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High pH Dissolution
of Quartz and Kaolinite

by

Nita L. Jenkins-Smith

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemical and Petroleum-Refining Engineering).

Golden, Colorado

Date 5/8/86

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Abstract

This research studied the dissolution of fine quartz powder, kaolinite particles and mixtures of the two materials in 0.1 N sodium hydroxide solutions at 70°C. The materials were chemically pretreated to remove surface amorphous layers and surface impurities. Solution concentrations of soluble silicon and aluminum were measured by atomic absorption spectrometry. The production of soluble silicon from the dissolution of quartz is examined at three different solids to solution ratios: 3.3 g/L, 6.7 g/L and 10 g/L. The dampening effect of three added soluble aluminum concentrations (7 ppm, 14 ppm and 20 ppm) on the production of silicon from quartz is shown.

Silicon and aluminum production from kaolinite dissolution was measured. Small amounts of soluble aluminum (14 ppm and 20 ppm) and significant amounts of soluble silicon (100 ppm and 150 ppm) were added to the caustic solution before kaolinite addition and the effects documented. The production of silicon and aluminum from dissolution of three different weight ratio mixtures of the two materials (95%, 90% and 85% weight percent of quartz) are reported. Evidence suggests the formation of a Si/Al species complex that is removed from solution by either a precipitation or an adsorption mechanism.

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Acknowledgements

Funding for this research was provided by the Colorado School of Mines Graduate Office. Equipment and technical assistance was provided by the Colorado School of Mines Department of Chemical Engineering and Petroleum Refining. Analysis Instruments were made available and maintained by the Colorado School of Mines Department of Chemistry and Geochemistry and the Department of Metallurgy.

I would like to thank: my advisor, Annette Bunge, for endless guidance; Ron Minor of the CPR department staff for his time and tools; my family, Rodger and Leon Smith, for the multitude of sacrifices required to make my work possible; my mother, Verna Miller, for aid in ways too numerous to mention.

Chapter 1

Introduction

The purpose of this research was to quantitatively study the dissolution of fine quartz powder (SiO_2) and kaolinite clay particles ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) in high pH solutions. The quartz and kaolinite studied were chemically pretreated to assure surface purity and to remove grinding-induced amorphous layers or attached fine particles. All experiments were conducted in 0.1 N sodium hydroxide (pH 13) maintained at 70°C with the production of soluble silicon and aluminum measured. Both the solubility and dissolution rates of these materials are known to depend strongly on pH. The effect of added soluble silicon and aluminum on the mineral dissolution rates was also examined.

High pH dissolution of siliceous minerals is important in two methods for improving oil recovery: caustic (or alkaline) waterflooding and steamflooding. Caustic waterflooding is the generic description of any process to inject high pH solutions into an oil reservoir for the purpose of mobilizing more oil. The extent of the reservoir which the high pH solution will contact is controlled largely by alkaline consumption by various chemical reactions with reservoir solids. Many reservoir formations are principally composed of quartz, amorphous silica and clay minerals.

The experimental temperature chosen approximates typical underground formation temperatures.

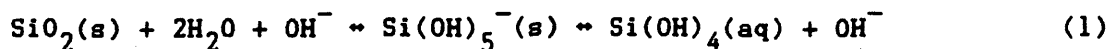
Steam injection (steamflooding) is used to recover heavy, viscous crudes. Steam at about 260^oF and 80% quality is injected into the formation (Reed, 1980). The condensate is highly caustic (pH 10.8 - pH 11.6) from HCO₃⁻ ions, which are present in the feed water, decomposing into carbon dioxide and hydroxide ions in the steam generation step (Reed, 1980). Near well-bore and gravel pack dissolution have been reported as significant problems (Reed, 1980; Bojes and Bulkowski, 1985). Previous research has considered varying the type or composition of packing material to increase its lifetime (Underdown and Das, 1985). One of the problems with the alternatives to conventional quartz packing considered in the Underdown study was cost.

The presence of dissolved aluminum strongly affects amorphous silica and quartz dissolution rates in nearly neutral solutions (Iler, 1973; Ballou et al. 1973). A few experiments report similar trends in high pH solutions (Ting, 1985). This phenomenon is important to both caustic waterflooding and steam injection. Since oil reservoirs always contain some aluminum-bearing minerals which will simultaneously dissolve, we can expect that quartz dissolution rates in aluminum-free caustic solutions will always be much greater than would actually occur in the reservoir. Gravel pack dissolution during steamflooding may be slowed by small additions of aluminum

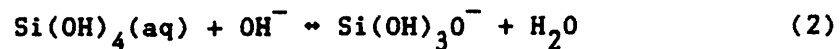
to the condensate or by mixing the sandpack with small amounts of readily available aluminum-bearing minerals like kaolinite or other clays. Consequently, this research examined the dissolution of pure quartz and pure kaolinite, quartz in the presence of aluminum, kaolinite in the presence of silicon and aluminum, and several mixtures of kaolinite and quartz.

For composite materials like clay minerals, dissolution can occur according to two broad classes of chemical reactions. Congruent dissolution occurs when the species existing in solution are in the same stoichiometric ratio as they occur in the crystal lattice structure. Incongruent dissolution occurs when the dissolved species react with one another to form another mineral of a different stoichiometric ratio than the parent mineral.

Silica dissolution is a depolymerization and hydrolysis process (Iler, 1979). Depolymerization reactions are normally catalyzed by soluble nucleophiles. For solutions near neutral to moderately alkaline (less than pH 10), the hydroxide ion acts as a catalyst to quartz dissolution. Chloride ions can also act as a catalyst even though they are weak nucleophiles. The hydroxide ion is chemisorbed onto the silica surface weakening the silicon-oxygen bond (Iler, 1979). The reaction can be written as follows:



As written here, the reaction product is monosilicic acid. At higher hydroxide concentrations, the weak monosilicic acid can lose a hydrogen ion which reacts with a free hydroxide ion thereby decreasing the pH:



The extent that silicic acid dissociates depends on pH. Figure 1.1, taken from Bunge (1982), shows speciation of monomeric silica as a function of pH. The solution pH expected during these studies varied between 12 and 13. Figure 1.1 shows that at these conditions, the monovalent and divalent species are prevalent. At higher silicon concentrations, the monomers that exist in solution can react with each other to form silica polymers. Conglomeration of the polymers to form solid silica precipitate is prevalent in neutral or acidic solutions but not common in the highly caustic solutions except at extremely high silica concentrations.

In these studies, a small amount of moderately large surface area materials was placed in a large volume of solution. The dissolution rates for siliceous minerals are known to be slow relative to most mass transfer limitations (Bunge, 1892). Changes in surface area are negligible over the experimental times of these experiments. Changes in pH depend on the amount of dissolution and are generally small. Only the forward rate of the silica

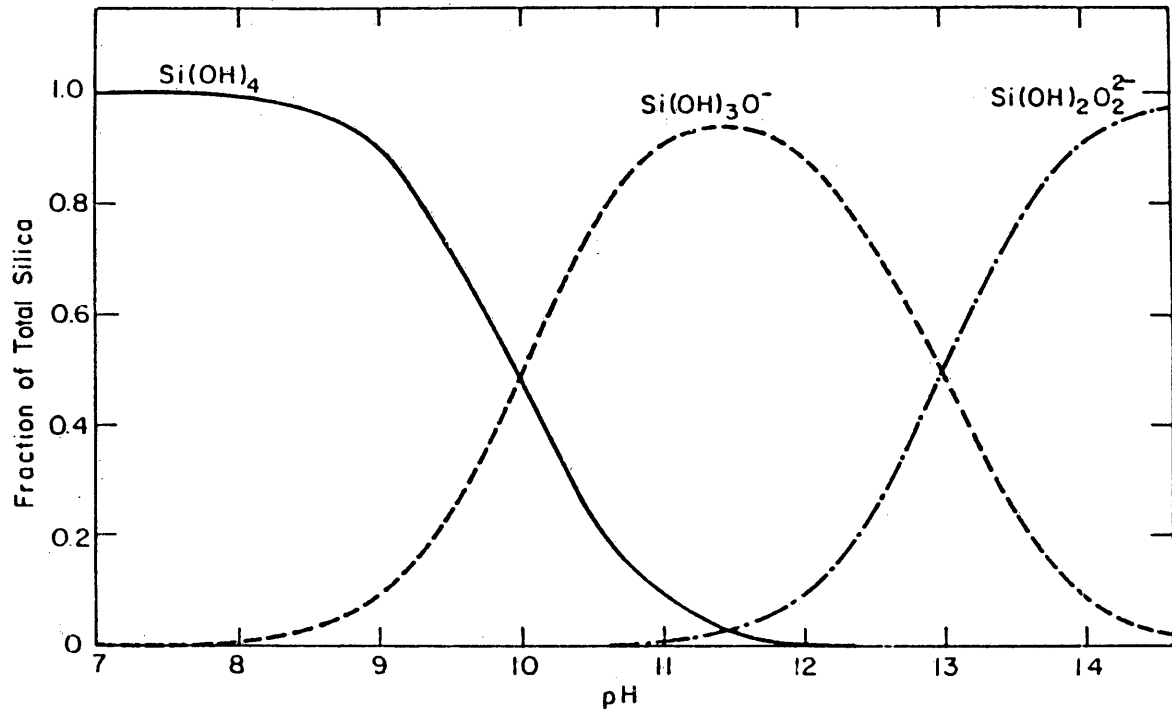


Figure 1.1 - Speciation of monovalent silicic acid as a function of pH.

depolymerization reaction is important since silica concentrations for even the longest experimental duration are much smaller than the solubility limits (Bunge, 1982; Stumm and Morgan, 1970). At high silica concentrations, the reverse silica-condensation reaction begins to contribute significantly (Thorton and Radke, 1985).

Previous studies of the high pH dissolution rates of amorphous silica and quartz suggest a dependence on the concentration of hydroxide ions (Bunge, 1982; Ting, 1985; Sydansk, 1983). The surface attack of the quartz by hydroxide ions during dissolution will begin at a surface imperfections and continue to be more rapid at these sites. The mechanism can be depicted by the steps shown in Figure 1.2 (Bunge, 1982). The hydroxylated silica surface has both oxygen ions and neutral hydroxyl groups bonded at the surface. Charge transfer can occur among the groups. An aqueous hydroxide ion attacks the surface causing a silicon atom to temporarily change from a coordination number of four to a higher coordination number allowing a bonding to occur. Cleavage takes place with monosilicic acid going into solution. Dissolution may be slowed by protecting the surface from attack. The rate equation suggested by the reaction scheme just described is:

$$dC/dt = k(A/V)(K_g[OH^-]/(1 + K_g[OH^-])) \quad (3)$$

where C is the concentration of silicon, t is time , k is the rate

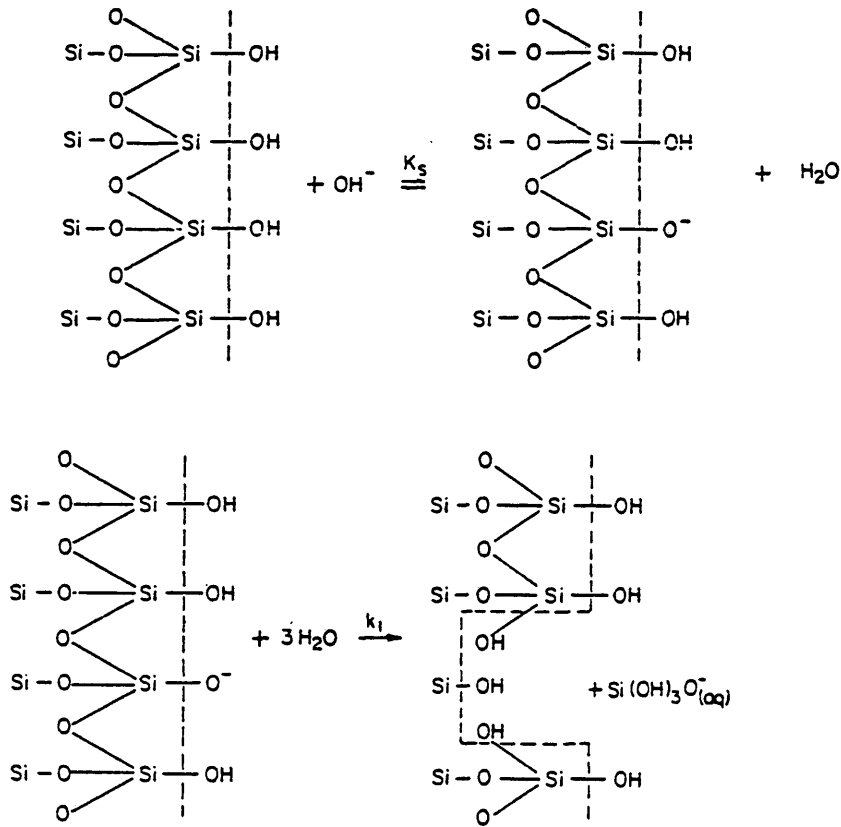


Figure 1.1 - Speciation of monovalent silicic acid as a function of pH.

constant, K_s is the dissociation constant for the surface silicic acid sites, A is the available surface area and V is the volume of solution. As long as the solution concentration of the hydroxide ions changes by only a small amount, the right side of the equation is essentially constant. Then, a pseudo rate constant can be defined and the rate equation becomes:

$$dC/dt = K'(A/V) \quad (4)$$

The next chapter describes the experimental procedures followed. The pretreatment procedures are discussed in detail. Surface areas of the experimental materials were determined using four-point BET nitrogen gas adsorption measurements. The surface areas are reported for materials that have been through the pretreatment procedure and compared with the surface areas of fresh materials. The experimental equipment used is documented along with the sampling procedures followed. The analysis procedures followed are also discussed.

The experimental results are presented and discussed in Chapter 3. Pure quartz dissolution is the first case study. The solution depletion effects are examined with an initial kinetics one day experiment. Initial dissolution rates are determined for all quartz studies followed by dissolution of quartz in the presence of added soluble aluminum. Pure kaolinite dissolution is addressed

next and then kaolinite dissolution in the presence of added soluble aluminum or silicon. Finally, mixtures of the two materials are dissolved with the solution concentrations of both silicon and aluminum are presented and compared to the first studies.

In the last chapter, the conclusions and recommendations are presented. The conclusions are drawn by comparing the results from the various types of experiments. An appendix is included which documents the solution concentrations measured at each sampling time for every experiment conducted.

Chapter 2

Experimental Procedures

The rates of dissolution were investigated for quartz (SiO_2), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and mixtures of the two materials. The quartz is obtained from Pennsylvania Glass Sand Corporation (Pittsburgh, Pennsylvania). Marketed under the name "Min-u-sil 5", the quartz is a fine powder with a reported nominal particle size of 5 μm . The kaolinite is obtained from Georgia Kaolin Company (Elizabeth, New Jersey).

