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The Management of Silica in Los Alamos National Laboratory Tap Water

A Study of Silica Solubility

Cornel Wohlberg
V. Peter Worland
Mark A. Kozubal
George F. Erickson
Heather M. Jacobson
Kevin T. McCarthy

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545

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THE MANAGEMENT OF SILICA IN
LOS ALAMOS NATIONAL LABORATORY TAPWATER
A STUDY OF SILICA SOLUBILITY

by

Cornel Wohlberg, V. Peter Worland, Mark A. Kozubal,
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ABSTRACT

Well water at Los Alamos National Laboratory (LANL) has a silica (SiO_2) content of 60 to 100 mg/L, with 4 mg/L of magnesium, 13 mg/L calcium and lesser concentrations of other ions. On evaporation in cooling towers, when the silica concentration reaches 150 to 220 mg/L, silica deposits on heat transfer surfaces.

When the high silica well water is used in the reprocessing of plutonium, silica remains in solution at the end of the process and creates a problem of removal from the effluent prior to discharge or evaporation.

The work described in this Report is divided into two major parts. The first part describes the behavior of silica when the water is evaporated at various conditions of pH and in the presence of different classes of anions: inorganic and organic. One aim of this work was to be able to increase the solubility of silica to 500 to 700 mg/L.

Solution pH has a strong effect on the solubility of silica in the LANL water. The minimum solubility of silica occurs at pH 8.2 to 8.4, the natural pH of the well water.

The halogen anions, chloride, bromide, and iodide showed no effect on silica solubility. Fluoride and the pseudo-halide, thiocyanate, increased the solubility markedly. The oxygenated anions showed the following order of effectiveness as solubilizers.

phosphate, PO_4^{-3} > sulfate, SO_4^{-2} > bisulfite, HSO_3^{-1} > sulfamate, $NH_2SO_3^{-1}$ > nitrate, NO_3^{-1} > nitrite, NO_2^{-1}

The solubility of silica in a solution of sodium metasilicate in deionized water at pH 8.2 was found to be infinite, within the limits of the experiment. This solubility is radically different from the silica solubility found in the natural LANL well waters.

The organic anion work showed that various functional groups and their configurations determine their solubilizing effect. The organic compounds used are grouped here according to their decreasing effect on silica solubility.

lignin sulfonates > di- and trihydroxybenzenes, oxalate, and Tiron
> citrate > ortho- and paraphathalate > EDTA > maleate > formate
> sebacate and paratoluene sulfonate

In the anion work, the major and perhaps controlling role of magnesium in silica solubility became evident. When magnesium was kept in solution (or complexed), the silica remained in solution. The goal of reaching silica solubilities greater than 500 mg/L was achieved with the following anions: phosphate, fluoride, sulfamate, oxalate, citrate, EDTA, ortho-phthalate, para-phthalate, catechol, Tiron, and three lignin sulfonates (Chelig 32, Marasperse N-22, and Maracell XE). Some other anions, for example sulfate and formate, which enabled silica concentrations in solutions to reach 500 mg/L may however cause supersaturation of silica (a sudden deposition of silica with increased concentration).

In the second part of this work it was found that precipitation (floccing) of silica was a function of solution pH and mole ratio of metal to silica. The following series shows the effectiveness of the metals in lowering silica solubility at pH 9.0.

$$Fe^{+2}\text{(deoxygenated)} > Mg^{+2} > Al^{+3} > Fe^{+2}\text{(oxygenated)} > Zn^{+2} > Fe^{+3} >> Ca^{+2}$$

The first five metals in the above series reduced the silica concentrations to the target level of 10 mg/L at pH 9.0. Preliminary work with titanium and copper also showed them to be effective in silica precipitation to some degree.

The silica removing capabilities of mixtures of divalent and trivalent metals (spinel type compositions such as $MgO \bullet Fe_2O_3$) generally showed intermediate silica removal between the divalent alone and the trivalent alone solutions. A resolubilization of silica, noticed in the trivalent alone solutions at pHs above 9.5 did not occur in the mixed metal solutions.

I. INTRODUCTION

The work described here concerns the chemistry involved in the solubility of silica in Los Alamos National Laboratory water (LANL well water, tap water). This is a "fossil" water in equilibrium with a volcanic glass, a common occurrence in volcanic areas. The problem associated with the high silica content of Los Alamos well water has been a perennial one. Table 1 shows a representative chemical analysis of LANL tap water.

Table 1

Representative Chemical Analysis of LANL Tap Water

Cationic Constituents	**mg/L**
Ca^{+2}	13
Mg^{+2}	4
Na^{+1}	14
K^{+1}	2
Fe^{+2}	< 0.1

Anionic Constituents	**mg/L**
Cl^{-1}	4
SO_4^{-2}	3
NO_3^{-1}-N	0.2
F^{-1}	0.2
HCO_3^{-1}	90

Other Constituents	**mg/L**
Total Silica	88 mg/L
Color-Reactive Silica	80 mg/L
Non-Reactive Silica	8 mg/L
Total Dissolved Solids	151 mg/L
*p*H	7.8 - 8.2

Silica is known for its tendency to deposit an opalene layer on heat exchanger surfaces making heat transfer less efficient. In cooling tower work in the early 1970s and mid-1980s, LANL water evaporated to silica concentrations of 160 to 220 mg/L was found to deposit silica.

Work has been done in the past to increase the solubility of silica by using anionic compounds. The aim of the present anion work was to increase the silica solubility by five to seven concentration factors (500 to 700 mg/L). This work, therefore, was planned to determine the solubility of SiO_2 in the presence of various types of anionic reagents, both inorganic and organic.

The solubility of silica in the natural LANL well water needed to be determined before the effects of additives could be studied. An evaporative technique was used to determine the silica solubility as a function of solution pH, concentration factor (mg/L Expected Silica), and time of standing following evaporation.

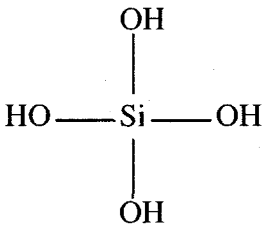
Work that had been published on the solubility of silica was usually done with simulated water containing sodium silicates or dissolved amorphous silica.[1] One of the purposes of the current work was to show that the solubility of silica in LANL well water is a function of its composition.

The work with cations was planned in 1994 when a Radioactive Liquid Waste Treatment Facility (RLWTF) was being planned. The plans called for zero liquid waste to be discharged to the environment.

A LANL facility that reprocesses plutonium is the major source of this element in the influent to the RLWTF. This facility and others at LANL use untreated tap water for their process water. The resulting high silica waste water undergoes treatment for removal of plutonium to the limits of current technology. At this stage, the waste water contains the remaining silica that has to be removed prior to final disposal.

It was decided that removal of the silica from the incoming well water used in the reprocessing facility would be easier than removing the silica from the radioactively contaminated waste water from the facility. The method of removal investigated was flocculation with cationic metal hydroxides.

