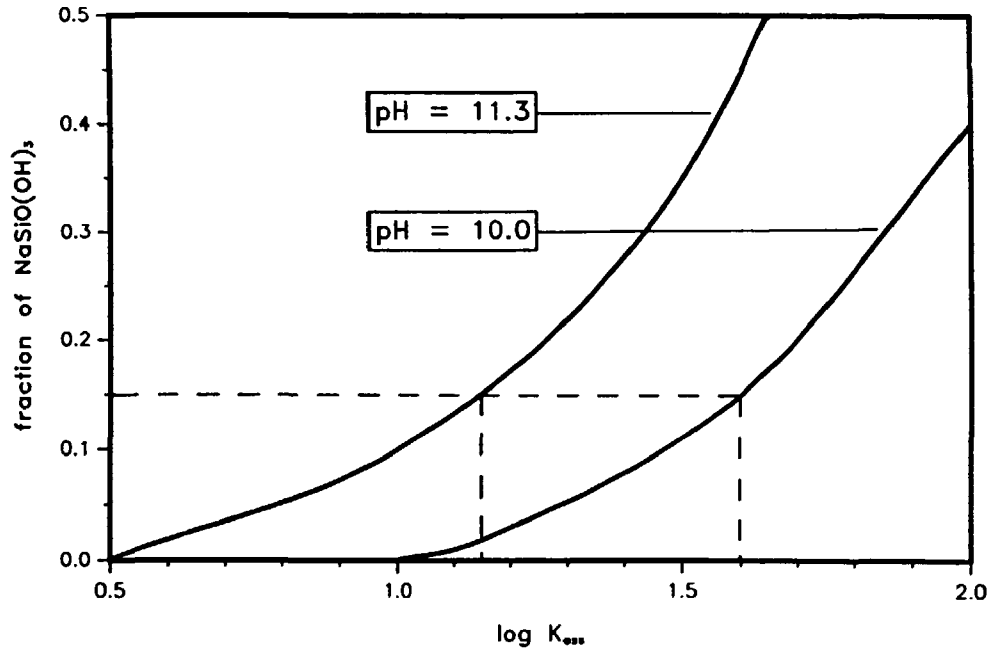


Figure 11: Fraction of NaSiO(OH)_3 in amorphous silica saturated NaOH solutions independence of $\log K_{oss}$ at a fixed pH of 10 and 11.3 and a temperature of 25°C.