Small amounts of impurities present in these materials and grinding induced damage can influence the rate of dissolution measured experimentally. Naturally occurring impurities, such as iron and alumina compounds, may slow the rate of silica dissolution. Grinding rock samples to obtain the desired range of particle sizes can leave damaged amorphous layers on crystal surfaces or extremely fine debris which rapidly dissolves.

To eliminate these effects, the materials were chemically pretreated before the dissolution studies. We use the pretreatment procedures followed by surface chemists studying the surface charge and adsorption properties of these materials (Reise, 1982). Since surface titrations and adsorption measurements are extremely sensitive to grinding alterations and surface impurities, procedures

demonstrated as adequate for these measurements should be satisfactory for the surface preparations of dissolution studies. The impurities trapped within the structure of the materials are not removed by the pretreatment procedures.

Quartz Pretreatment

The quartz studied is reported by the manufacturer to contain a level of 0.023% Fe_2O_3 and 0.10% Al_2O_3 by weight along with other impurities. These contaminants can be removed from the exterior crystal surfaces by leaching the quartz with an acid solution. An equimolar acid mixture, 2.5 N HCl-HNO_3 prepared by adding equal volumes of 2.5 N HCl and 2.5 N HNO_3 , is employed. Fifty grams of quartz are contacted with 150 mL of the acid mixture in each of four polypropylene bottles (250 mL capacity) designed for use in the centrifuge. The solids are kept in a suspension by a wrist action shaker and the suspension is kept at a temperature of 80°C by an immersion water bath for a period of 18 hours. The solids and acid solutions are separated by centrifugation. The solution above the settled solids is decanted away and discarded. Each sample is contacted with 150 mL of fresh acid mixture, stirred into suspension, and boiled for one hour. After centrifugation, the acid solutions are decanted away and discarded.

To insure that the surface and particulate iron and aluminum contaminants are removed, a dilute acid treatment follows the leaching. Each quartz sample is mixed into suspension with 100 mL of 0.12 N HCl and then allowed to settle at room temperature overnight. After centrifugation, the solution is decanted away and discarded. This process is repeated to obtain a total of three treatments with the dilute acid. The excess acid is removed by a similar series of three deionized water rinses.

Grinding induced amorphous surface layers and fine debris present in the quartz samples can be removed by treatment with sodium hydroxide solutions. The caustic solution dissolves disturbed surface layers at a much faster rate than the more structured, undamaged quartz crystals. The quartz samples are contacted long enough with sodium hydroxide solutions to insure that surface layers and debris are removed, typically overnight.

One hundred milliliters of 2 N NaOH are added to each bottle containing the acid rinsed quartz. The resulting suspensions are allowed to settle overnight at room temperature followed by centrifugation. This separation is more difficult than the previous separations from acid solutions because the particles are highly negatively charged hindering settling. The recovered caustic solution is decanted away and discarded. This process is repeated to obtain a series of three caustic treatments. Some of the excess caustic is removed by a similar series of three deionized water

rinses.

To complete the rinse, the quartz in each bottle is made into a slurry using a small amount (less than 50 mL) of deionized water and transferred from the bottle into a length of 5/8 inch filled diameter regenerated cellulose dialysis tubing which has a reported average pore radius permeability of 24 angstroms (VWR #25225-281). The dialysis bags are soaked in a flask of deionized water which is changed periodically until the overall solution pH drops below 9. The pH measurements are taken at room temperature with the electrode calibrated using pH 7 and pH 10 buffer solutions. After the pH reading is acceptable, the quartz is removed from the tubing, dried in a 100°C oven, and stored in a dessicator.

Kaolinite Pretreatment

Kaolinite (105 g) is placed into a large flask and 2 liters of deionized water are added. The solids are mixed into a suspension by constant stirring. The clay particles tend to clump together initially which inhibits the bar magnet rotation. The suspension is maintained at room temperature for one week. After one week, the suspension is allowed to settle at room temperature for 48 hours. The clarified solution, which contains the very fine particles (less than about 0.2 μm diameter) that did not settle, is decanted away

and discarded. The remaining slurry is separated by centrifugation.

The surface and particulate iron contamination present in the kaolinite is removed by acid leaching. Two liters of 0.2 M ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and the settled kaolinite are contacted with the overall pH of the solution adjusted to pH 4 using drops of 1.2 N HCl. The resulting suspension is maintained by constant stirring at room temperature for one week and then allowed to settle for 48 hours. The clarified solution is decanted away and discarded. The remaining slurry is separated by centrifugation.

The amorphous silica present in the kaolinite is removed by treatment with caustic. The acid rinsed kaolinite is divided equally among four polypropylene bottles. To each bottle, 150 mL of 0.5 N NaOH are added. The mixtures are stirred into suspensions and boiled for one hour. The clay particles are collected from the suspensions by centrifugation with the resulting liquid decanted away and discarded. The clay particles in each bottle are rinsed three times with 100 mL of deionized water to remove some of the excess caustic. The remaining kaolinite is made into a slurry and transferred into lengths of regenerated cellulose dialysis tubing. The filled dialysis bags are soaked in a flask of deionized water which is changed periodically until the pH drops to below 9. After the rinse is completed, the kaolinite is removed from the tubing, dried in a 100°C oven and stored in a dessicator.

The specific surface area of each material is determined by 4-point BET nitrogen gas adsorption method (Micromeritics AccuSorb 2100E). The samples were outgassed overnight at a minimum temperature of 350°C. The untreated quartz is found to have a surface area of about $6.6 \text{ m}^2/\text{g} \pm 2 \text{ m}^2/\text{g}$. The surface area of the treated silica is about $4.5 \text{ m}^2/\text{g} \pm 1.2 \text{ m}^2/\text{g}$. This value compares to the value of $4.15 \text{ m}^2/\text{g}$ reported after a similar pretreatment of material obtained from the same source (Riese, 1982). The surface area of the raw kaolinite is about $17.4 \text{ m}^2/\text{g} \pm 2.2 \text{ m}^2/\text{g}$. After treatment, the surface area of the kaolinite is about $15.9 \text{ m}^2/\text{g} \pm 1.5 \text{ m}^2/\text{g}$. This value compares to the value of $12.3 \text{ m}^2/\text{g}$ reported after a similar pretreatment of kaolinite obtained from a different source (Riese, 1982). The lower surface area of the pretreated materials principally reflects the loss of fines.

Dissolution Experimental

After the pretreatment procedures are completed, the materials are ready for dissolution measurements. A dissolution temperature of $70^\circ\text{C} \pm 2^\circ\text{C}$ is maintained using a constant temperature immersion bath controlled by a Haake thermostat. The reaction vessel is a 250 mL nalgene bottle which is occasionally shaken by hand. Dissolution rates are so slow that contributions from mass transfer effects are not expected. Preliminary experiments show faster

dissolution occurs when the bottle contents are mixed constantly by a wrist action shaker. This rate increase could be due to self abrasion of the particles (Southwick, 1985). An unstirred reaction vessel was chosen to circumvent this possibility.

Into each bottle, 150 mL of 0.1 N NaOH was carefully measured. The desired 0.1 N ($0.1 \text{ N} \pm 0.02 \text{ N}$) concentration is achieved by diluting concentrated NaOH with deionized water. Since these NaOH solutions will dissolve the vitreous silica present in laboratory glassware, storage vessels are nalgene plastic and contact time with volumetric flasks and other glassware is limited. The dilute solution normality is checked against standardized HCl solution by titration. The solution in the reaction vessel was heated to the dissolution temperature by immersion in the water bath for at least one hour prior to the start of the experiment.

To start the dissolution, the doping solutions and solids are added to the reaction vessel. To add dissolved aluminum ions, a small volume of a concentrated solution of alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) was used. To add dissolved silicon ions, a small volume of 1000 ppm analytical standard silicon solution was used. The amount of solids by weight is determined to the nearest hundredth of a gram before addition. When mixtures of solids (quartz/kaolinite) were to be studied, the fraction of each component was determined by its weight on the basis of a 10 g total mixture weight.

The mouth of the bottle is covered with a membrane consisting

of a 2 mm thick rubber disk which is 22 mm in diameter and has a teflon coating on one surface (Alltech #95322). The teflon coating is placed toward the bottle contents because preliminary experiments indicated that the high pH and temperature degraded the rubber. The bottle is sealed by a screw on cap which is open at the top. The capping arrangement is designed to allow samples to be withdrawn from the bottle without uncapping, minimizing evaporation losses. The cap also serves to sandwich the teflon and rubber disks which sometimes separate. The bottles were kept in an upright position during an experiment to prevent solids from becoming trapped in the pocket between the disks. Preliminary experiments were conducted to determine that the reaction vessels and caps did not leak.

Samples are withdrawn from the reaction vessel by a 3 inch, 22 gauge hollow needle attached to a syringe. The glass syringe has a 20 cm³ capacity and is equipped with a luer-lock tip. After sample withdrawal, the needle is replaced with the filtering assembly consisting of a three piece swin-lok filter holder and a nuclepore filter. The nuclepore filters are 25 mm in diameter with a nominal pore diameter of 0.2 μ m. The solution in the syringe is forced through the filter by applying pressure to the plunger. Care must be taken in this step since excess pressure can puncture the filter or cause fluids to leak around the filter. All particulates must be removed from the sample solution to prevent further

dissolution and to prevent them from contributing in the analysis. The clear solution is collected in a small, clean, dry vial which is afterwards capped with parafilm and a screw on top. The silicon and aluminum ion concentrations in the caustic solutions should not exceed the solubility limits even as they are cooled to room temperature. Visible solid particles are not present.

The volume of the sample withdrawn is about 10 mL. The sample volume was estimated from the markings on the body of the syringe. The solution volume inside the reaction vessel is reduced during a dissolution experiment due to repeated sample withdrawal. The total amount of reaction vessel volume reduction was determined by the sampling volume and by the number of samples taken. The exact amount of solution depletion is not measured but a limit of five samples were withdrawn from any single reaction vessel during the dissolution studies.

To avoid cross contamination of samples, the filtering equipment must be cleaned between each use. The syringe and plunger were rinsed with deionized water, rinsed with acetone, and shaken dry. The filter holder is disassembled and the filter discarded. The three pieces of the filter holder were rinsed with deionized water, shaken dry and allowed to air dry for about 20 minutes. Several sets of filter holders were employed to minimize sampling time.

The sample solutions were analyzed for species concentration using atomic absorption spectrometry. The instrument ionizes all species in a liquid sample by atomizing into a flame. A beam of light, of selected wavelength, passes through the flame and the species of interest absorbs light in proportion to its concentration. The total amount of the species present is determined regardless of the form(s) present in solution. For silicon, the concentration versus the measured absorbance is linear up to 150 ppm. The recommended operating range is between 18 and 150 ppm. The silicon absorbance takes place only in a very narrow region within the flame so both flame height and burner head height are critical parameters. For aluminum, the concentration versus absorbance relation is linear up to 60 ppm. The recommended operating range is between 10 and 60 ppm.

Species standards of known concentration were used to calibrate the absorbance. These standards are prepared by diluting analysis grade reagents with deionized water. Anticipated sample solution concentrations were estimated from preliminary experiments. A sample solution aliquot is diluted by the required amount of deionized water to obtain a solution concentration within the linear absorbance range. After the absorbance of the dilute sample is measured, its concentration is determined from the linear absorbance calibration of the standards. The original sample concentration is deduced by the amount of dilution performed.

Chapter 3

Results and Discussion

Table 3.1 summarizes the experiments performed in this study. All of the experiments were conducted at 70°C in a 0.1 N sodium hydroxide solution with an initial volume of 150 mL. The dissolving solids for each experiment were either quartz, kaolinite, or a mixture of the two. The amount of solids reported for each experiment is a target amount with the actual amount of solids added to each bottle varying by a small amount. When a mixture of materials was used in an experiment, the weights of quartz and kaolinite reported are on the basis of a 1.5 g total sample weight. When doping ions are reported, the initial amount added is shown. The initial soluble ion concentrations are determined from the total volume of solution in the bottle and the known volume of added solution. A parallel experiment is performed with 150 mL of 0.1 N NaOH and the added doping solution with no added solids to verify the initial ion concentration. The duration of each run is also reported. Most experiments lasted for about one week.

The amount of dissolved material that appears in a fixed solution volume depends on the amount of solids added. To put similar runs on a comparable basis, we normalized the measured concentrations by the ratio of the target solid mass to the actual

Table 3.1

Tabulation of Experiments Performed

Experimental Conditions: 70°C in 150 mL of 0.1 N NaOH

Run Number	No. of Bottles	Quartz (g)	Kaolinite (g)	Al (ppm)	Si (ppm)	Duration (hrs)
4	4	1.5	-	14	-	80
8	2	0.5	-	-	-	122
9	2	1.5	-	-	-	122
10	4	1.5	-	-	-	120
11	4	-	1.5	-	-	171
12	3	1.5	-	7	-	171
13	4	1.5	-	20	-	169
14	4	-	1.5	14	-	169
15	4	1.0	-	-	-	28
16	4	1.0	-	-	-	168
17	4	1.5	-	14	-	168
18	4	-	1.5	20	-	173
19	3	1.35	0.150	-	-	173
20	3	1.425	0.075	-	-	170
21	2	1.20	0.30	-	-	141
22	2	-	1.5	-	100	170
23	2	-	1.5	-	150	170
24	2	-	1.5	-	-	170

solid mass in all of the following reported results. Typically, this ratio deviates from one by no more than 3%. The normalized concentration is used in reporting the solution concentration of ions produced from the dissolution of minerals. The normalization is not used in reporting the aluminum solution concentrations of the soluble aluminum doped quartz experiments since the effect is negligible. All solution concentrations are reported on the basis of milligrams of solute per kilogram of solution (ppm). On all figures shown, the curves connecting the data points are included to illustrate trends rather than generated from theoretical models.