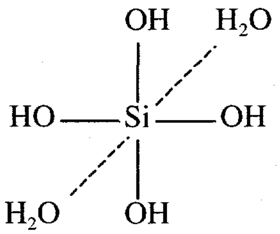
The solubility in this work involved the interactions of additives with silica. As we use it here, silica represents the hydrous orthosilicic acid. The generally accepted structure[2] of orthosilicic acid we have used in this report is shown below.



$\mathrm{Si(OH)_4}$

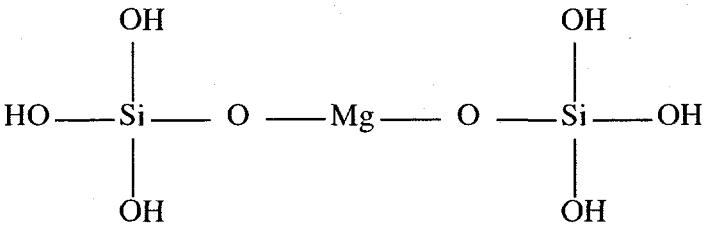
The structure's first ionization constant is about 10^{-10}. The structure is a tetrahedral form, a very compact entity. [3,4]

There is a possibility that silica in solution exists as a hexa coordinate structure, an octahedral configuration with two, coordinated water molecules.



It was assumed that the anions, both inorganic and organic, might react with the (OH) groupings on the orthosilicic acid group. This could increase the solubility.

In addition to the discussion of the tetrahedral or the octohedral models, we might show the following structure which involves two or more, orthosilicic nuclei bonded by a magnesium ion. Magnesium may be present in such a form in the original solution and influence the solubility behavior of silica during the evaporation of water.



$\mathrm{(HO)_3Si{-}O{-}Mg{-}O{-}Si(OH)_3}$

It could also be possible that what is involved, particularly in the case of organic anions, is a chelation of the silica to form a five-membered ring. Also, it may be that the effect of some of the organic and oxygenated inorganic anions, such as phosphate, etc., is to chelate magnesium and calcium, thus altering the solubility of silica.[5]

In the planning of this work, the following questions were formulated:

Question #1

How long a time of rest is required for silica to reach a steady state solubility following evaporation at 50° C?

Question #2

What is the effect of pH on silica solubility in LANL tapwater?

Question #3

How reproducible is data in the solubility of silica?

Question #4

What is the effect of anionic additives, both inorganic and organic, on the solubility of silica is LANL tap water?

Question #5

Is silica above 160 mg/L in evaporated solutions in true solution or supersaturated (thermodynamically unstable)?

Question #6

What is the chemistry involved in the solubility of silica in the presence of anionic additives?

Question #7

What is the effect of common flocculating cations, such as magnesium, calcium, iron, aluminum, etc., on the solubility of silica?

The answers to these questions are found in the discussions and are summarized in the section "Final Summary and Conclusions."

II. EXPERIMENTAL PROCEDURES

The variables to be investigated were pH and the effects of various inorganic and organic anions as additives at various mole ratios to SiO_2. In addition, the effects of inorganic cations (flocculators) were investigated. Control runs in parallel were included so as to closely define the effects of the variables.

The ideas for this work are based on work done at LANL by Wohlberg and Bucholz[6] and Wohlberg and Strickler.[7] These previous efforts were influenced by the research and writings of Iler.[8]

The two techniques used in this study were evaporation in the anion studies and insolubilization (floccing with metal ions) in the cation studies.

A. Anion Work

The anion studies involved the use of "inverse solubility," which can be determined by the evaporation of solutions to various concentration factors. Concentration factor is defined as the silica expected in solution divided by the silica concentration in the original solution. What is actually determined is the concentration at which insolubilization occurs. The effect on silica solubility of varying conditions of pH, additives, etc., can be quantified in this way.

Pure solutions of silica were not used in this experimental work, because such solutions do not represent a realistic model of silica in local well waters. Ions present in the well water probably influence the solubility and stability of silica markedly. The silica content in LANL well water varies between 80 and 100 mg/L.

Under the conditions of our technique, solutions were heated on a water bath at a mean temperature between 50-55°C. The water baths were in a hood with a rapid flow of air over the beakers, so that the water was in a steady, uniform state of convection and evaporation rates were uniform for all the beakers. The importance of these conditions lies in the tendency of silica to supersaturate and to be in a thermodynamically unstable state. Supersaturation is an excess of solubility over the thermodynamic solubility. Under ideal conditions, if the temperature, pressure or even the roughness of the container is changed by an infinitely small increment, the solubility of the substance in a saturated solution will change. In an ideal solution, as soon as the stress is relieved, the compositions of the solution should revert to their original state. Silica solutions are usually not reversible; thus, a rise in solubility of the silica will cause more to stay in solution than would be normal at a lower temperature. This is of vital importance when the solutions, as in our beaker work, are concentrated. Some of the chemicals we have used caused some rather strong supersaturation, rather than a true solubility, to appear. Any nonuniformity in turbulence, surface conditions, or container can thus lead to solubility results that are not duplicable. Figure 1 summarizes the results of 57 "control" or "blank" runs in which the solubility of silica in the tap water was determined in parallel with its solubility in the presence of the anion additives.