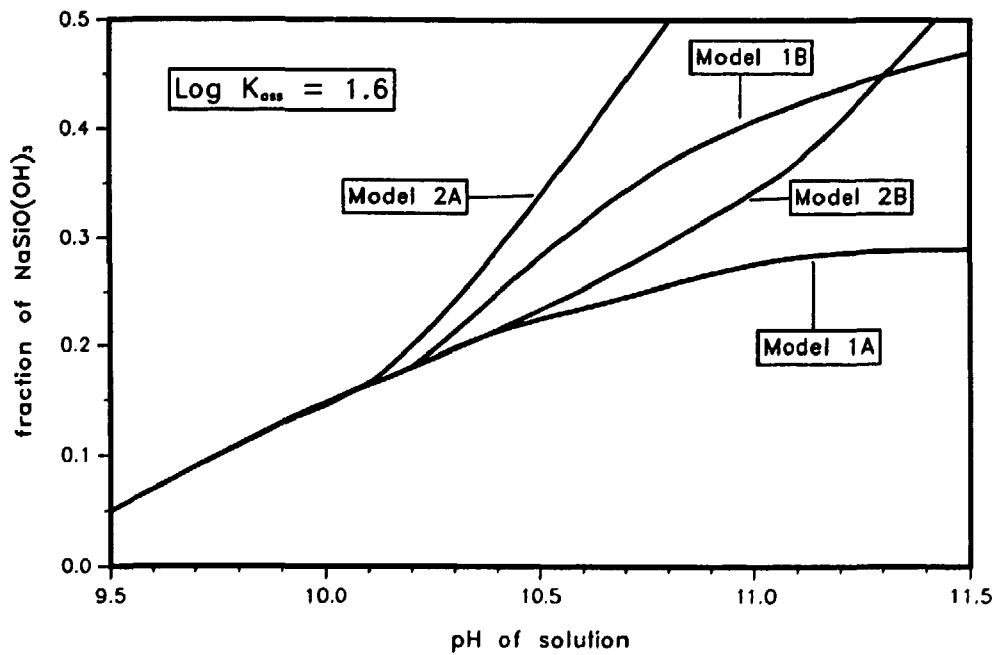


Figure 12: Fraction of NaSiO(OH)_3 in amorphous silica saturated NaOH solutions in dependance of pH at a fixed $\log K_{oss}$ of 1.6 and a temperature of 25°C.

4.4 Conclusions

The solubility of silica at high pH was evaluated in this study. Such estimations are important as it is predicted that the interaction between ground water and a cement based near field repository causes a high pH plume which intrudes into the silica rich geologic environment. In order to evaluate the quality of thermodynamic constants of silicic acid, a parameter variation modelling study was initiated, based on a comparison of model calculations using different equilibrium constants and analytical data taken from the literature. All work was performed by the use of the geochemical speciation code MINEQL/EIR for the system $\text{Na}_2\text{O}-\text{H}_2\text{O}-\text{SiO}_2$ at 25 and 90°C, as most analytical data refer to these temperatures. Besides a discussion of different reactions involving monomeric and polymeric silica species, the influence of silica ion pairing was considered. The equilibrium constants recommended from the comparison study are summarized in table 7 and have been selected for the following reasons:

1. Up to pH 9 the solubility of the SiO_2 minerals quartz, chalcedony and amorphous silica is generally believed to be determined by the hydrolysis reaction $\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4(\text{aq})$. Whereas the solubility product for quartz in pure water is well known, slightly different values have been reported for amorphous silica. A model using the most widely recommended value of $\log K_s = -2.7$ agrees with most of the literature data considered.
2. Solubility data measured in weak sodium hydroxide solutions are best explained with the equilibrium $\text{Si}(\text{OH})_4(\text{aq}) = \text{SiO}(\text{OH})_3^- + \text{H}^+$ and a dissociation constant of $\log K_{1,1} = -9.8$. This value agrees with most of the data derived by potentiometric and colorimetric measurements and needs no further investigation.

Table 7: Compilation of the recommended equilibrium constants between silica species at 25°C and 90°C.

	25°C	reference
$\log K_{\text{am.silica}}$	-2.70	Rimstidt and Barnes (1980)
$\log K_{\text{quartz}}$	-3.97	Rimstidt and Barnes (1980)
$\log K_{1,1}$	-9.81	NEA-TDB (1989, draft)
$\log \beta_{1,2}$	-23.14	NEA-TDB (1989, draft)
$\log \beta_{2,1}$	-8.1	NEA-TDB (1989, draft)
$\log \beta_{2,2}$	-19.0	NEA-TDB (1989, draft)
$\log \beta_{3,3}(\text{cyclic})$	-28.6	NEA-TDB (1989, draft)
$\log \beta_{3,3}(\text{linear})$	≤ -30.0	this study
$\log \beta_{4,3}$	-25.5	NEA-TDB (1989, draft)
$\log \beta_{4,4}$	≤ -38.0	this study
$\log K_{\text{ass}}$	$\leq +1.7$	this study
	90°C	
$\log K_{\text{quartz}}$	-3.14	Rimstidt and Barnes (1980)
$\log K_{1,1}$	-9.17	Schwarzenhuber et al. (1987)
$\log \beta_{1,2}$	-19.87	Schwarzenhuber et al. (1987)
$\log K_{\text{ass}}$	$\leq +1.2$	this study

3. The sharp rise in the measured solubility of amorphous silica above pH 10.5 cannot be explained by the first dissociation reaction only. This phenomena has to be explained by either a low pK of the second deprotonation reaction of $\text{Si}(\text{OH})_4$ or by formation of additional silica polymers. In a model which disregarded polymer formation, the elevated silica solubility data were fitted by the use of an unrealistically high value of about -21 for $\log \beta_{1,2}$ at 25°C. This value is not reasonable because of disagreement with thermodynamic data reported in the literature. From the present work, it is concluded that $\log \beta_{1,2}$ is less than -22 and thus the species $\text{SiO}_2(\text{OH})_2^{2-}$ does not contribute significantly to the total silica solubility even in strongly alkaline media. A value of $\log \beta_{1,2} = -23.14$ calculated by the NEA is recommended (NEA-TDB, 1989).