Quartz Dissolution

In Figure 3.1, the production of silicon from quartz dissolution is presented. The three different initial weights of quartz studied were 0.5 g, 1.0 g and 1.5 g. The solids to solution volume ratios were approximately 3.33 g/L, 6.67 g/L and 10 g/L, respectively. As expected, an increase in the surface to volume ratio increases the solution concentration of silicon at a given time. However, the increase in solution concentration is not always directly proportional to the increase in available surface area. When the initial weight of quartz was doubled from 0.5 g to 1.0 g, the measured concentrations of soluble silicon is about doubled. When the initial weight is increased to 1.5 g quartz, the increase in soluble silicon

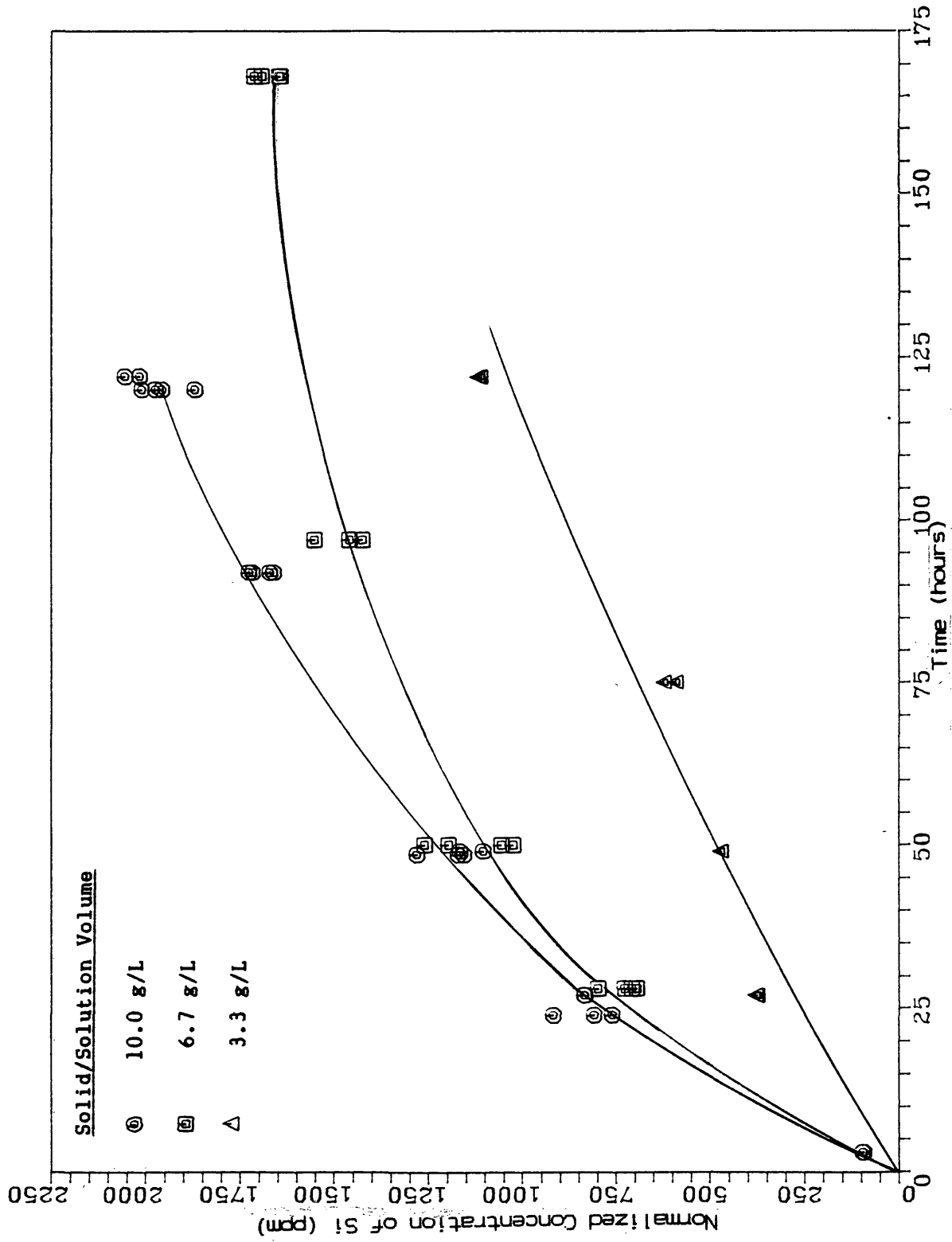


Figure 3.1 - Silicon concentrations from quartz dissolution for three different solid to solution volume ratios.

is not increased proportionally.

The rate of dissolution is always faster during the first few hours. The initial dissolution may be influenced by an amorphous silica layer deposited during the pretreatment rinsing procedures. Later, the dissolution rate slows. This effect may be due to contaminants within the quartz matrix which are released by dissolution and then depress the rate (Ting, 1985). This rate decrease may also be from a drop in solution pH as free hydroxide ions are complexed with soluble silicon ions. Assuming two hydroxide ions are consumed for every silicon ion produced, a concentration of 1000 ppm silicon will cause solution normality to drop to 0.03 N NaOH resulting in a solution of pH 12.5. Assuming one hydroxide ion is consumed, a concentration of 1000 ppm silicon will cause solution normality to drop to 0.06 N NaOH resulting in a pH of 12.8. From Figure 1.1, at these pH values the silicon speciation would be approximately evenly divided between the monovalent and divalent forms. This change in hydroxide ion concentration would cause the less than proportional increase in soluble silicon observed at higher initial quartz (1.5 g) experiments.

To study the initial kinetics of quartz dissolution, an experiment was conducted with a deviation from the one week experimental duration. The same number of samples were taken but the total time allowed for dissolution is only one day instead of one week. The amount of quartz added was 1.0 g with a solids to

solution volume ratio of approximately 6.67 g/L. The results of the short time experiment are presented in Figure 3.2. The fast initial dissolution forms a linear relation lasting the first hours of the experiment. The two lines presented are linear regression best fits. Case one uses the average measured silicon concentrations of only the first four sampling times. Case two is based on the average concentration measurements of all points.

Table 3.2 shows the initial rate calculated for each silica weight basis presented in Figure 3.1 and the linear regression results from the two cases described above. The calculated initial rates are found by the change in silicon concentration divided by the time increment of the first sample (about 28 hours) and the sample surface area. The value reported is an average of all bottles in the experiment. The linear regression rates are given for both case one and case two.

The effect of solution depletion on the concentration measurements is illustrated by comparing the results of the experiments with the same surface to volume ratios but different time frames. Both experiments have a sample withdrawn at about 28 hours but the measured silicon concentrations show a difference of about 20%. The difference in silicon concentration at about 28 hours in Figure 3.1 for the 1.0 g of quartz case (731.6 ppm) and Figure 3.2 at about 27.5 hours (910.4 ppm) is probably at least partly due to sampling effects.

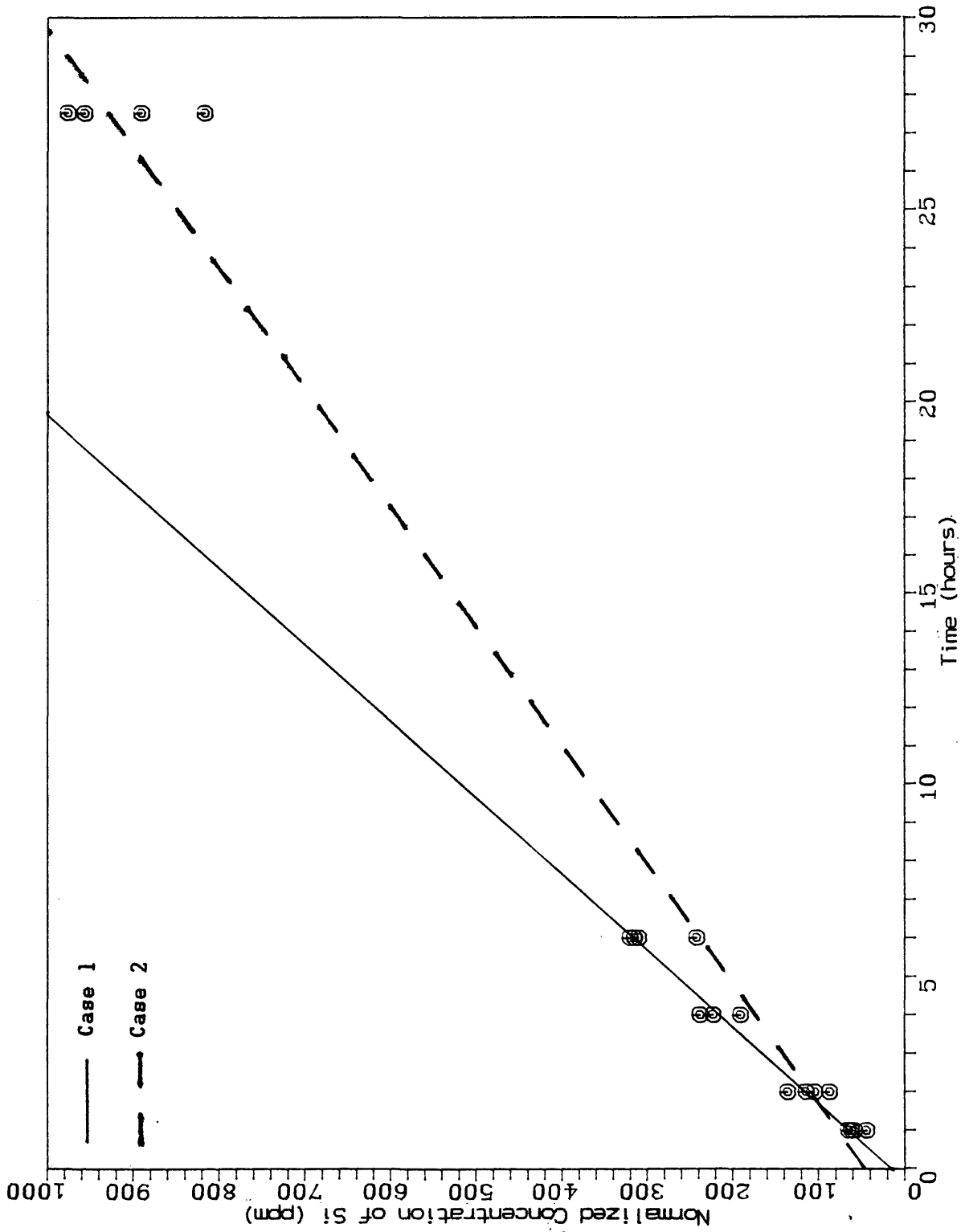


Figure 3.2 - Silicon concentrations from short time quartz dissolution for a solid to solution volume ratio of 6.67 g/L.

Table 3.2
Comparison of Initial Silicon Production Rates

Quartz Mass (grams)	Correction Applied	Initial Rate (g/m ⁵ hr)	Linear Regression	
			Case 1	Case 2
1.5	none	7.7	-	-
1.0	none	6.0	10.8	6.9
1.0	depletion	-	10.4	6.5
0.5	none	6.1	-	-

After a sample withdrawal, the volume of solution in contact with the solids is reduced. Dissolution proceeding at the same rate in two bottles will give a higher concentration of solute in the bottle with the smaller volume of solution. The short experimental duration run has the last in a series of five samples withdrawn at about one day. With normal experimental duration, the first sample is withdrawn at about one day.

The sampling effects can be examined in more detail by assuming the volume of each sample withdrawn is exactly 10 mL and by assuming the dissolution rate is not influenced by the sample withdrawal. In Table 3.3, the sampling effect is quantified by correcting each sampling time average concentration for the short time experiment by the solution depletion effect. The 27.5 hour sample can then be compared directly with the long time experiment 28 hour sample by correcting the measured value with the cumulative corrections. With the correction, the difference between the 27.5 hour soluble silicon concentration (842 ppm) and the first sample taken for the same solid to solution volume ratio in Figure 3.1 (731.6 ppm) is about 15%. Figure 3.3 repeats the data from Figure 3.2 with the solution depletion effect correction. The initial rates calculated for the corrected data by the two cases of linear regression are also given in Table 3.2.

The rate constants for all of the above quartz dissolution cases can be found by examining the rates presented in Table 3.2. The

Table 3.3

Correction for Solution Depletion Effect

C = solution concentration before time increment (ppm Si)

C_o = solution concentration if no sample was removed (ppm Si)

C_1 = solution concentration when a sample of 10 mL is removed (ppm Si)
(average for all bottles in the experiment)

V_o = initial volume of solution (mL)

V_1 = volume of solution after a 10 mL sample is withdrawn (mL)

$$\text{Mass Balance: } (C_o - C) * V_o = (C_1 - C) * V_1$$

Time (hours)	C	C_1	C_o	$(C_1 - C_o)$
1	-	57.1	-	-
2	57.1	110.2	106.7	3.5
4	110.2	222.1	214.1	8.0
6	222.1	296.8	291.0	5.8
27.5	296.8	910.4	859.3	51.1
			Total	68.4

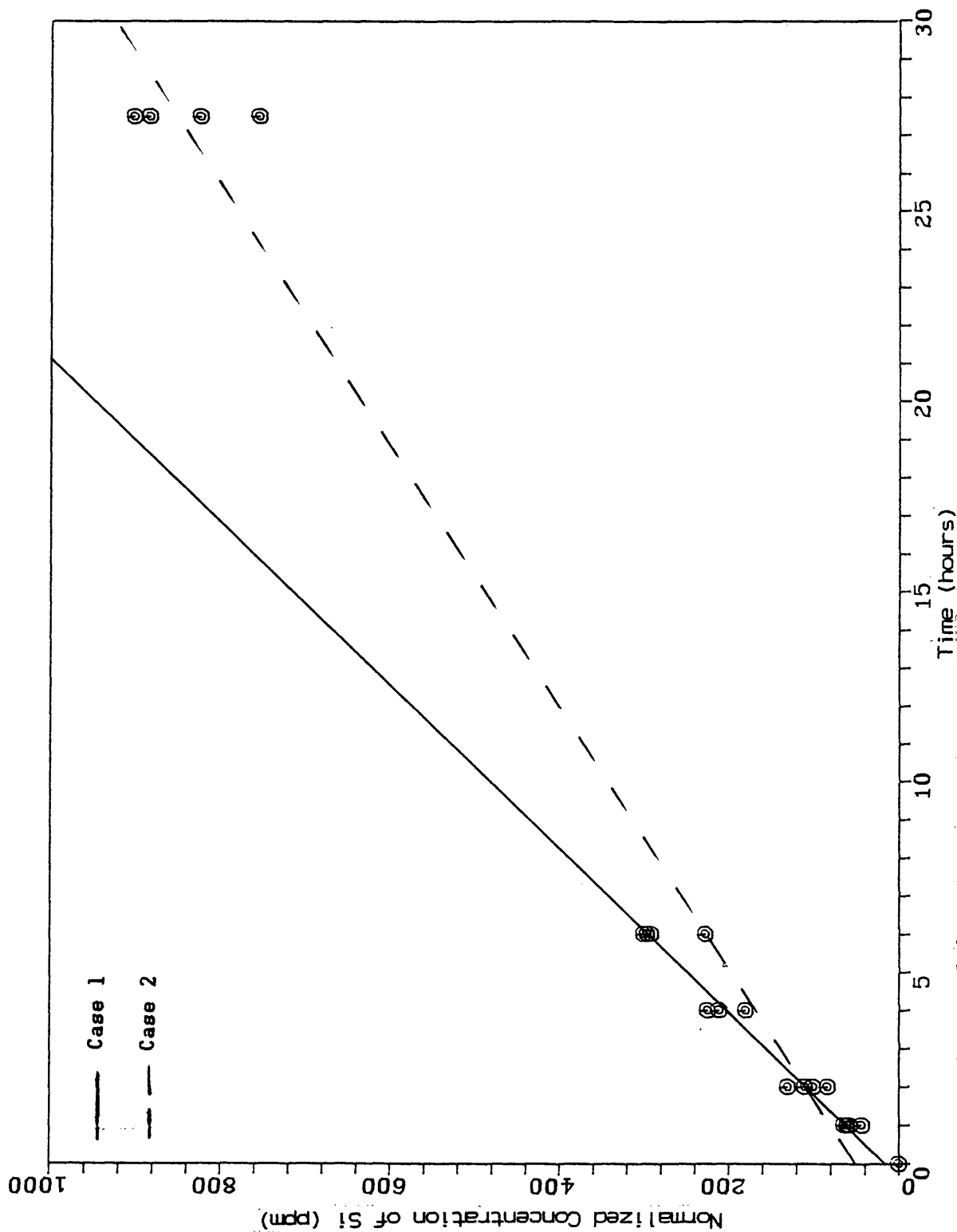


Figure 3.3 - Silicon concentrations from short time quartz dissolution for a solid to solution volume ratio of 6.67 g/L including correction for solution depletion.

rate constant can be calculated as the rate times the solution volume (150 mL) divided by the hydroxide concentration (0.1 N) by assuming first-order kinetics. A rate constant of 9.7×10^{-9} cm/sec is calculated using the linear regression rate of 6.5 g/m⁵hr which incorporated all of the initial data points corrected for solution depletion effect. This rate constant can be compared with the values reported by others. The value is one order of magnitude higher than the value of 4.1×10^{-10} cm/sec reported for quartz at 52°C in 0.1 N NaOH (Bunge, 1982). The 52°C value is one order of magnitude higher than the value of 3.3×10^{-11} reported at 25°C in 0.1 N NaOH (Van Lier, 1960). The rate depends exponentially on temperature so these values are consistent.