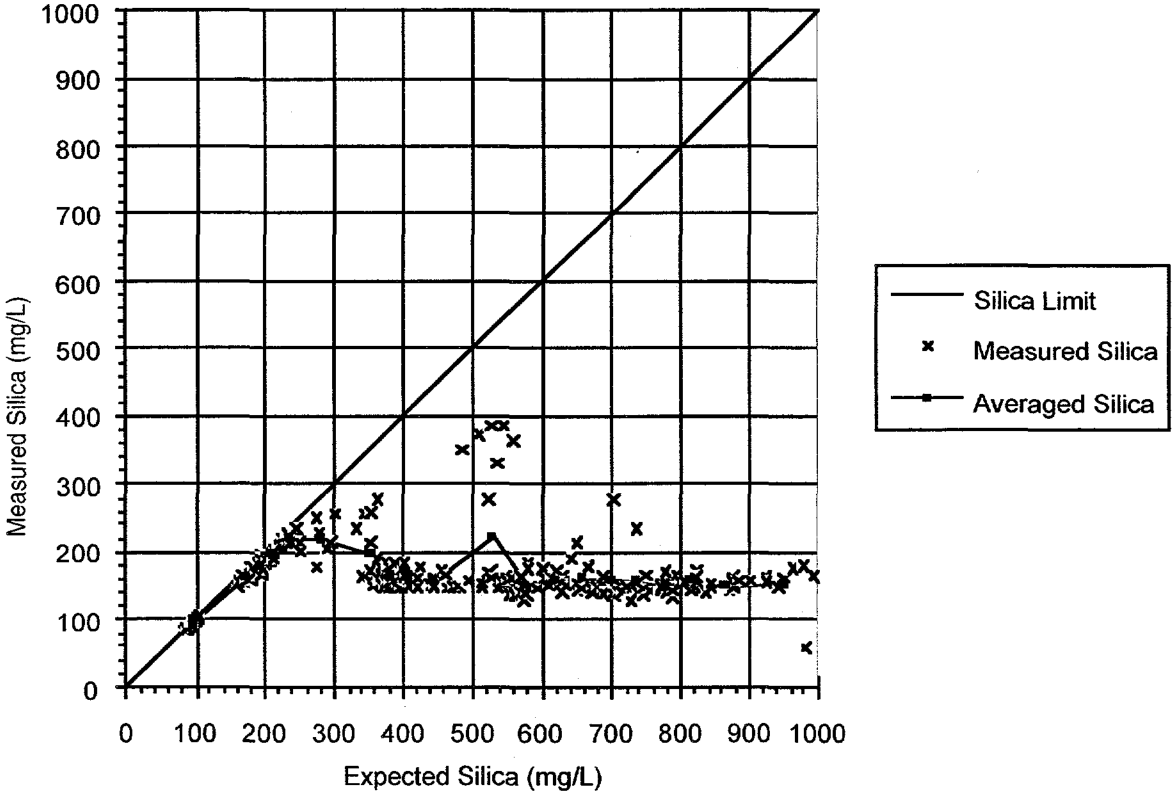


Figure 1. Accumulated Silica Solubility Results in Control Runs.

In general, the graph describes the average control curves found in the evaporative (anion) work rather well. It is obvious that there is considerable scatter. Also present are several clusters of a few points that seem to be outliers or anomalous data points that show appreciably higher solubility than expected.

Supersaturation is not readily controllable in silica solutions and may occur seemingly at random. The technique, therefore, had to be as rigorously uniform as possible to control random nucleation.

There have been complaints in the past about indefinite conditions in work with silica solutions. We attempted to use conditions as uniform as possible from experiment to experiment.

Since silica has greater solubility at the temperature of evaporation[9] of about 50°C than at room temperature of 22°C, the time required for stabilization had to be determined. Stabilization was achieved by letting solutions stand for various lengths of time after evaporation and cooling to room temperature prior to filtration (see Appendix C).

1. Experimental Procedures

Experimental procedures included the following:

a. Preparation of Solutions

To make up the solutions, the mole ratios of reactant to silica (SiO_2) were usually varied over a range of 0.1 to 4.0. The mole ratio of reactant to SiO_2 and the pHs were adjusted to the requirements of the experiment. The details are given in Appendix A.

b. Evaporation of Solutions

The evaporation procedure was performed in smooth-surfaced polypropylene beakers that had been carefully cleaned prior to use. The experimental batches were heated on a steam bath in a fume hood with rapid air circulation, providing rapid evaporation without permitting crusting or nucleation on solution surfaces. The contents of each beaker were evaporated to a predetermined concentration (final volume), then taken off and allowed to cool to room temperature.

This approach enabled the solution at the surface to cool, sink down, and be replaced by a increment of solution, thus providing good circulation and mixing. Details are given in Appendix B.

c. Time of Standing to Steady State

Reference has been made to the increased solubility of silica at higher temperature.[10] Appendix C describes the procedure used to determine time required for solutions to reach a steady state solubility. It was found that approximately 48-50 hours of standing were required.

d. Filtration of Solutions

The solutions from evaporation and nonevaporation experiments were filtered, following the 48-50 hour time of standing. Pressure filtration was done with an Antlia Pneumatic Hand Pump System. The filters were 47 mm diameter, 0.2 µm Supor™ polysulfone membranes. Appendix D details the filtration procedures.

e. Sample Preparation

The filtrate through the Supor™ membrane filters was placed in a new 60 ml polypropylene sample bottle that had been rinsed with deionized water. The pH of this filtered solution was determined.

f. Beaker Preparation

The polypropylene beakers used in the experiments were subjected to a rigorous cleaning and inspection protocol to ensure that none were reused that had any extraneous inorganic (seeding) material left in them. Those that did not pass visual inspection were discarded. Details are given in Appendix E.

g. Analytical Techniques

The solutions were analyzed spectroscopically for silicon and metals using an inductively coupled plasma optical emission spectrometer (ICP-OES). Other water quality parameters were also analyzed by standard methods. See Appendix F for details.

2. Interpretation of Data-Anions

The analytical data from the various evaporation experiments were plotted as Measured Silica (mg/L) against Expected Silica (mg/L) on a linear graph. Usually the plots are interpreted by determining where inflection points on the graphs show changes in the solubility behavior of the silica. Linearity on the plot is important and in many cases slopes of the lines are indicated in the tables to help in the interpretation of the various parts of the curves discussed. The straight lines follow the theoretical 45° line closely, but usually not exactly. They may continue in a straight line, but at a slight angle or offset. When a solubility limit is reached, there is a sharp break. If a true solubility were reached, the maximum solubility would continue at the same concentration to higher Expected Silica concentrations.

The captions of the figures for solubility data show the purpose of the experiment and the conditions used; a sidebar on the graph shows the identification of the various curves (lines). The Measured Silica found values are plotted on the left ordinate against the Expected Silica content in each graph. The pH values are plotted on the right side against the Expected Silica values. Silica values are identified by solid markers and pH values are identified by open markers.

The discussions of each evaporation experiment (with inorganic and organic additions) include a table which summarizes the slopes of the silica solubility curves and the maximum silica solubility. The curves have an initial slope, S_a, which begins at the point where the measured silica curve breaks from the 45° line on the graph. Slope, S_a, ends where the measured silica curve changes slope. Slope, S_a, is determined by dividing the change in Measured Silica by the change in Expected Silica over this portion of the curve. Additional slope changes in the silica curve, if they exist, are identified by S_b and S_c. Slopes, S_b and S_c, are determined in a similar manner as S_a.

The table also gives the Expected Silica concentration range over which the slopes S_a, S_b, and S_c continue. Furthermore, the table lists the maximum Measured Silica concentration and its corresponding Expected Silica concentration in each evaporation experiment. The usefulness of this data is mainly indicative. The greater the slope, the higher the solubility. If the slope is negative, it usually indicates that the maximum silica solubility has already been attained in the experiment.

The data on the solubility of silica as a function of mole ratio of additive to silica are summarized at the end of each section of both the inorganic anion work and the organic anion work. This was done by taking a "cut" at the iso-theoretical concentration of 600 mg/L through the lines representing the original data of Measured Silica versus Expected Silica. The corresponding measured values for each silica content were then plotted as a function of mole ratio of additive to silica.

B. Cation Work

In the cation work, precipitation (floccing) was the method used to reduce the solubility of the silica. The silica was precipitated by addition of various mole ratios of cations as a function of pH (see Appendix A). Then the solutions were allowed to stabilize and the residual silica was determined.

1. Experimental Procedures

The cation work was divided into two parts:

In Part 1, solutions were stirred with a magnetic stir bar over a set period of time. The interactions of silica with cations in LANL tap water were investigated by the addition of the following cations to the water: Mg^{+2}, Al^{+3}, Ca^{+2}, Ti^{+4}, Fe^{+3}, Cu^{+2}, and Zn^{+2}. The nitrate salts were used except for Ti^{+4}. After standing for 48 hours, the solutions were filtered and analyzed. Details are given in Appendix G.