4. The strong increase in the solubility of amorphous silica at $\text{pH} \geq 10.5$ is most likely to be the result of association of $\text{SiO}(\text{OH})_3^-$ ions into low molecular weight polynuclear species. The total silica curve, calculated by using the most recently proposed polymerisation constants (NEA-TDB, 1989), does not fit the analytical solubility data. The model predicts a much higher solubility above $\text{pH} 10.5$ because of a strong increase of the polymeric species $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$ (linear trimer) and $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$. By variation of $\log\beta_{3,3}$ (linear) from -27.5 to -30 and $\log\beta_{4,4}$ from -34.9 to -38 the model can be fit to the measured solubility data of amorphous silica. If this model describes the silica speciation correctly, then the increase in the solubility of amorphous silica at least between $\text{pH} 10.5$ and 11.3, results mainly from the polymeric species $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$, $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$ (cyclic trimer), $\text{Si}_4\text{O}_7(\text{OH})_5^{3-}$ and $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$.
5. At higher pH , there are some indications of additional polymeric species (such as pentamers) or Na-Si-complexes. Thus the solubility is probably further enhanced. Unfortunately, due to the lack of analytical data and due to the high ionic strength of such solutions, no reasonable model predictions could be made. Nevertheless, the dissolution of silica will proceed until, in very strong (about 5 molar) sodium hydroxide media, viscous silica water glasses will be formed. This is partly because some of the water molecules are bound in the silica species, but mainly because the free water molecules from the solvent build up hydrated layers around the surfaces of the negatively charged silica species on the one hand, and the Na^+ ion on the other, so that a gelatinous structure results.
6. Polynuclear species are only stable at $\text{pH} \geq 10.0$ (amorphous silica) and $\text{pH} \geq 11.3$ (quartz) and at total silica concentrations ≥ 0.01 M. At lower concentrations, only monomeric species will be formed over the whole pH range. In this case (conc. ≤ 0.01 M), the species $\text{Si}(\text{OH})_4(\text{aq})$ controls the solubility of silica in equilibrium with solid SiO_2 up to $\text{pH} 9.8$. Between $\text{pH} 9.8$ and, probably, about 13, it is controlled by the species $\text{SiO}(\text{OH})_3^-$ and by $\text{SiO}_2(\text{OH})_2^{2-}$ in concentrated sodium hydroxide solutions.
7. The possibility of silica-sodium ion pairing in strongly alkaline media cannot be excluded. Unfortunately the association constant $\log K_{a,s}$ for the proposed reaction $\text{Na}^+ + \text{SiO}(\text{OH})_3^- = \text{NaSiO}(\text{OH})_3$ has been determined at higher temperature only. In order to determine the influence of silica sodium complex formation at lower temperatures, $\log K_{a,s}$ was varied in a sensitivity study. The modelling study revealed that $\log K_{a,s}$ does not exceed a value of 1.6 at 25°C . No evidence has been

found, however, for the formation of a complex of the form $\text{Na}_2\text{SiO}_2(\text{OH})_2$ or $\text{NaSiO}_2(\text{OH})_2^-$ resulting from ion pairing of Na^+ with $\text{SiO}_2(\text{OH})_2^{2-}$. This indicates that the concentration of $\text{SiO}_2(\text{OH})_2^{2-}$ must be low, even in SiO_2 saturated strong sodium hydroxide solutions.