The rate constants and the corresponding dissolution temperatures can be used to determine the heat of dissolution of quartz by using an Arrhenius plot. Figure 3.4 shows the Arrhenius plot for the three data points. The heat of dissolution determined from the linear relation slope is 25.6 kcal/mol. Greenberg (1957) has previously reported a value of 26.2 kcal/mol for the dissolution of quartz in an alkaline solution.

Quartz Dissolution in the Presence of Soluble Aluminum

With the dissolution rate of pure quartz established, the effect of dissolved aluminum on the production rate of silicon was studied.

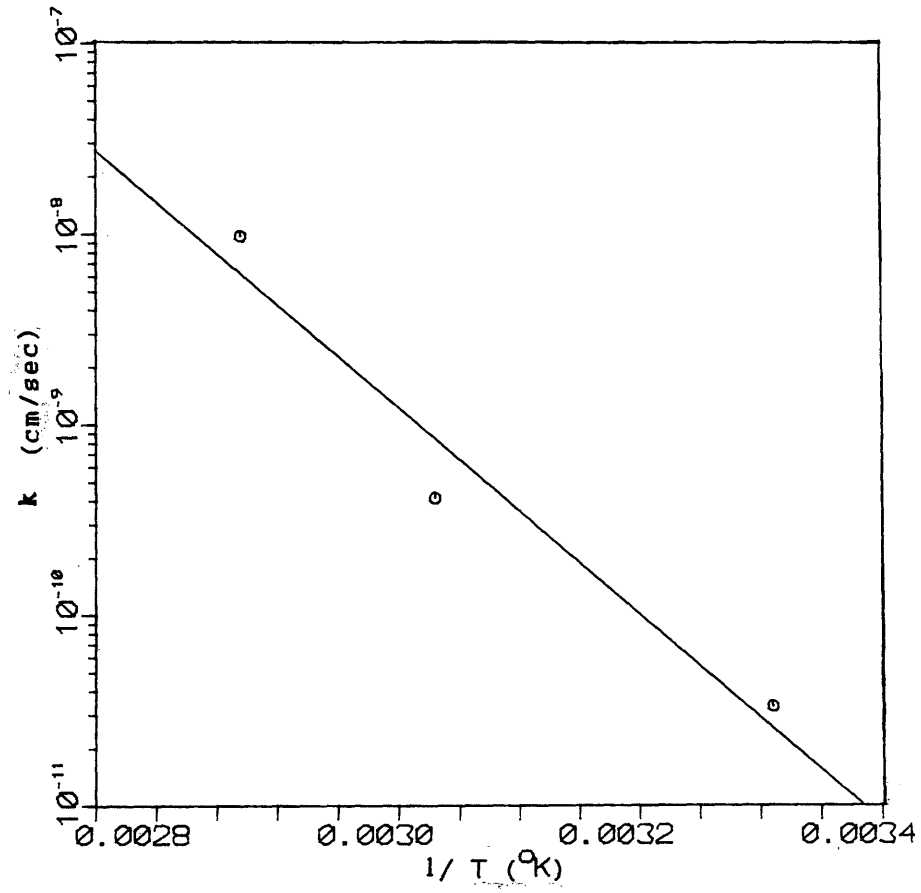


Figure 3.4 - Arrhenius plot to obtain the heat of dissolution for quartz.

The solution concentration of the soluble aluminum can also be studied as a function of experimental duration. Three different initial aluminum solution concentrations were studied: 7 ppm, 14 ppm, and 20 ppm. The three concentrations were chosen in an effort to discover the minimum amount of soluble aluminum to have an effect. The amount of solid quartz added to the aluminum-doped caustic solutions is 1.5 g which gives a surface to volume ratio of about $45 \text{ m}^2/\text{L}$. In Figure 3.5, the normalized solution concentrations of silicon are presented. In Figure 3.6, the solution concentrations of aluminum are reported.

The addition of soluble aluminum to the sodium hydroxide solutions drastically reduces the dissolution rate of quartz. The initial steep climb of the silicon production versus time relation is less pronounced. The highest aluminum concentration allows about 350 ppm silicon in solution compared with over 2000 ppm silicon measured when no added aluminum is present. The effect of the two lower aluminum concentrations on the dissolution rates are reversed. That is, 14 ppm added aluminum depressed the rate less than the 7 ppm aluminum addition. The final silicon concentrations achieved in these solutions are almost identical. It can also be seen that the final aluminum concentrations in these two experiments dropped to almost zero. The final measurements of silicon solution concentrations show a more pronounced plateau when soluble aluminum is present.

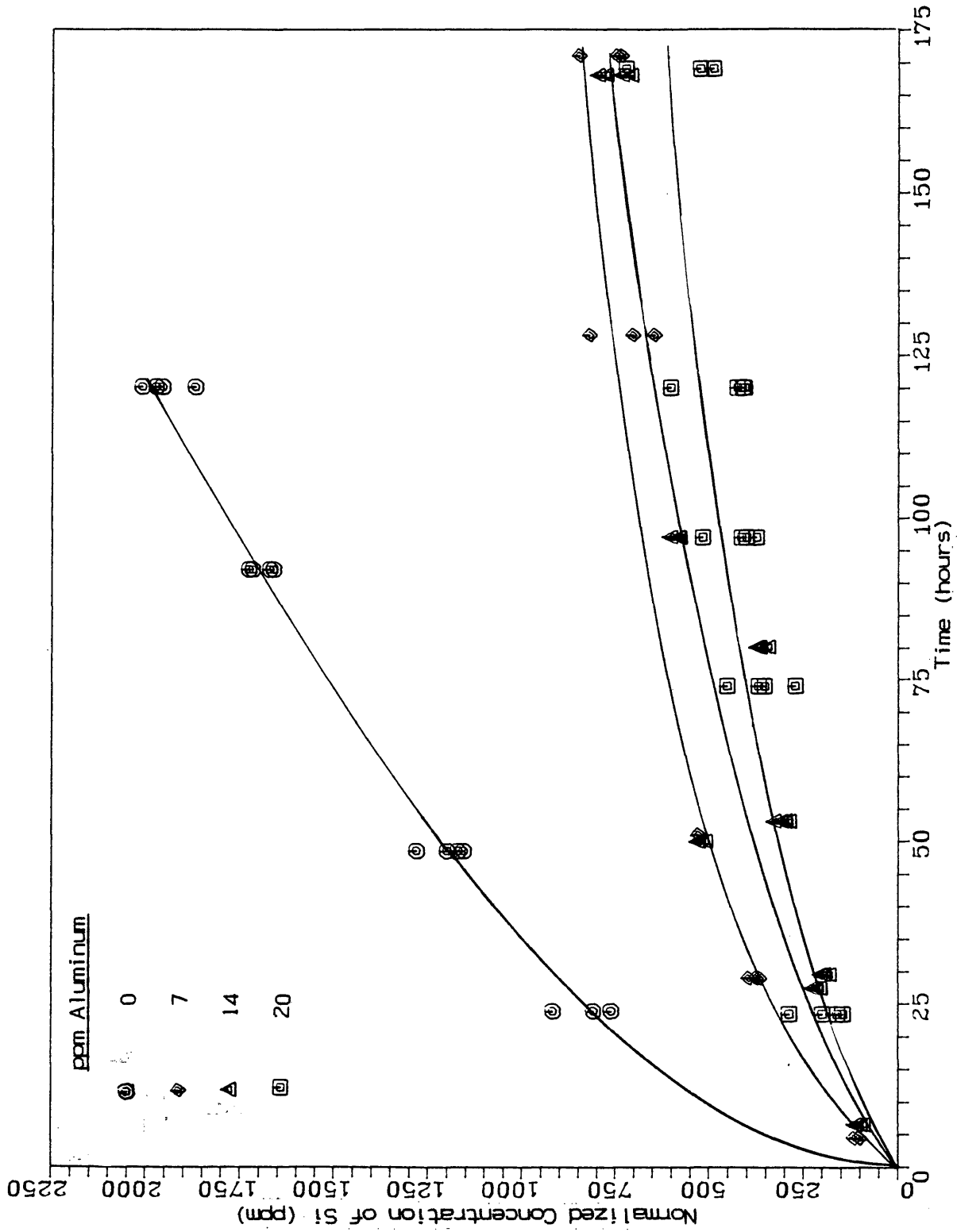


Figure 3.5 - Silicon concentrations from quartz dissolution in the presence of three concentrations of added soluble aluminum for a solid to solution volume ratio of 10.0 g/L.

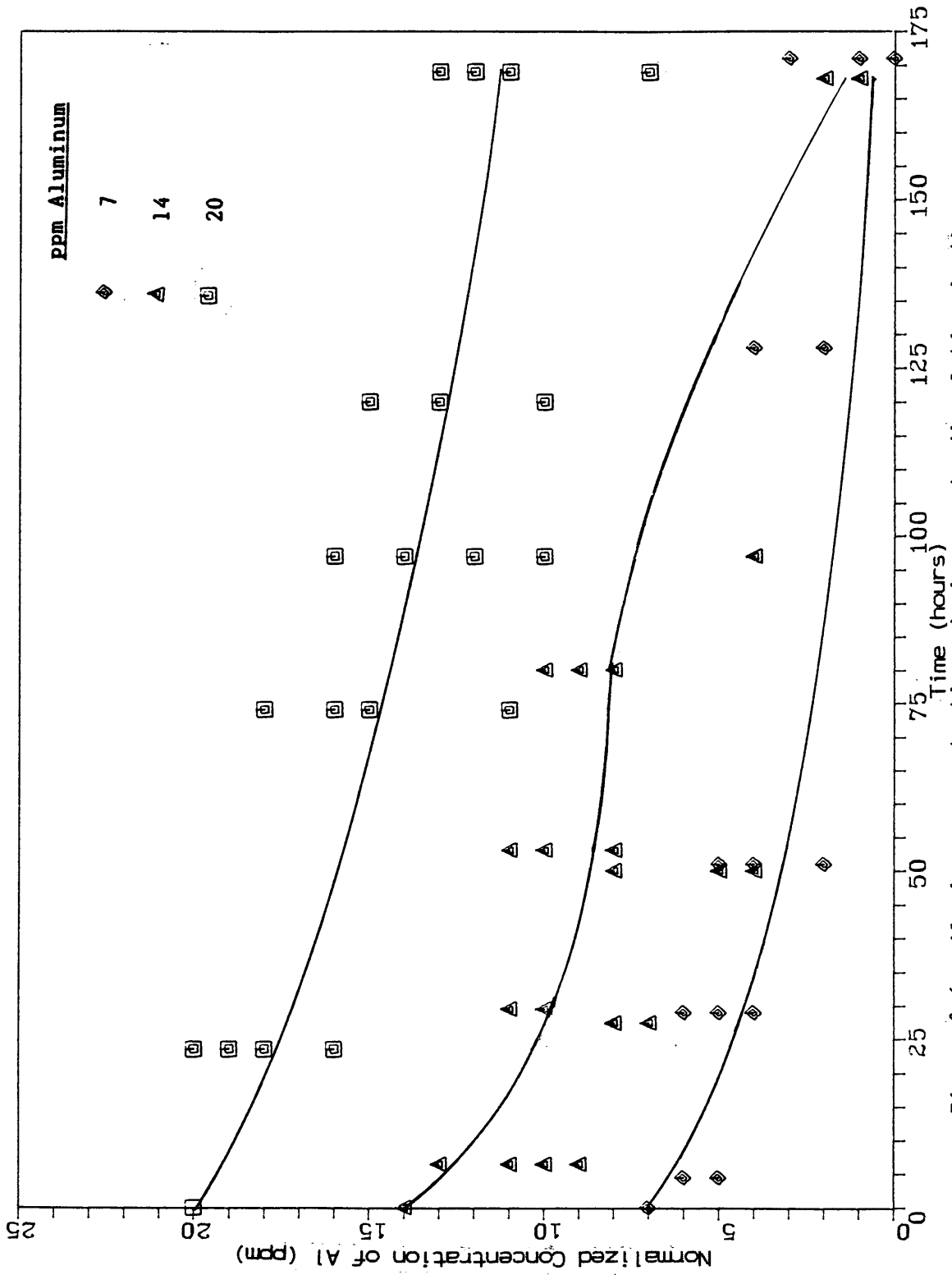


Figure 3.6 - Aluminum concentrations during quartz dissolution in the presence of three concentrations of added soluble aluminum for a solid to solution volume ratio of 10.0 g/L.

In the concentration measurements of aluminum, some interesting trends can be seen. During the initial dissolution of quartz, there is an apparent rapid decline in the solution concentration of soluble aluminum. This drop could be due to adsorption of aluminum onto the quartz surfaces. For the surface to volume ratios studied, a drop of 10 ppm in aluminum concentration would place each aluminum atom adsorbed onto the quartz surface at approximately 250 pm apart. For reference, the atomic radii of the soluble species of interest are as follows: 140 pm for a hydroxide ion, 40 pm for silicon and 53 pm for aluminum (assuming a coordination number of four for the elements) (Huheey, 1980). So, one explanation of the the reduction in dissolution rate is that the adsorbed aluminum ions create a dissolution barrier that reduces the available surface area. The plateau in silicon concentration observed could be due to nearly complete surface coverage.

The decline in aluminum concentration continues throughout the duration of the dissolution even though the available surface area of quartz is approximately constant or declining slightly. The continuous decline in aluminum concentration suggests a Si/Al species forms and is removed from solution by either adsorption onto the quartz surface or precipitation. If this hypothesized Si/Al species adsorbs or precipitates onto the quartz surface, it might block further surface attack by hydroxide ions and slow silicon production.