In Part 2 of the cation work the procedures were similar to those used in the Part 1 metals work. The difference lay in the use of mixed valence metals approximating the 1:1 compositions of the spinel types (i.e., $MgO \cdot Al_2O_3$) as a function of pH. For all these experiments a Phipps & Bird™ mechanical six-unit stirrer was used to mix the solutions. The detailed procedure used in the Part 2 cation work is presented in Appendice H.

2. Interpretation of Data-Cations

The following data were plotted for Cations 1 work:

1. Solubility as a function of pH for each cation addition.
2. Solubilities as a function of mole ratio of metal ions added at a pH of 9.0 (see Figure 59).

For Cation 2 work, the data plotted were:

1. Solubility as a function of pH for each cation mixture and for the corresponding individual metal additives.
2. Solubilities as a function of mole ratio of metal ions to silica at a pH of 9 (see Figure 80).

III. EXPERIMENTAL RESULTS

A. Evaporation Work

1. Preliminary Work

This section describes some of the experimental results obtained as a preliminary to the major work on the effects of anion additions.

Three areas of work provided information necessary to performing the later evaporation runs with additives (see Appendices B, C, and D for details).

a. Effect of Filtration on Silica Solubility

Effects of Filtration on total silica as solutions are concentrated. Filtration did not substantially change the results obtained in evaporation runs. See Appendix I for details.

b. Effect of Time of Standing on Silica Solubility

Time of Standing required for supersaturated solutions to reach a steady state silica concentration after supersaturation. As already mentioned, solutions reached a steady state saturation after approximately 48-50 hours of standing. See Appendix C for details. Solubility of silica also seems to have a definite temperature dependence.[10]

c. Effect of pH on Silica Solubility

Prior to beginning the work with additives, the effects of pH on the solubility of silica in LANL water was determined. Previous work has shown that pH has a very appreciable effect on the solubility of silica.

The effect of pH on solubility has been reviewed by Wohlberg[11] and others.[12] Probably the most typical of the early work with amorphous silica on opal, Alexander[13] has shown that when working with pure amorphous solid silica there is little resolubilization until pH range 9.5-10. The minimum solubility of silica is shown by Alexander and various workers to be in the range of 8.0-8.6.

Figure 2 shows the effects of pH in this work over the range of 3.0 to 7.8. The pH 3.0 and 4.0 curves are linear with no breaks. Definite breaks occur in the pH 5.0, 5.5, 6.0, and 7.8 curves. The pH 7.8 approximates the control. Thus, as pH is increased to 7.8, we have the appearance of supersaturation, as shown by the curves.

Figure 3 shows the results obtained at higher pHs. The solubility values over the pH range 6.5-9.0 resemble "control" curves, many examples of which are shown in Figure 1 in this report.

Figure 4 shows the effect of pH on solubility over the range of pH 7.8-11.0. It shows that beyond pH 8.5 there is an increase in apparent solubility, but the results seem to be very erratic and seem to represent supersaturation rather than solubility within the pH ranges of this work.

Results are summarized best in Figure 5. The data has been replotted along lines of constant expected silica concentration (iso-concentration) as a function of final pH values. This plot shows very clearly the minimum solubility values cluster sharply around the values of 8.3-8.8, which is close to the value of 8.2-8.4 usually found in LANL tap water. In the pH range 9.0-11.0, instabilities are found in the solubility curves which may be due to the ionization of the orthosilicate anion. However, an expected upward trend is found. See also Appendix J for the analytical data used to plot Figures 2, 3, and 4.

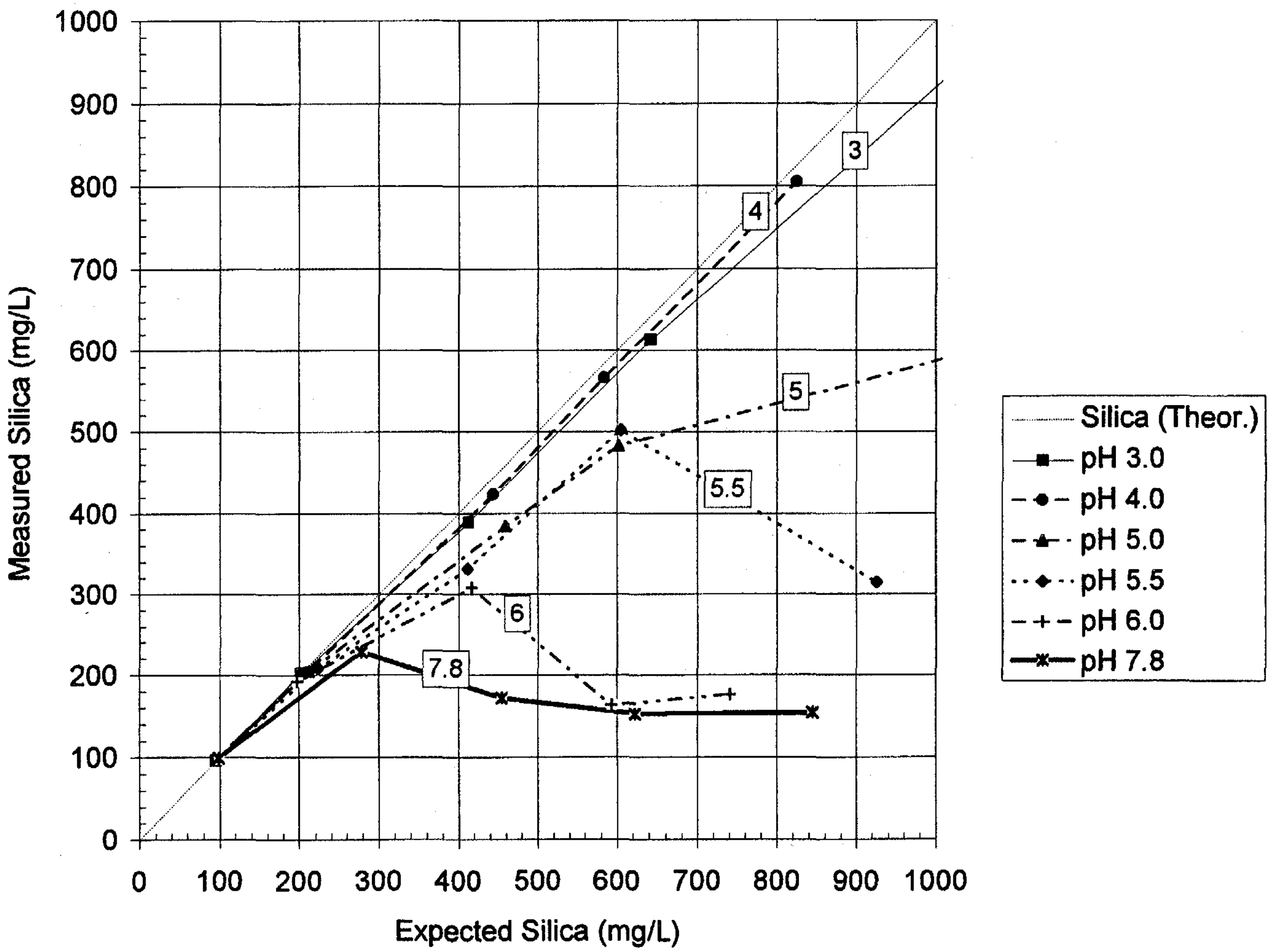


Figure 2. Effect of pH on the Solubility of Silica in Water.
Initial Solution pHs: 3.0, 4.0, 5.0, 5.5, 6.0, and 7.8.