8. Although the solubility of silica increases strongly with temperature, the tendency of monomers to form polymers decreases with temperature. A comparison of model predictions with analytical data obtained at 90°C indicates that, in NaOH media up to 0.1 M, mainly mononuclear silica species are present if the solution is in equilibrium with quartz. There are indications, however, that in stronger NaOH solutions at elevated temperatures, silica sodium ion pairing gains importance.

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Appendix A: Analytical Data

Table 8: Analytical data for amorphous silica saturated sodium hydroxide solutions at 25°C.

SiO ₂ (tot) (mMol/l)	pH	Reference
1.7	7.0	Alexander et al. (1954)
1.9	8.0	
2.5	9.0	
3.4	9.5	
8.9	10.28	
18.2	10.60	
43.7	10.85	
120.2	11.04	
3.6	7.0	Goto (1955)
4.3	8.5	
8.9	10.0	
15.8	10.3	
2.0	7.50	Greenberg and Price (1957)
2.0	8.30	
2.2	8.60	
4.6	9.50	
5.5	9.85	
6.6	10.05	
7.9	10.15	
21.9	10.60	
33.1	10.70	
53.7	10.80	
17.0	10.45	Greenberg (1958)
1500	11.3	
2.2	7.55	Marsh et al. (1975)
2.2	10.05	
3.4	9.55	
5.0	9.98	
6.9	10.20	
9.3	10.40	
11.2	10.50	
2.9	8.5	Iler (1979)
3.7	9.0	
4.3	9.5	
13.2	10.0	
15.8	10.5	

Table 9: Analytical data for quartz saturated sodium hydroxide solutions at 25°C and 90°C.

SiO₂ (tot) (mMol/l)	NaOH (tot) (mMol/l)	pH	temp. (°C)	reference
0.2	0.1	9.6	25	van Lier et al. (1960)
50.0	921	12.3	25	
0.11		8.0	25	Henderson et al. (1970)
0.15		9.0	25	
2.51		10.0	25	
0.9	0.1	7.51	90	van Lier et al. (1960)
1.5	1.0	8.88	90	
6.8	10	10.04	90	
67.6	100		90	
10.7	20		90	Schwarzenhuber et al. (1987)
61.7	115		90	
388	505		90	

Appendix B: Correction for Ionic Strength

According to the law of mass action, the thermodynamic equilibrium constants are dependent on the **activity** of the different species in the equilibrium under consideration. Experimentally, however, only the **concentration** of a species can be determined. The relation between the activity of a species i , $\{A_i\}$, and its concentration $[C_i]$ is given by the activity coefficient f_i .

$$\{A_i\} = [C_i]f_i \quad (25)$$

The databases provided with geochemical codes contain medium independent equilibrium constants that refer to standard conditions, i.e., $I = 0$. For the correction of these standard equilibrium constants to real conditions ($I > 0$) different models may be used, depending on the ionic strength and the ionic interactions to be expected. The code MINEQL/EIR which was used in the present modelling study uses the Davies approximation (Schweingruber, 1980, 1981),

$$\log f_i = -bz_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - cI \right) \quad (26)$$

with the following parameters: f_i = activity coefficient; b = temperature dependant parameter of the density and the dielectric constant of liquid H_2O ; c = empirical constant; z_i = charge of the species; I = ionic strength of the solution. The code MINEQL/PSI uses values of 0.5 and 0.2, respectively for b and c at $25^\circ C$. The ionic strength of an aqueous solution is a function of the total ionic concentration and their respective charges:

$$I = 0.5 \sum z_i^2 [C_i] \quad (27)$$

With the Davies-approximation, f_i can be reasonably approximated up to a ionic strength of 0.5 M (Stumm and Morgan, 1981). In higher molar media, this relation is, however, limited because its only ion-specific parameter is the charge. At higher concentrations, short range non-electrostatic interactions also have to be taken into account, which require additional information of often rather uncertain parameters. Therefore, in the present study, all model calculations have been performed only up to $I = 0.5$ M. Note, that a guideline for the extrapolation of equilibrium constants to zero ionic strength has been presented recently by the NEA (NEA-TDB, 1988). In this guideline the Bronsted - Guggenheim - Scatchard approach, which includes a specific ion interaction term, has been recommended.