If a Si/Al precipitate forms but does not protect the surface, then continuing silicon production would eventually exhaust the available supply of soluble aluminum. In this situation, the silicon concentration should begin to increase once the soluble aluminum concentration reaches zero. These experiments are not conclusive since the effective consumption of all soluble aluminum would be seen at longer times.

Looking at the small differences between the measured aluminum concentrations, it is not surprising that the silica production rates are close to the same for all the aluminum doped quartz doped experiments. The aluminum concentrations show little difference at long experimental times despite the variable initial amount. In looking at the 20 ppm run, it can be seen that one bottle in the run was at a slightly lower aluminum concentrations for all sampling times. In the silicon production curve, the same bottle exhibits a slightly higher silicon concentration than the other bottles of that run. In reviewing these results, the reader should also keep in mind the recommended detection range for aluminum (10-60 ppm). Most of the data reported have solution concentrations of aluminum below 10 ppm.

Kaolinite Dissolution

The dissolution of kaolinite produces both soluble silicon and

aluminum into the caustic solution. The stoichiometric ratios of silicon and aluminum in the kaolinite crystal structure are equal. If the dissolution proceeds in a congruent fashion, dissolved aluminum and silicon should appear in equal molar amounts. The amount of kaolinite added to the sodium hydroxide solutions is 1.5 g which gives a surface to volume ratio of nearly $160 \text{ m}^2/\text{L}$. Two identical experiments were conducted with pure kaolinite.

The normalized silicon production rates are presented in Figure 3.7. The silicon production rate is much lower for kaolinite than the production rate for the same mass of quartz even though the available surface area of the kaolinite is much higher than for quartz.

The normalized aluminum production rates are presented in Figure 3.8. The results of the two experiments are not in agreement. Both runs show similar rates for silicon production. However, the production rate of aluminum was significantly lower in run 11 than for run 24. The difference is clearly demonstrated in a plot of the molar ratio of silicon to aluminum concentrations as shown in Figure 3.9. The molar ratio should be approximately equal to one during congruent dissolution. Since congruent fashion dissolution is reported by others (Ting, 1985), the results of run 24 were taken as more accurate and used in the production rate comparisons with the soluble silicon and aluminum doped solution results presented below.

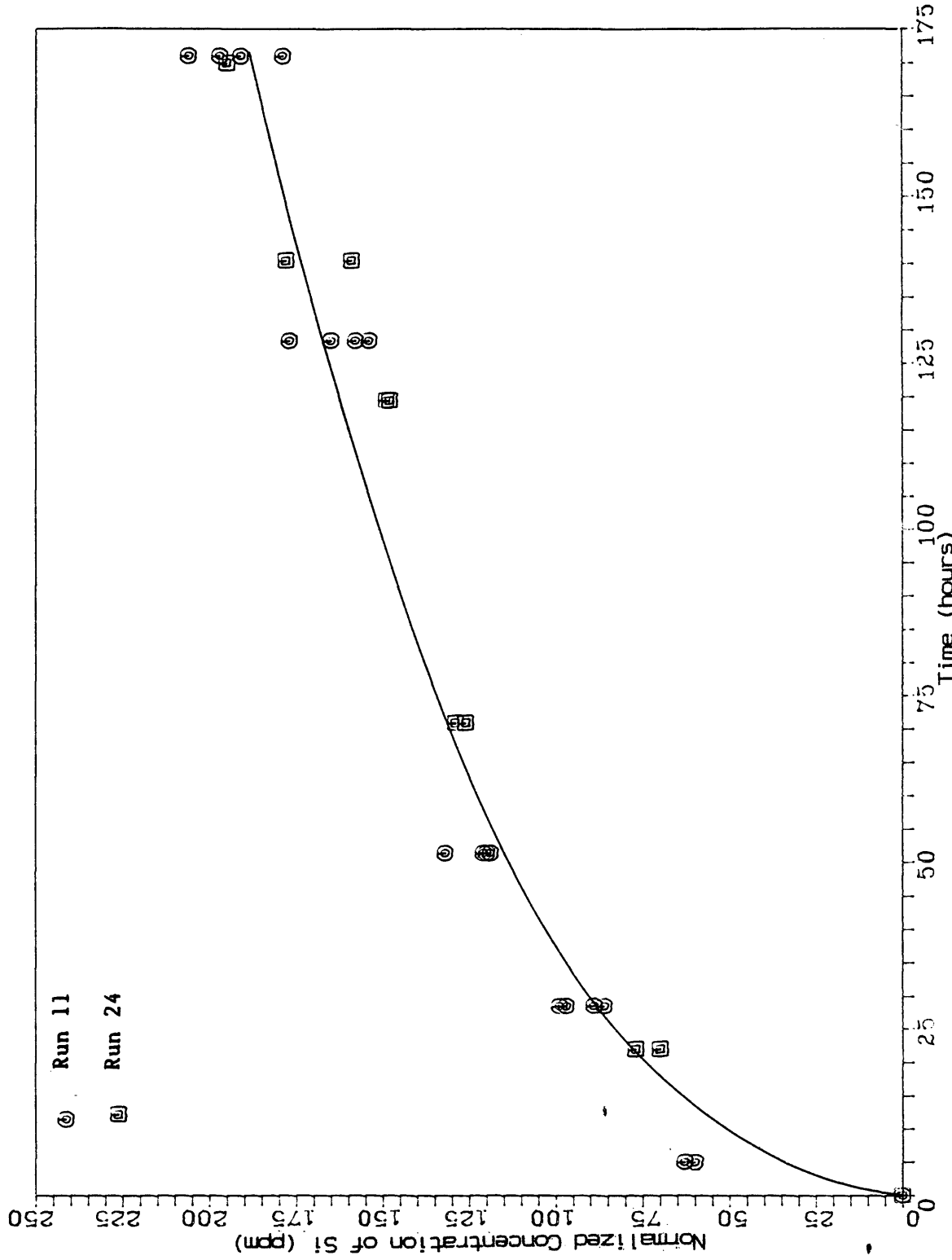


Figure 3.7 - Silicon concentrations from kaolinite dissolution for a solid to solution volume ratio of 10.0 g/L.

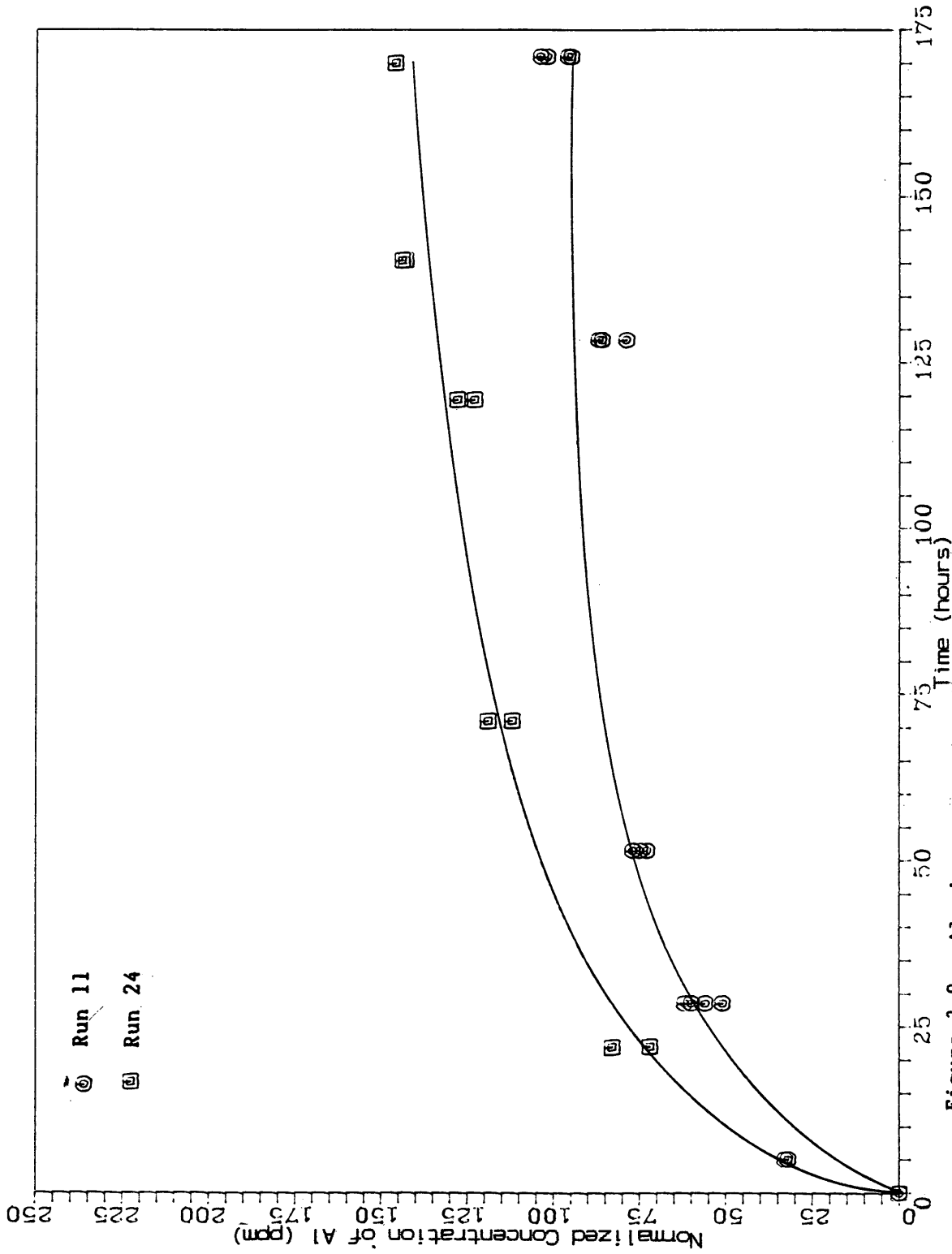


Figure 3.8 - Aluminum concentrations from kaolinite dissolution for a solid to solution volume ratio of 10.0 g/L.

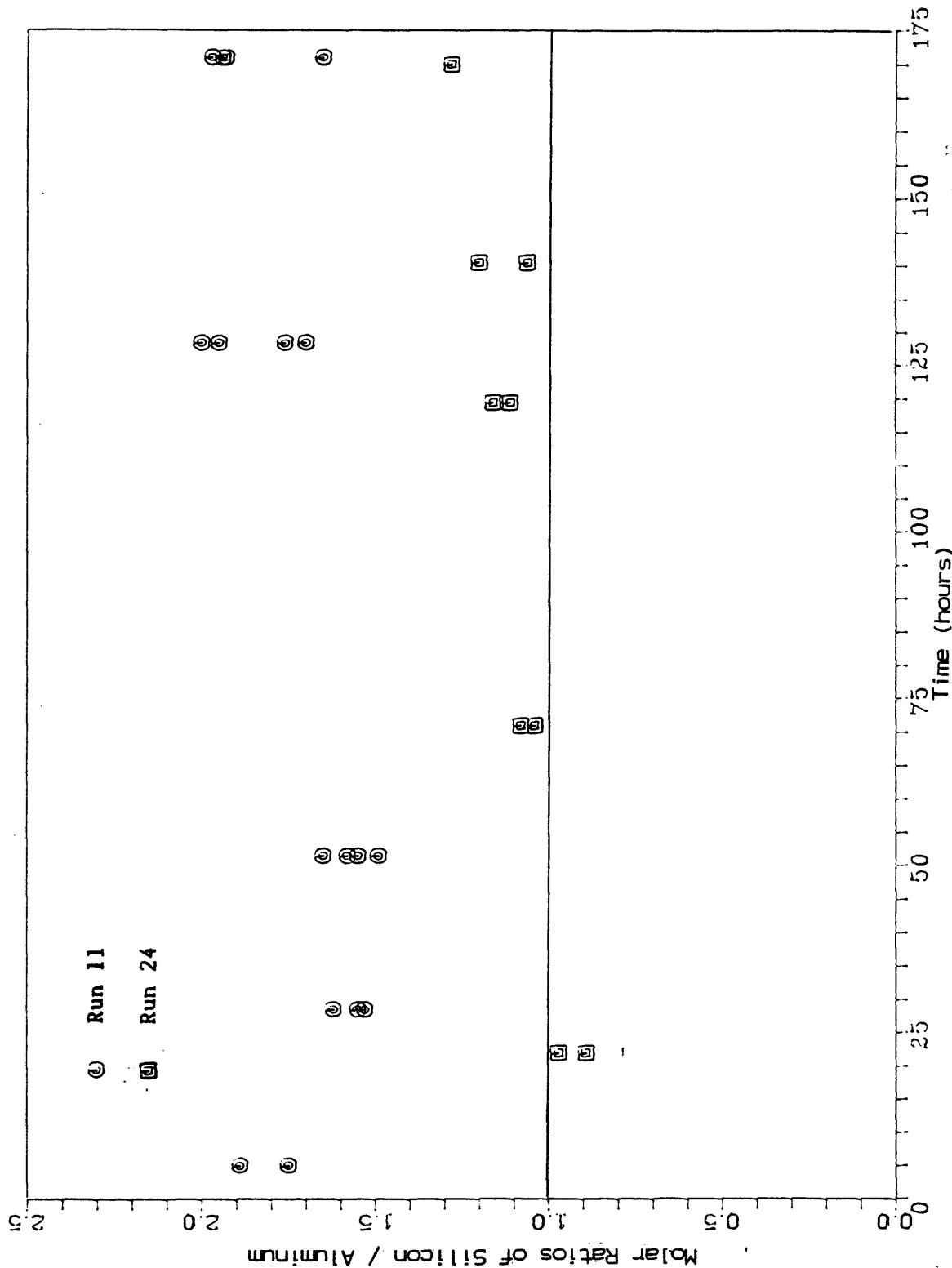


Figure 3.9 - Molar ratios of silicon to aluminum from kaolinite dissolution for a solid to solution volume ratio of 10.0 g/L.

Kaolinite Dissolution in the Presence of Soluble Silicon/Aluminum

The production rates of silicon and aluminum from kaolinite dissolution change slightly by doping the solutions with either soluble aluminum or silicon. The production rates of silicon and aluminum seem to show little effect from small amounts of soluble aluminum. Two initial concentrations of aluminum (14 and 20 ppm) were chosen because of their drastic effect on quartz dissolution. The normalized silicon production rates for the aluminum-doped kaolinite experiments are presented in Figure 3.10. The normalized aluminum production rates presented in Figure 3.11 are the measured concentrations minus the amount of aluminum initially added. The addition of soluble aluminum seems to have no effect on production rates of either silicon or aluminum except for a more pronounced plateau observation. The molar ratios of the produced silicon to aluminum are close to one throughout the experimental duration and are presented in Figure 3.12.