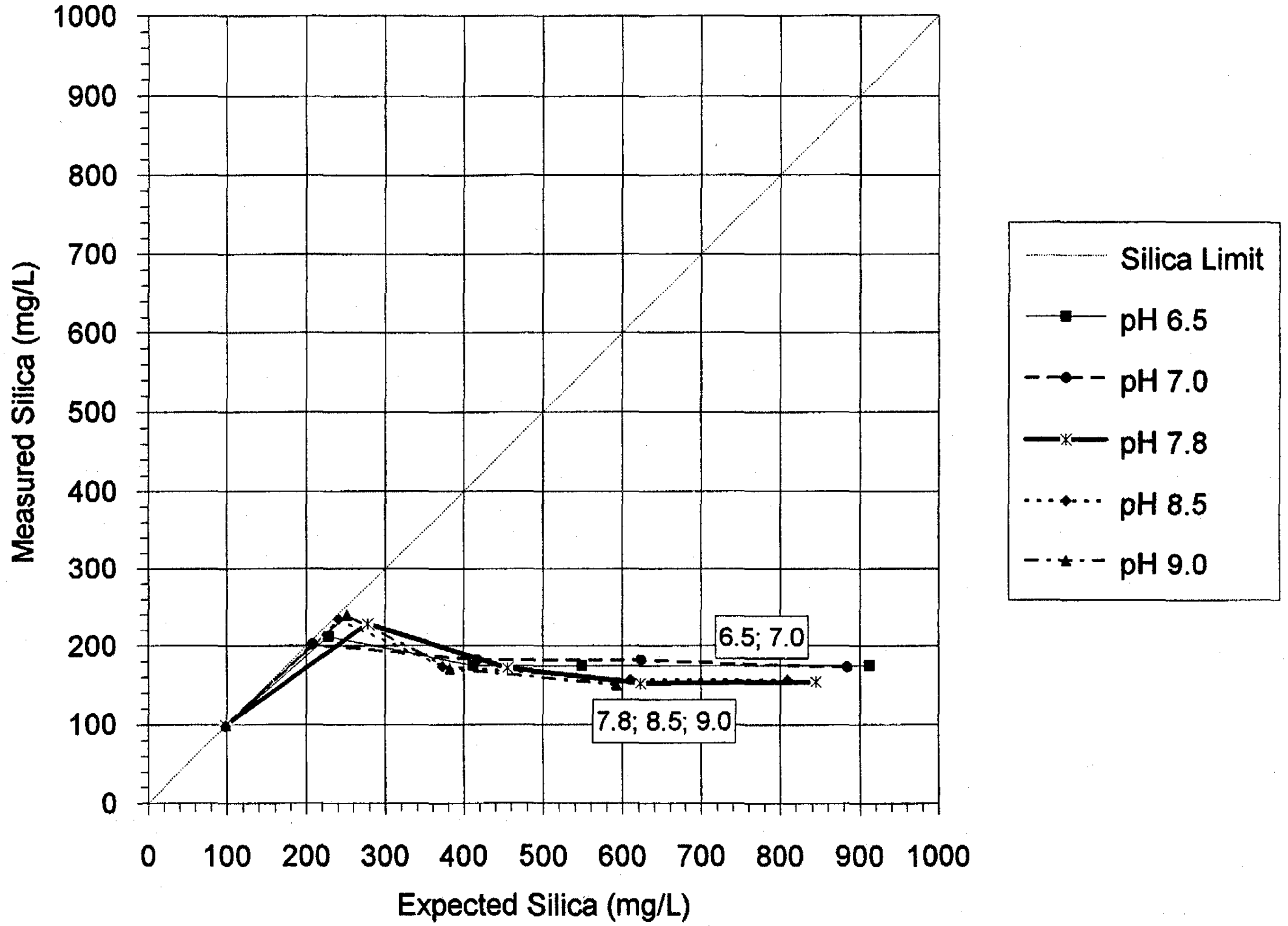


Figure 3. Effect of pH on the Solubility of Silica in Water.
Initial Solution pHs: 6.5, 7.0, 7.8, 8.5, and 9.0.

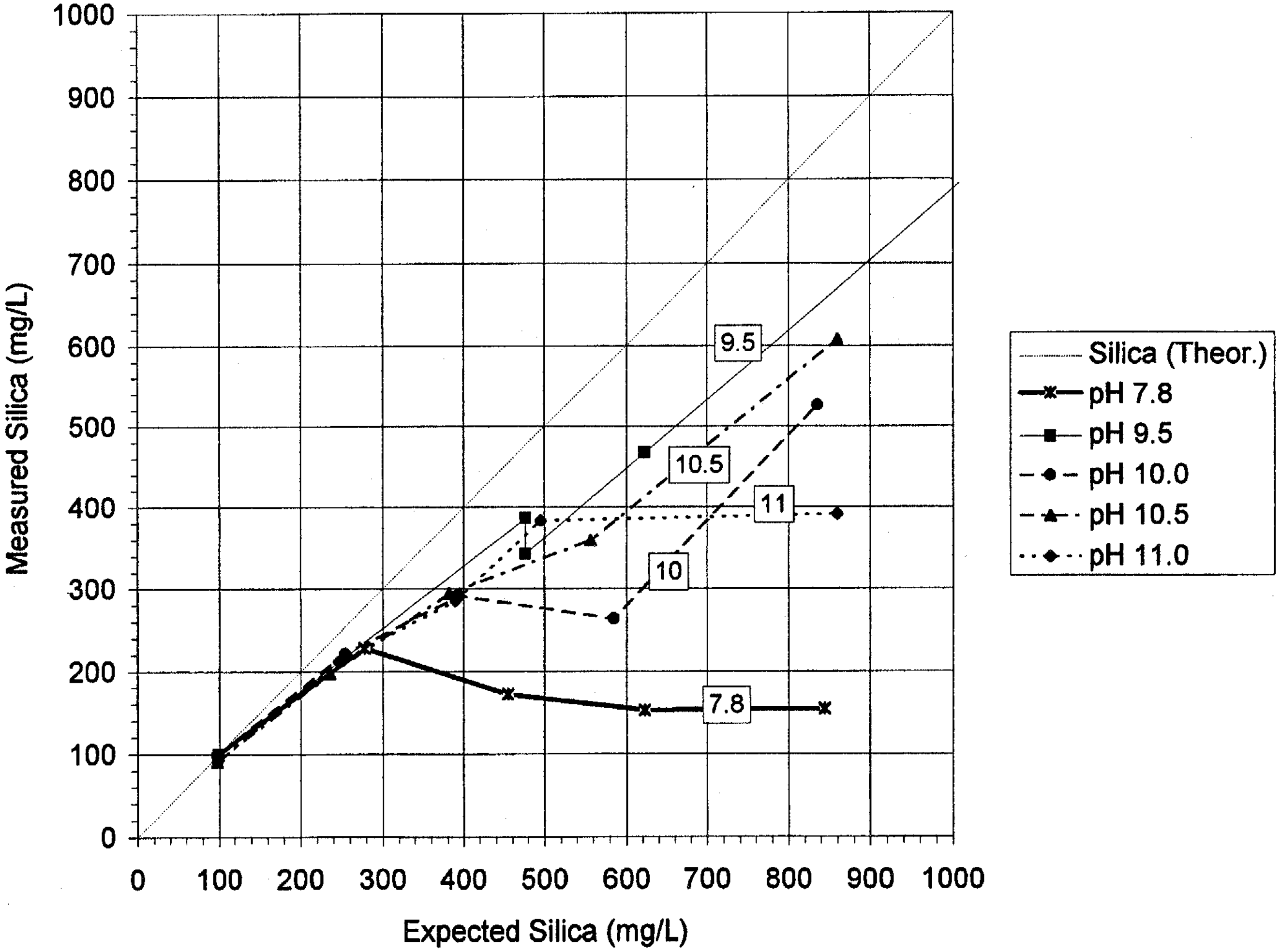


Figure 4. Effect of pH on the Solubility of Silica in Water.
Initial Solution pHs: 7.8, 9.5, 10.0, 10.5, and 11.0.

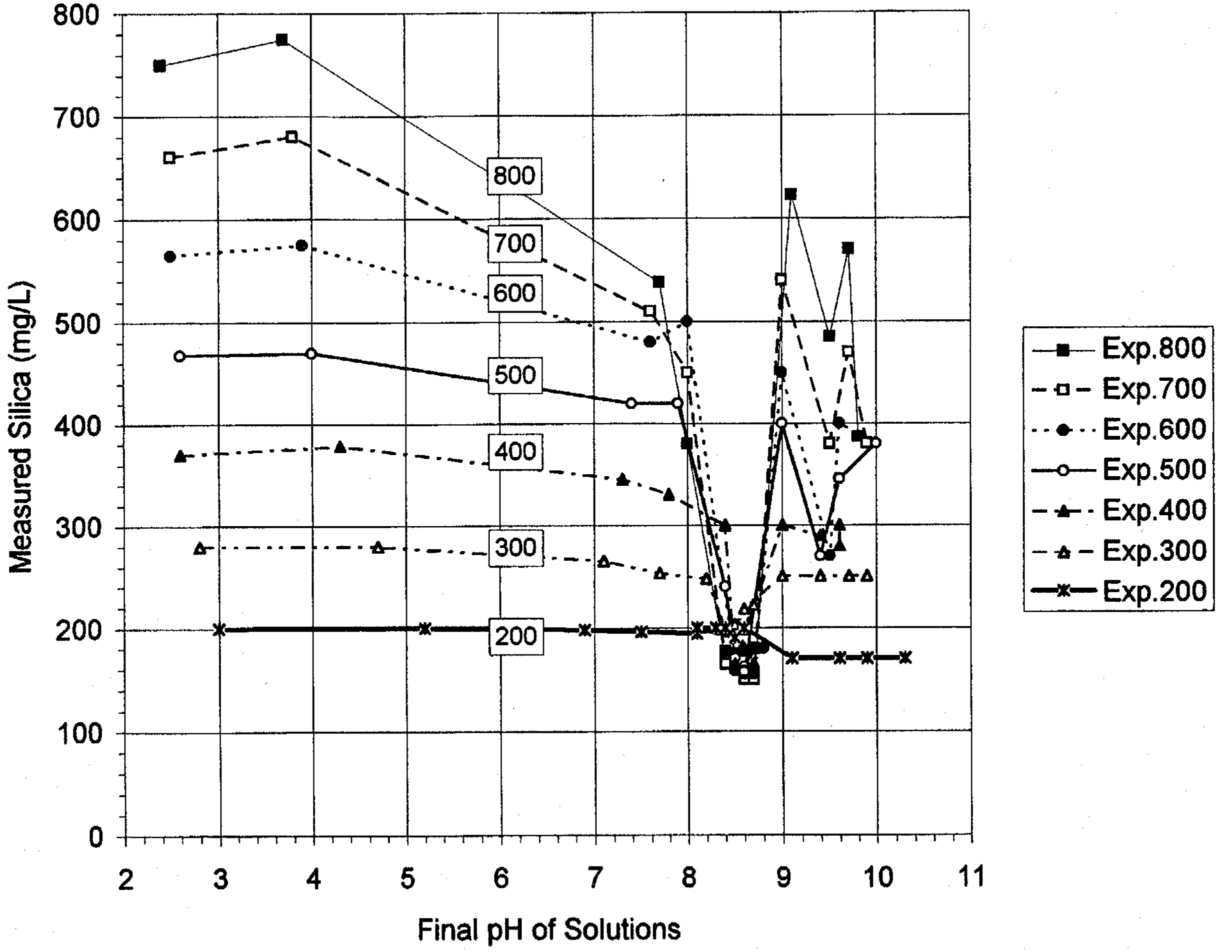


Figure 5. Solubility of Silica at Constant Expected Silica Concentrations
As a Function of Final Solution pH. Expected (Theor.) Concentrations 200, 300, 400, 500, 600, 700, and 800.

2. Variability of Measured Silica, Magnesium, and Calcium in Control Evaporation Experiments

a. Variability of Measured Silica

To determine the effect of additives on the solubility of silica, a control evaporation run was also performed with tap water. In these control evaporation runs, a water sample with no additive was evaporated under the same conditions and subjected to the same physical processing as all the rest. This information is summarized in Appendix K. Figure 1K shows the silica remaining in solution after evaporation in 59 control tap water runs.

b. Variability of Measured Magnesium and Calcium

As a result of concentrating the water (solution) by evaporation, a great deal of data were collected on the solubility of magnesium and calcium in addition to that of silica. These are summarized in Appendix K as a function of Expected Silica concentration and pH.

The curve in Figure 2K shows the magnesium remaining in solution after evaporation in 59 control tap water runs. Figure 4L in Appendix L shows the effect of pH on the magnesium remaining in solution. All the curves show sharp breaks in magnesium contact beyond a pH 8.0.

Between pH 8.6 and 9.6 there is a rise in magnesium solubility which, with our present knowledge, can only be described as a region of uncertain magnesium solubility.

Above pH 9.6, the magnesium solubility is close to zero. Wey and Siffert[14] showed a minimum solubility of magnesium in a magnesium and silica solution at pH 9.2.