Also studied were the effects of added soluble silicon on the dissolution of kaolinite. The two initial concentrations of silicon chosen were 100 ppm and 150 ppm. The normalized silicon production rates presented in Figure 3.13 are the measured concentrations minus the initially added silicon ion concentrations. The silicon production seems unaffected by the addition of silicon to the reaction solution.. The normalized production rates of aluminum

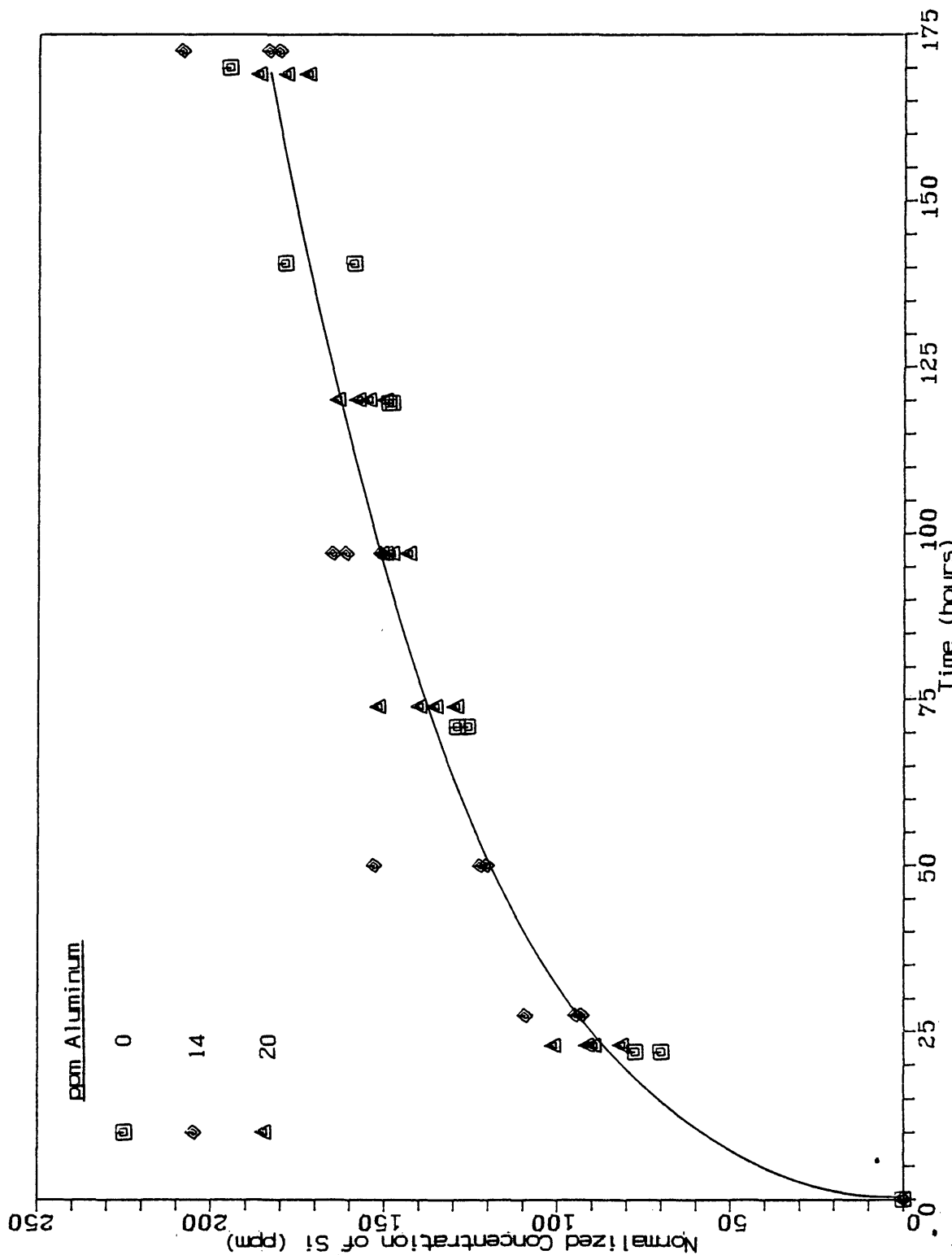


Figure 3.10- Silicon concentrations of added soluble aluminum for a solid to presence of two concentrations of added soluble aluminum for a solid to solution volume ratio of 10.0 g/L.ons from kaolinite dissolution in the

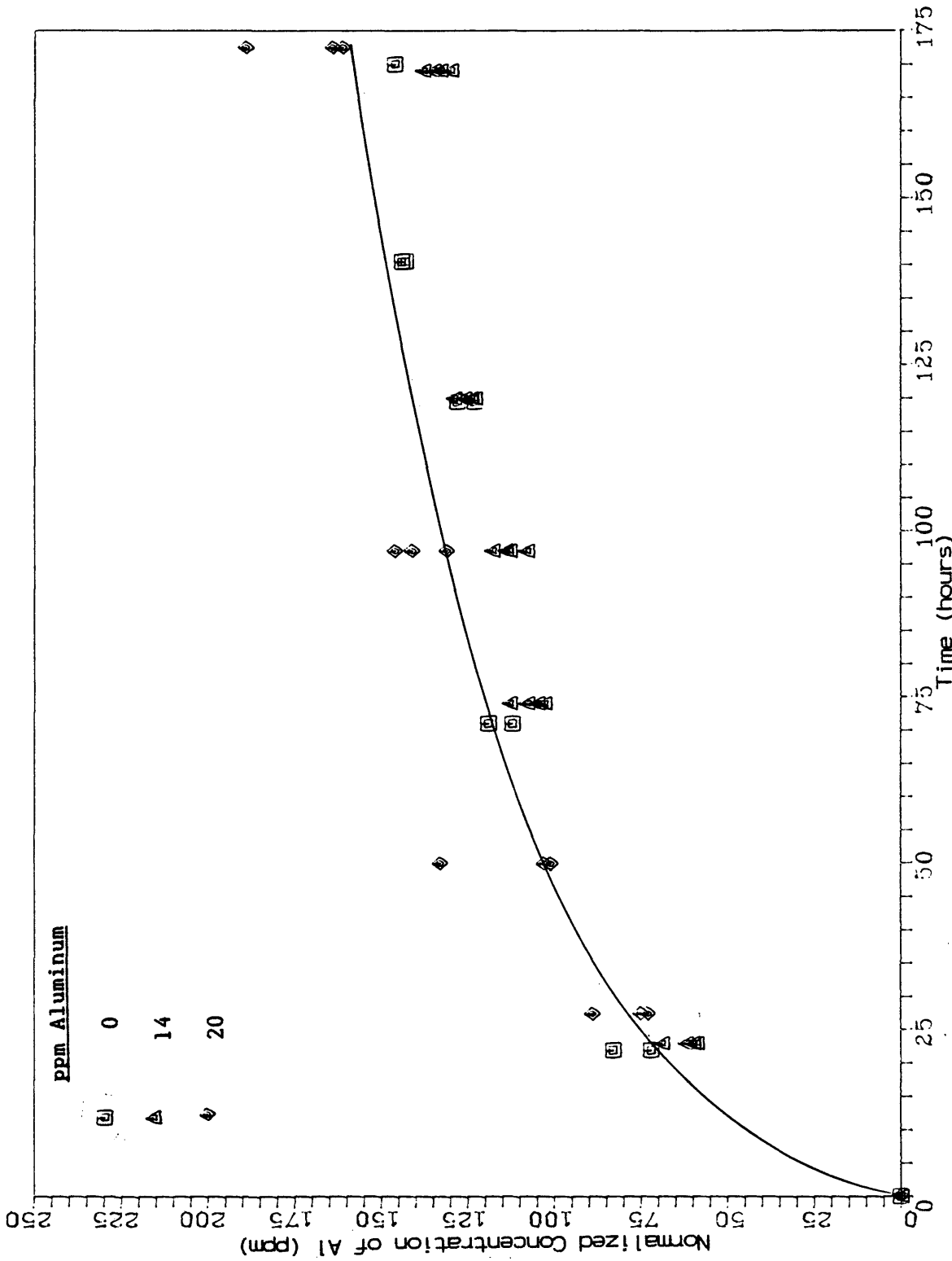


Figure 3.11 - Aluminum concentrations from kaolinite dissolution in the presence of two concentrations of added soluble aluminum for a solid to solution volume ratio of 10.0 g/L. Reported concentrations do not include the amount of added soluble aluminum.

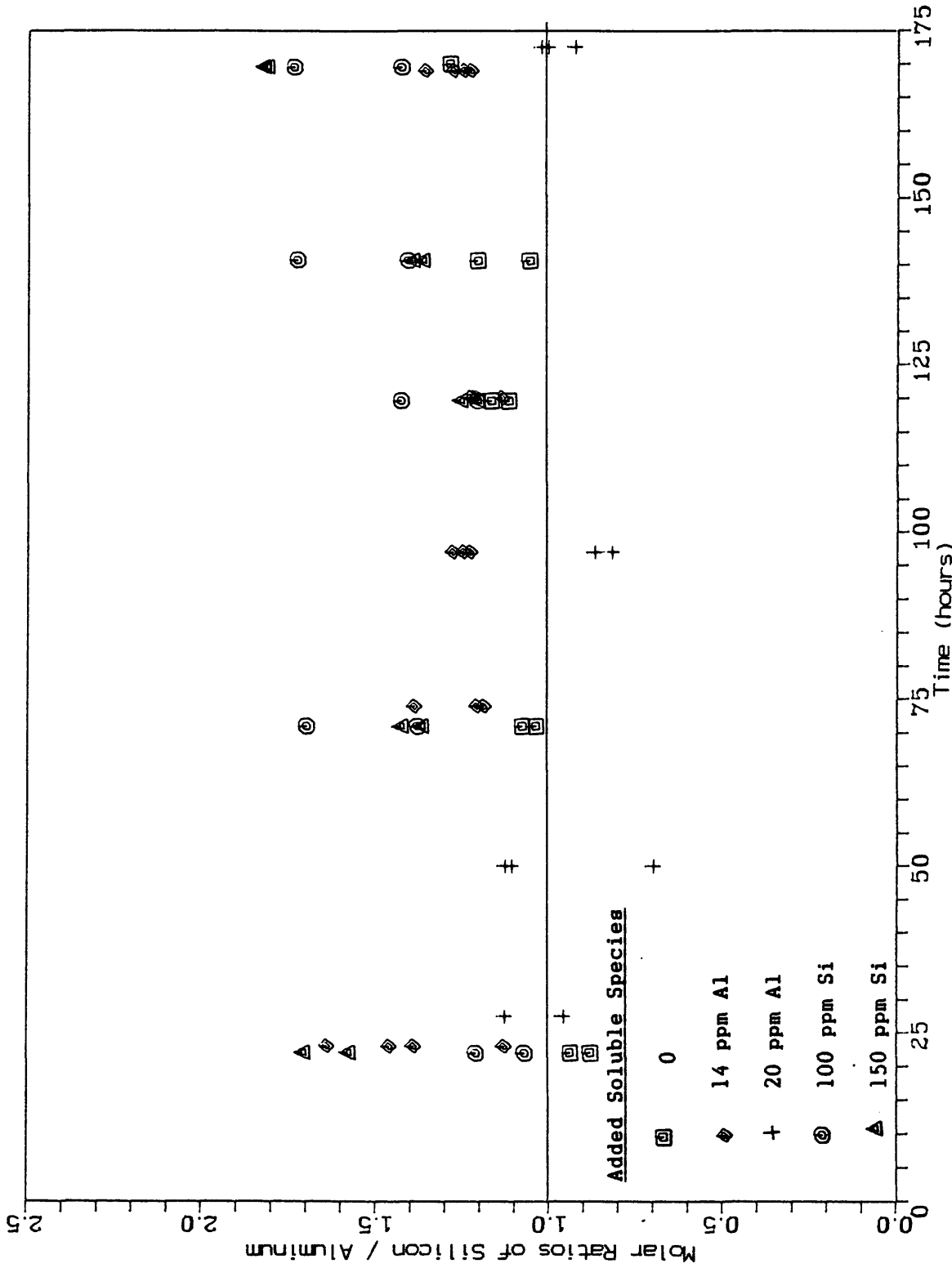


Figure 3.12 - Molar ratios of silicon to aluminum from kaolinite dissolution in the presence of added soluble aluminum or soluble silicon. Reported ratios do not include the amount of added soluble species.

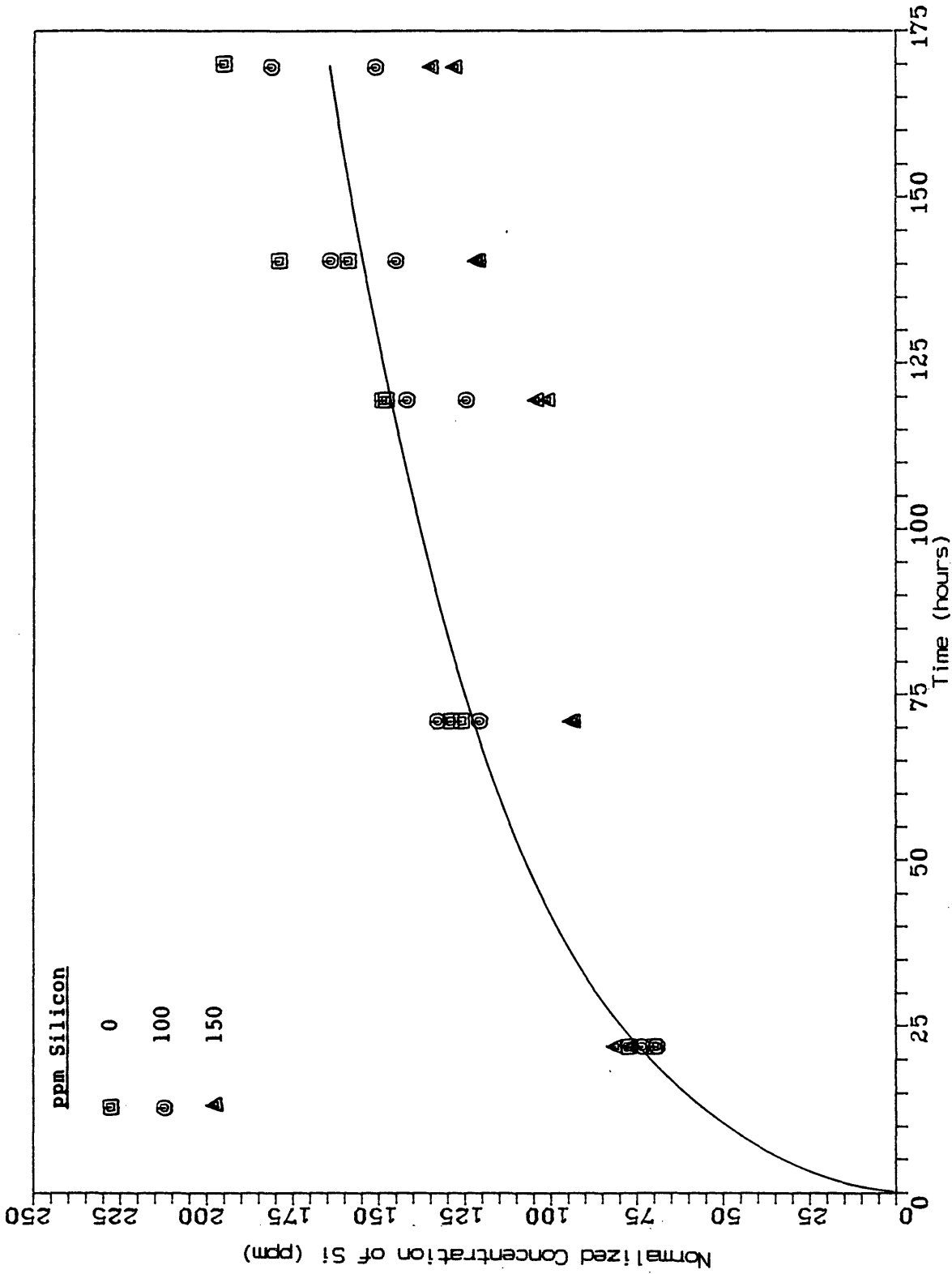


Figure 3.13 - Silicon concentrations from kaolinite dissolution in the presence of two concentrations of added soluble silicon for a solid to solution volume ratio of 10.0 g/L. Reported concentrations do not include the amount of added soluble silicon.

are presented in Figure 3.14. Again, the effects of the soluble silicon are not large but some effect is evident in the values of the plateaus. The production rates of aluminum seem to show a lower plateau value and also the turn around point is earlier in the experiment. These effects could be due to the formation of a Si/Al complex being removed from solution. The molar ratios of the normalized silicon moles (corrected by the added initial amount) to the normalized aluminum moles are also reported in Figure 3.12.