Figure 3K shows the solubility of calcium as a function of concentration factor of silica. Figure 4M in Appendix M shows the solubility of calcium as a function of pH; the individual curves represent the expected concentration of calcium in the solution. This shows that there is a sudden drop in the concentration of calcium in the neighborhood of pH 8.4-8.6, then a more gradual decrease of 2-4 ppm in the neighborhood of pH 9.6 onward.

The effects of magnesium and calcium on silica solubility are considered later in this report under metal cation effects.

B. Effect of Anion Additions on Silica Solubility in LANL Water

1. Inorganic Anions

a. Introduction

The effects of various types of inorganic and organic anions on silica solubility in LANL tap water (well water) were studied by the evaporation technique. The anions are shown in Tables 1 and 13.

First, however, the effects of time of standing and pH on solubility of silica in the water had been determined. Minimum solubility was found to be at the natural pH of LANL water around 8.2.

The final Measured Silica values are plotted on the left ordinate against the Expected Silica content in each graph.

The two classes of inorganic compounds were halides and oxygen-containing anions. Table 2 lists the specific compounds used.

Table 2
Inorganic Anions Studied for Their Effect on Silica Solubilities in LANL Tap water

Inorganic Anions			
Figure	**Chemical Additive**	**Mole Ratio of Additive to Silica**	**Initial pH of Solutions**
HALIDES			
6	Sodium Fluoride NaF	0, 0.21, 0.83, 3.3	8.2
7	Sodium Chloride $NaCl$	0, 0.2, 0.78, 3.1	8.2
8	Sodium Bromide $NaBr$	0, 0.21, 0.83, 3.3	8.2
9	Sodium Iodide NaI	0, 0.21, 0.83, 3.3	8.2
10	Sodium Thiocyanate $NaSCN$	0, 0.22, 0.86, 3.44	8.2
OXYGEN-CONTAINING			
12	Sodium Nitrate $NaNO_3$	0, 0.2, 0.81, 3.23	7.8
13	Sodium Nitrite $NaNO_2$	0, 0.21, 0.83, 3.3	8.2
14	Sodium Sulfate Na_2SO_4	0, 0.21, 0.83, 3.33	8.2
15	Ammonium Sulfamate $NH_2SO_3NH_4$	0, 0.2, 0.78, 3.14	8.2
16	Sodium Bisulfite $NaHSO_3$	0, 0.2, 0.79, 3.2	8.2
17	Disodium Phosphate Na_2HPO_4	0, 0.23, 0.9, 3.7	8.2
19	Sodium Metasilicate $Na_2SiO_3 \cdot 9H_2O$	113 mg/L SiO_2 Total + CR SiO_2	8.0
20	Sodium Metasilicate $Na_2SiO_3 \cdot 9H_2O$	111 mg/L SiO_2 Total SiO_2	3.0, 6.0, 9.0, 10.5
21	Sodium Metasilicate $Na_2SiO_3 \cdot 9H_2O$	111 mg/L SiO_2 CR SiO_2	3.0, 6.0, 9.0, 10.5

b. Halides

Effect of Sodium Fluoride on Silica Solubility in Water[1]

Figure 6 shows the effect of various mole ratios (MR) of added fluoride ion, F^-, on the solubility of silica in the tap water. The LANL tap water naturally contains approximately 0.2 milligrams per liter (mg/L) of fluoride. Mole ratios of fluoride to silica added were 0.21, 0.83, and 3.3.

The MR 3.3 solution (run) showed a straight line silica solubility with a slope of 0.8 as shown in Table 3. The MR 0.83 run shows approximately 360 mg/L as a solubility limit; hence, it is (probably) a supersaturated solution. The MR 0.21 solution shows no effect, as it seems to be the same as the control run.

The slope of the measured silica solubility line for the MR 3.3 suggests that indeed some reaction has occurred. In the MR 3.3 solutions substantially all the magnesium and calcium are missing (Table 4N, Appendix N).

The pH curves in Figure 6 show an increase in the pH, indicating possible replacement of OH ions by fluoride. As a type of reaction, fluoride at the mole ratio of 3.3:1 (but not the lower MRs used) indicates a definite strong solubilizing effect.

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[1] See Appendix N, Tables 1N–4N for data.