Dissolution of Quartz/Kaolinite Mixtures

Whenever a mixture of materials is prepared containing a variety of particle sizes and particle densities, a problem of homogeneity develops. A ten gram sample of mixture was prepared by combining the quartz and kaolinite needed to reach the desired weight percent of each. The mixing procedure was shaking, rolling and stirring with a spatula. The mixtures studied have a weight percent of quartz of 95%, 90% and 80%. The amount of the solids mixture added to the 150 ml of reaction solution is always about 1.5 g. The solids to surface to volume ratios are; 3.33 g/L, 6.67 g/L, and 10 g/L respectively. The production rates of silicon for the mixtures is presented in Figure 3.15. The reference curve presented in Figure 3.15 is the silicon production measured for pure quartz. The rates follow the predictable pattern of the more

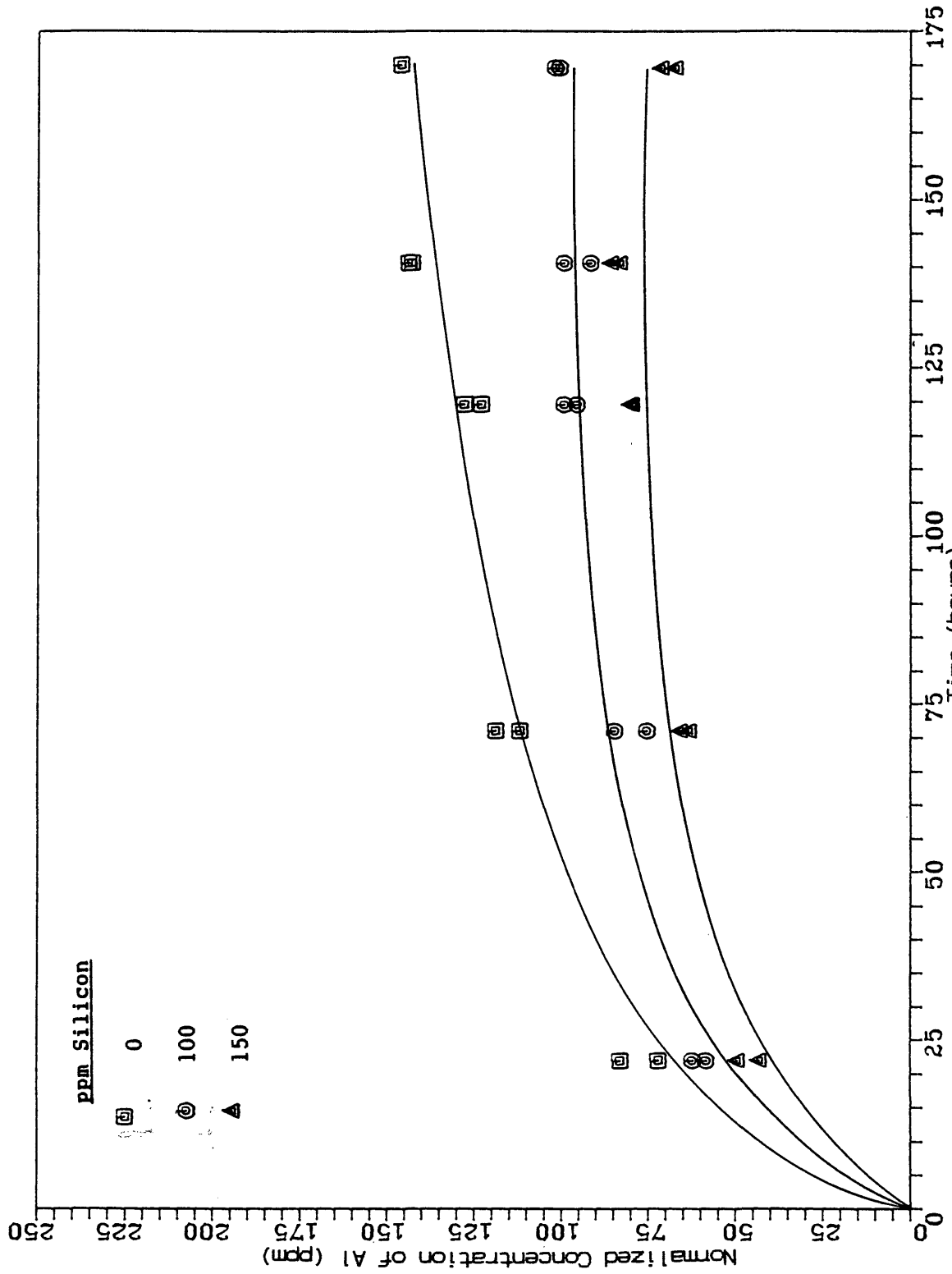


Figure 3.14 - Aluminum concentrations from kaolinite dissolution in the presence of two concentrations of added soluble silicon for a solid to solution volume ratio of 10.0 g/L.

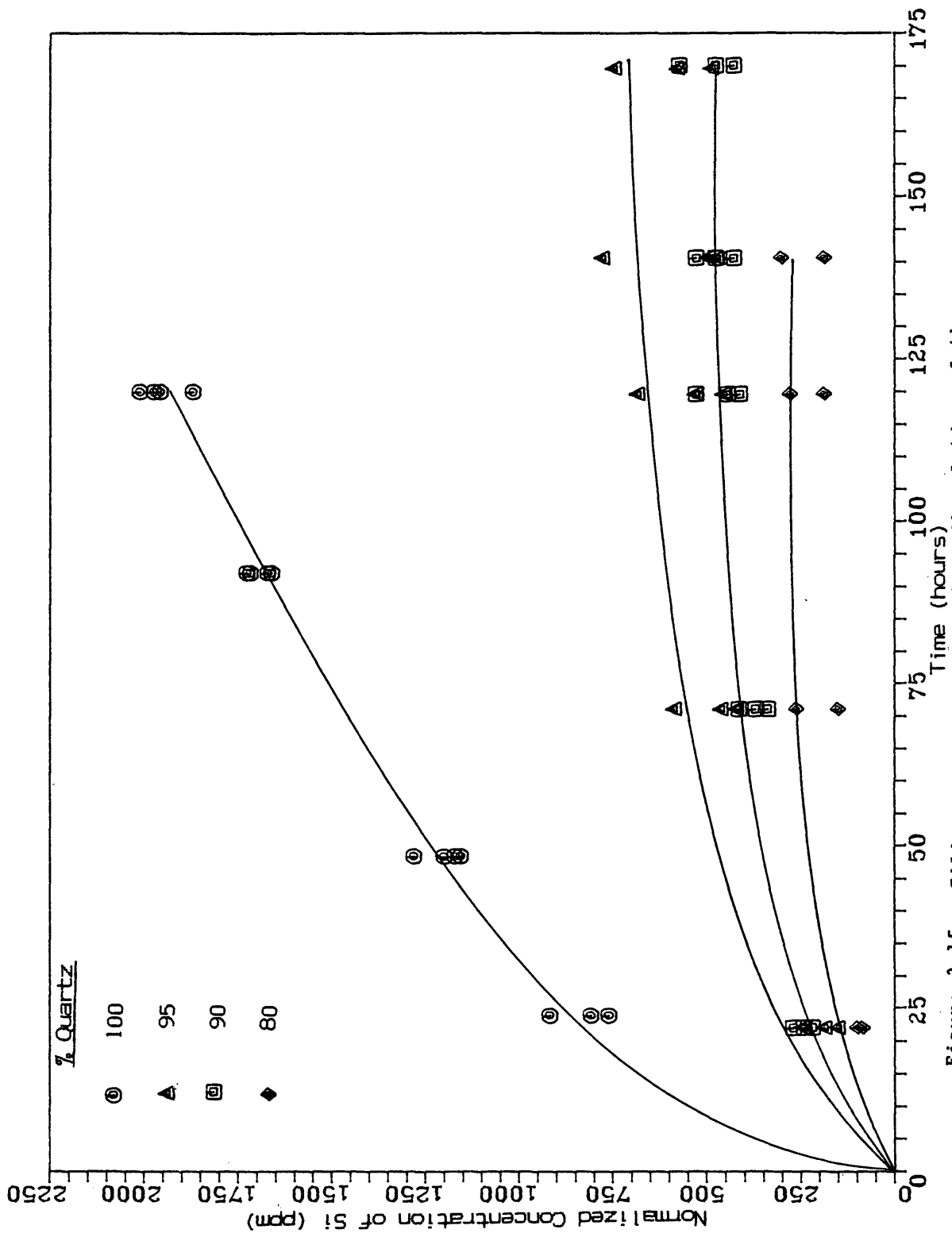


Figure 3.15 - Silicon concentrations from dissolution of three quartz/kaolinite mixtures for a solid to solution volume ratio of 10.0 g/L.

quartz, the higher the rate of silicon production. The normalized silicon production rates are substantially below the production rates of pure quartz. The plateau observations in all mixture experiments are again more pronounced similar to the observed plateaus for quartz dissolution in the presence of aluminum.

The production rates of aluminum are presented in Figure 3.16. The reference curve presented is pure kaolinite aluminum production. A maximum in the aluminum concentration is observed for all mixtures. This is consistent with the results reported by others (Bunge, 1981; Mohnat, et al 1984). The maximum is a product of the release of aluminum from kaolinite consumed by free silicon released by the quartz and the kaolinite. Initially, there is a limited amount of silicon to complex with the aluminum. As the dissolution proceeds, the amount of silicon present increases to the point where all aluminum is complexed as soon as it is produced. Also the kaolinite dissolution would be depressed in the same manner as the silicon-doped kaolinite experiments.

As the amount of kaolinite is increased, one would expect to see an increase in the amount of aluminum measured in solution. An unexpected phenomenon occurred in the 90% quartz mixture and the 95% quartz mixture. The 95% mixture produced more aluminum in solution than the 90% quartz mixture. A problem with the concentrations being low in the detection limit might be the first reason to suspect this observation but there was good

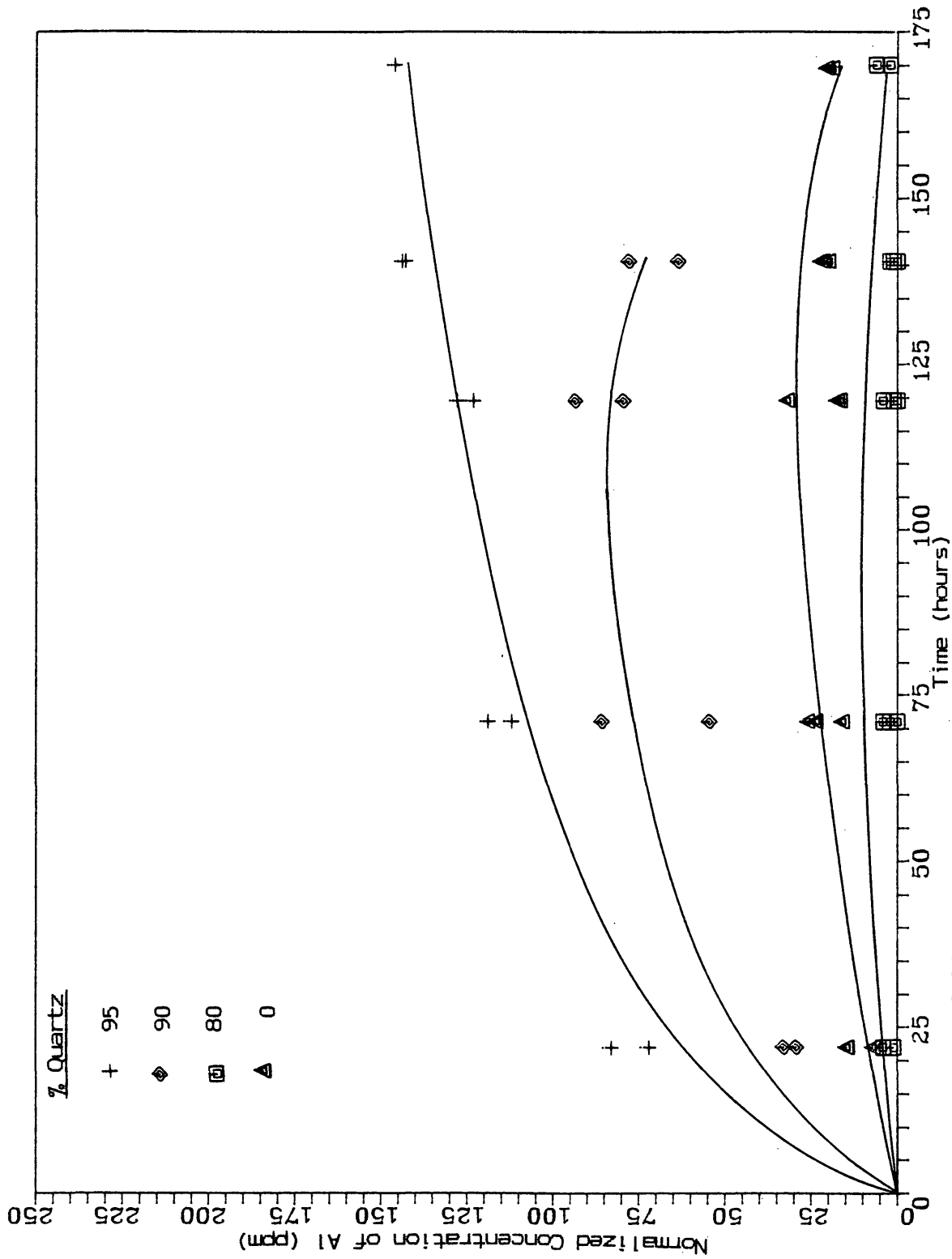


Figure 3.16 - Aluminum concentrations from dissolution of three quartz/kaolinite mixtures for a solid to solution volume ratio of 10.0 g/L.

reproducibility between the bottles.

Competing effects may cause this phenomenon. Perhaps there is a threshold amount of silicon needed in solution (or a large enough Si/Al ratio) before the suspected complex can form. The complex may not be forming in the 0% quartz case or in the 80% quartz case. The removal rate of the complex from solution could also be dependent on the amount of available surface area. The 95% quartz mixture has a lower surface area than the 90% quartz mixture. Perhaps, the amount of surface area combined with the silicon and aluminum concentrations in the 90% quartz experiment is just enough to essentially remove all soluble aluminum as it is being produced by the kaolinite dissolution.

Chapter 4

Conclusions and Recommendations

The silicon production rates increase about proportionally for the 3.3 g/L and the 6.7 g/L quartz cases. Increasing the solid to solution volume ratios to 10.0 g/L showed less than a proportional increase in silicon production. This result can be attributed to the depletion of hydroxide ions changing the dissolution rate. The solution concentrations of silicon should be at low values during the entire duration of the experiment to insure hydroxide is not depleted from solution. To achieve these solution concentrations, the recommended amount of pure quartz to use in 150 mL of 0.1 N NaOH is 1.0 g or less.

The dissolution comparison between the one week duration experiment and the one day duration experiment using the same solid to solution volume ratios, highlighted some interesting phenomenon. The solution depletion correction had a measurable effect (changing the measured concentrations by about 5%). The future work in this area should measure the sample volumes accurately to allow correction of each subsequent data point by the depletion amount. The most practical way to accurately measure the amount of solution withdrawn is to weight the reaction bottles both before and after a sample withdrawal. Since the density of the

solution is known to be 1 g/l, the weights can be directly related to the volume of the sample taken.

The rate constants calculated assuming dissolution rates are first-order with respect to hydroxide ion concentrations compare favorably with results reported by others. The rate constants were larger than those reported at a temperature of 52°C. But since the dissolution rate would increase as the temperature increases, the value reported in this research is reasonable. The heat of dissolution of quartz in 0.1 N NaOH found using the rate constants in an Arrhenius plot also compares favorably to reported values.

Quartz in a pure form dissolves much faster than kaolinite with the same solid to solution volume ratio. Only one solid to solution volume ratio of kaolinite was studied. It is recommended different solid to solution volume ratios of kaolinite be investigated. By adding soluble aluminum to the quartz, dissolution production of silicon can be strongly decreased. In this case, 1.5 g of pure quartz used in each experiment is satisfactory since the solution concentrations of silicon are well above the detection limit but not high enough to cause hydroxide ions to be depleted. The silicon production rates of the mixtures studied also show a decrease in silicon production as the ratio of kaolinite in the mixture is increased.

Evidence is strong supporting the hypothesized formation of a Si/Al complex in solution which is removed by an unknown

precipitation or adsorption mechanism. The quartz experiments where a small amount of soluble aluminum is added show the soluble aluminum decreasing steadily. The experimental duration chosen was not conclusive about the effect on the silicon production rates when all the soluble aluminum is depleted. If precipitation onto the quartz surface or adsorption is occurring, the rate of production would not increase at longer times. However, if the Si/Al complex is removed from solution without affecting the silica surface, then the rate of silicon production would increase when the soluble aluminum is depleted. Adding lower amounts of soluble aluminum would be one way of determining the effect on silicon dissolution when all soluble aluminum has been removed without increasing the experimental duration. The problem of moving solution concentrations of aluminum below the detection limits could be solved by the addition of a known amount of soluble aluminum to a known amount of withdrawn solution.

The silicon doped kaolinite experiments and the mixture experiments also lend evidence to the Si/Al complex formation hypothesis. The soluble aluminum production from kaolinite dissolution is decreased by the addition of soluble silicon while the silicon production seems unaffected. This implies soluble aluminum removal by some mechanism. The mixtures show a decreased amount of aluminum produced when quartz is present.

Because of the variances between bottles of the same run and

between these results and the reported results of others, it is recommended that better analysis techniques and instrumentation be explored. The experimental procedures followed may have some room for improvement. If more data is collected at the same experimental conditions and sampling times some statistical work can be done to arrive at a more accurate set of data.

References Cited

- Ballou, E.V., M.I. Leban and T. Wydeven, "Solute Rejection by Porous Glass Membranes," J. Appl. Chem. Biotech., 23, 119-130, (1973).
- Bojes, J.M and P.B. Bulkowski, "Cyclic Steam Injection: Interpretation of Some Results from Field Fluids Analysis Program," paper SPE 13568 presented at the 1985 SPE Annual Technical Conference and Exhibition, Phoenix, AZ, April 9-11, 1985.
- Bunge, A.L., "Transport of Electrolytes in Underground Porous Media," Ph.D. Thesis, University of California, Berkeley, CA (1982).
- Greenberg, S.A., "The Depolymerization of Silica in Sodium Hydroxide Solutions," J. Phys. Chem., 61, 960-965, (1957).
- Huheey, J.E., Inorganic Chemistry: Principles of Structure and Reactivity, 72-74, Harper and Row, New York, (1978).
- Iler, R.K., "Effect of Adsorbed Alumina on the Solubility of Amorphous Silica in Water," J. Colloid Interface Sci., 43, 399-412, (1973).
- Iler, R.K., The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry, John Wiley and Sons, New York, (1979).
- Mohnat, S.M., J.H. Bae and W.L. Foley, "A Study of Mineral-Alkali Reactions," paper SPE 13032 presented at the 1984 SPE Annual Technical Conference and Exhibition, Houston, TX, September 16-19, 1984.
- Riese, A.C., "Adsorption of Radium and Thorium onto Quartz and Kaolinite," Ph.D. Thesis, Colorado School of Mines, Golden, CO (1982).
- Reed, M.G., "Gravel Pack and Formation Sandstone Dissolution During Steam Injection," J. Pet. Tech., 32, 941-949 (1980).
- Southwick, J.G., "Solubility of Silica in Alkaline Solutions: Implications for Alkaline Flooding," Soc. Pet. Eng. J., 25, 857-864 (1985).
- Stumm, W. and J.J. Morgan, Aquatic Chemistry, Wiley-Interscience, New York, (1970).
- Sydansk, R.D., "Elevated Temperature Caustic/Sandstone Interaction: Implications for Improving Oil Recovery," Soc. Pet. Eng. J., 22, 435-462 (1982).

Ting, D.C., "The Kinetics of Alkaline Consumption of Silicate Minerals, M.S. Thesis, University of California, Berkeley (1985).

Thornton, S.D. and C.J. Radke, "Dissolution and Condensation Kinetics of Silica in Alkaline Solution," paper SPE 13601 presented at the 1985 California REgional Meeting, Bakersfield, CA, March 27-29, 1985.

Underdown, D.R. and K. Das, "Stability of Gravel-Packing Materials for Thermal Wells," J. Pet. Tech., 37, 2006-2012 (1985).

Van Lier, J.A., P.L. De Bruyn and J.G. Overbeek, "The Solubility of Quartz," J. Phys. Chem., 64, 1675-1682 (1960).

Appendix A

Experimental Solution Concentration Measurements

Run Number: 4

Description: 1.5 g of quartz with 14 ppm Al

Time (hours)	Bottle #			
	1	2	3	4
	Concentration of Si (ppm)			
6.5	114	90	114	100
29.5	198	180	210	201
53	312	296	336	292
80	370	340	380	380
	Concentration of Al (ppm)			
6.5	11	10	9	13
29.5	10	11	10	11
53	8	8	11	10
80	8	10	8	9
Weight of Solids (grams)	1.51	1.48	1.53	1.52

Run Number: 8

Description: 0.5 g of quartz

Time (hours)	Bottle #	
	1	2
	Concentration of Si (ppm)	
27	387	375
49	481	472
75	604	624
122	1136	1120
Weight of Solids (grams)	0.51	0.50

Run Number: 9

Description: 1.5 g of quartz

Time (hours)	Bottle #	
	1	2
	Concentration of Si (ppm)	
3	92	97
27	835	850
49	1166	1127
122	2016	2096
Weight of Solids (grams)	1.50	1.52

Run Number: 10

Description: 1.5 g of quartz

Time (hours)	Bottle #			
	1	2	3	4
	Concentration of Si (ppm)			
24	930	-	846	750
48.5	1298	1232	1210	1155
92	1749	1716	1738	1694
120	2000	1920	2048	1984
Weight of Solids (grams)	1.52	1.54	1.57	1.48

Run Number: 11

Description: 1.5 g kaolinite

Time (hours)	Bottle #			
	1	2	3	4
	Concentration of Si (ppm)			
5	63	62		
28.5	90	100	102	88
51.5	120	126	136	122
128.5	159	159	183	168
171	180	204	213	195
	Concentration of Al (ppm)			
5	32	34		
28.5	56	62	64	52
51.5	78	78	80	74
128.5	87	90	90	81
171	105	99	105	97
Weight of Solids (grams)	1.51	1.55	1.55	1.53

Run Number: 12

Description: 1.5 g of quartz plus 7 ppm Al

Time (hours)	Bottle #		
	1	2	3
	Concentration of Si (ppm)		
4.5	100	105	115
29	374	410	365
51	-	550	528
128	704	672	819
171	735	777	848

Time (hours)	Concentration of Al (ppm)		
	1	2	3
4.5	6	5	5
29	6	5	4
51	5	4	2
128	2	4	2
171	1	3	0
Weight of Solids (grams)	1.50	1.56	1.50

Run Number: 13

Description: 1.5 g of quartz plus 20 ppm Al

Time (hours)	Bottle #			
	1	2	3	4
	Concentration of Si (ppm)			
23.5	146	164	200	298
74	276	363	372	471
97	407	385	418	539
120	418	418	429	627
169	496	-	528	752
	Concentration of Al (ppm)			
23.5	19	18	20	16
74	18	16	15	11
97	16	14	12	10
120	15	13	13	10
169	13	11	12	7
Weight of Solids (grams)	1.52	1.54	1.51	1.56

Run Number: 14

Description: 1.5 g of kaolinite plus 14 ppm Al

Time (hours)	Bottle #			
	1	3	3	4
	Concentration of Si (ppm)			
23	80	94	102	92
74	149	133	141	139
97	147	147	152	152
120	147	159	165	162
169	183	177	180	177
	Concentration of Al (ppm)			
23	82	76	74	78
74	117	120	128	125
97	125	125	133	131
120	138	141	144	141
169	144	147	153	153
Weight of Solids (grams)	1.47	1.54	1.51	1.54

Run Number: 15

Description: 1.0 g of quartz

Time (hours)	Bottle #			
	1	2	3	4
	Concentration of Si (ppm)			
1	64	46	62	58
2	112	91	137	104
4	218	200	240	238
6	304	254	318	320
27.5	957	858	900	957
Weight of Solids (grams)	0.98	1.05	1.01	1.00

Run Number: 16

Description: 1.0 g of quartz

Time (hours)	Bottle #			
	1	2	3	4
	Concentration of Si (ppm)			
28	715	814	715	748
50	1232	1045	1067	1298
97	-	1584	1440	1504
168	1743	1680	1659	1764
Weight of Solids (grams)	1.03	1.02	1.01	1.03

Run Number: 17

Description: 1.5 g of quartz plus 14 ppm Al

Time (hours)	Bottle #			
	1	2	3	4
	Concentration of Si (ppm)			
27.5	206	208	224	224
50	534	531	528	522
97	605	583	605	572
168	800	736	736	768
	Concentration of Al (ppm)			
27.5	7	8	8	8
50	8	5	5	4
97	4	4	4	4
168	1	2	2	1
Weight of Solids (grams)	1.50	1.50	1.55	1.48

Run Number: 18

Description: 1.5 g of kaolinite plus 20 ppm Al

Time (hours)	Bottle #		
	1	2	3
	Concentration of Si (ppm)		
27.5	110	94	96
50	154	122	124
97	162	153	168
172.5	210	186	183
	Concentration of Al (ppm)		
27.5	114	114	116
50	126	126	126
97	204	189	207
172.5	201	195	209
Weight of Solids (grams)	1.51	1.52	1.52

Run Number: 19

Description: 1.5 g of 90% quartz and 10% kaolinite

Time (hours)	Bottle #		
	1	2	3
	Concentration of Si (ppm)		
22	242	286	220
71	374	440	341
119.5	448	560	416
140.5	480	560	432
170	480	608	432
	Concentration of Al (ppm)		
22	4	1	4
71	2	0	4
119.5	1	0	4
140.5	1	0	2
170	2	2	6
Weight of Solids (grams)	1.51	1.59	1.51

Run Number: 20

Description: 1.5 g of 95% quartz and 5% kaolinite

Time (hours)	Bottle #		
	1	2	3
	Concentration of Si (ppm)		
22	187	154	253
71	462	429	605
119.5	528	464	704
140.5	496	480	800
169.5	576	496	768
	Concentration of Al (ppm)		
22	7	15	15
71	16	24	27
119.5	32	17	18
140.5	20	22	23
169.5	19	21	21
Weight of Solids (grams)	1.49	1.52	1.54

Run Number: 21

Description: 1.5 g of 80% quartz and 20% kaolinite

Time (hours)	Bottle #	
	1	2
	Concentration of Si (ppm)	
22	88	99
71	154	264
119.5	192	280
140.5	192	304
	Concentration of Al (ppm)	
22	30	33
71	88	55
119.5	96	80
140.5	80	64
Weight of Solids (grams)	1.54	1.51

Run Number: 22

Description: 1.5 g of kaolinite plus 100 ppm Si

Time (hours)	Bottle #	
	1	2
	Concentration of Si (ppm)	
22	171	173
71	224	232
119.5	228	241
140.5	249	263
169.5	255	280

Time (hours)	Concentration of Al (ppm)	
22	64	58
71	87	75
119.5	102	95
140.5	102	91
169.5	104	100
Weight of Solids (grams)	1.54	1.49

Run Number: 23

Description: 1.5 g of kaolinite plus 150 ppm Si

Time (hours)	Bottle #	
	1	2
	Concentration of Si (ppm)	
22	228	232
71	245	245
119.5	256	252
140.5	273	273
169.5	280	286
	Concentration of Al (ppm)	
22	44	50
71	67	64
119.5	81	81
140.5	84	87
169.5	68	72
Weight of Solids (grams)	1.52	1.51

Run Number: 24

Description: 1.5 g of kaolinite

Time (hours)	Bottle #	
	1	2
	Concentration of Si (ppm)	
22	70	78
71	126	130
119.5	148	150
140.5	159	180
170	-	196
	Concentration of Al (ppm)	
22	72	84
71	112	120
119.5	128	124
140.5	144	144
170	-	147
Weight of Solids (grams)	1.50	1.51