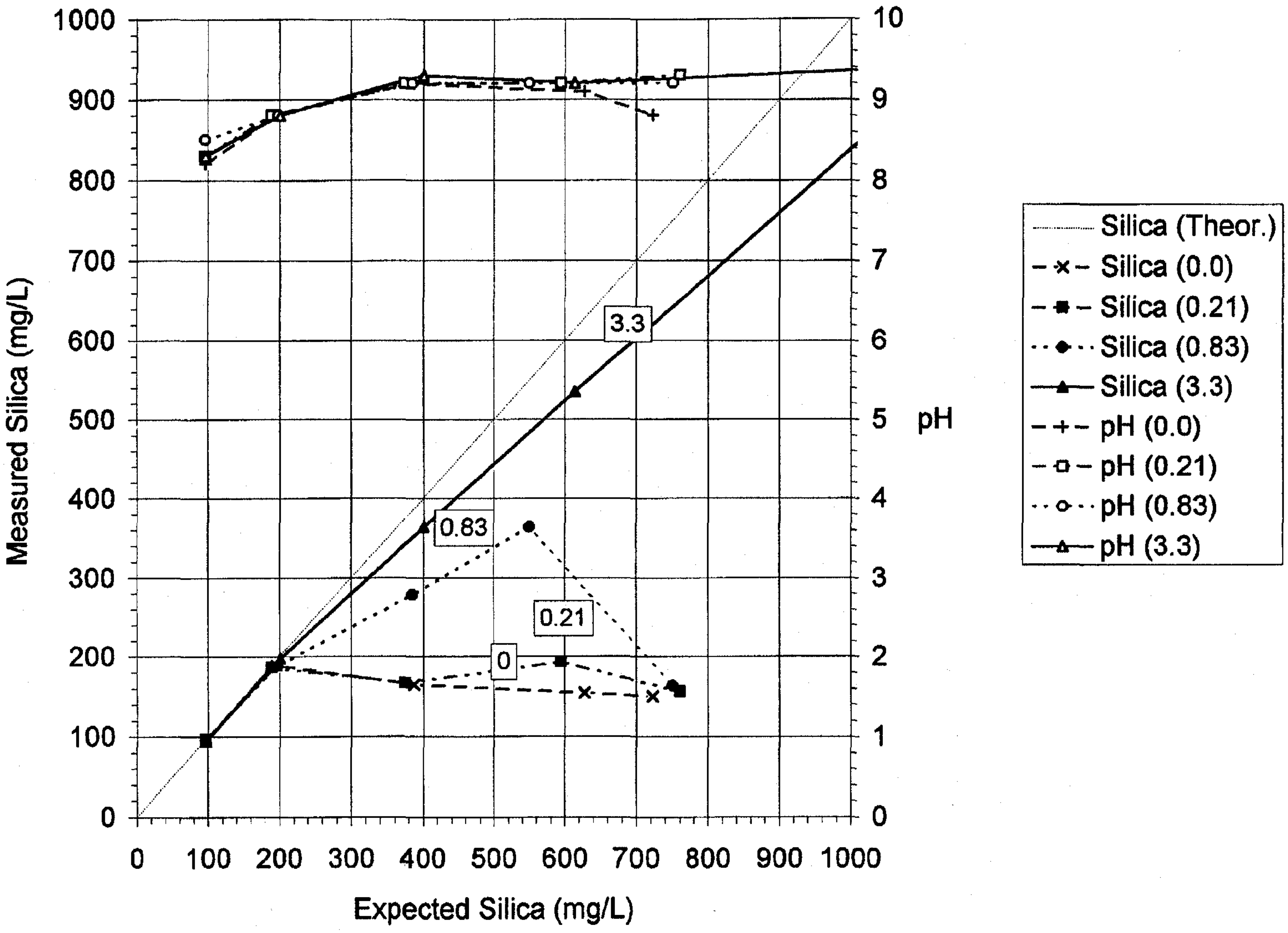

Figure 6. Effect of Fluoride on the Solubility of Silica in Water.
Fluoride:Silica MRs = (0), (0.21), (0.83), (3.3).

Table 3
Slope and Maximum SiO_2 Solubility Data for Sodium Fluoride Evaporation Experiments Shown in Figure 6

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (196-722)	-----	-----	**188** (196)
0.21	**-0.1** (190-375)	**+0.1** (375-596)	**-0.2** (596-760)	**193** (596)
0.83	**+0.5** (199-550)	**-1** (550-750)	-----	**364** (550)
3.3	**+0.8** (201-1376)	-----	-----	**1134** (1376)

Effect of Sodium Chloride on Silica Solubility in Water[1]

Figure 7 shows the effect of various MRs of added chloride ion Cl^- on the solubility of silica in the tap water. MRs of chloride to silica added were 0.2, 0.78, and 3.1.

The LANL tap water naturally contains 4 mg/L of chloride. The addition of chloride had no significant effect on silica solubility, except for an anomalous result in the MR 0.78 experiment at 615 mg/L expected silica, which, however, could also occur in control runs.

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[1] See Appendix N, Tables 5N–8N for data.

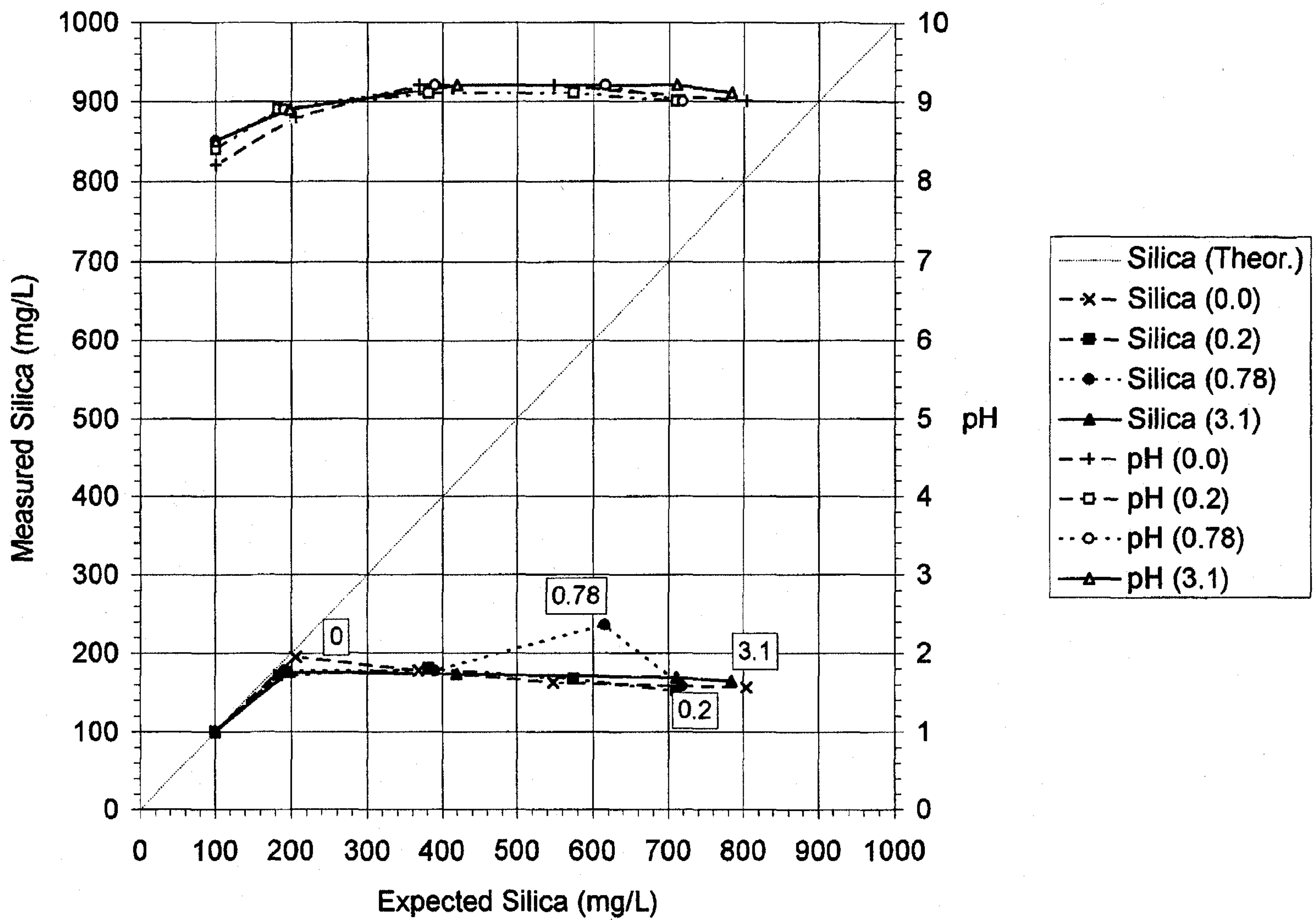

Figure 7. Effect of Chloride on the Solubility of Silica in Water.
Chloride:Silica MRs = (0), (0.2), (0.78), (3.1).

Table 4
Slope and Maximum SiO_2 Solubility Data for Sodium Chloride Evaporation Experiments Shown in Figure 7

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (206-805)	-----	-----	**195** (206)
0.2	**0** (183-710)	-----	-----	**180** (382)
0.78	**0** (192-389)	**+0.3** (389-616)	**-0.8** (616-718)	**235** (616)
3.1	**0** (198-784)	-----	-----	**176** (198)

Effect of Sodium Bromide on Silica Solubility in Water[1]

Figure 8 shows the effect of various MRs of added bromide ion Br^- on the solubility of silica in the tap water. MRs of bromide to silica added were 0.21, 0.83, and 3.3.

The addition of bromide revealed no effect on silica solubility significantly different from the control.

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[1] See Appendix N, Tables 9N–12N for data.

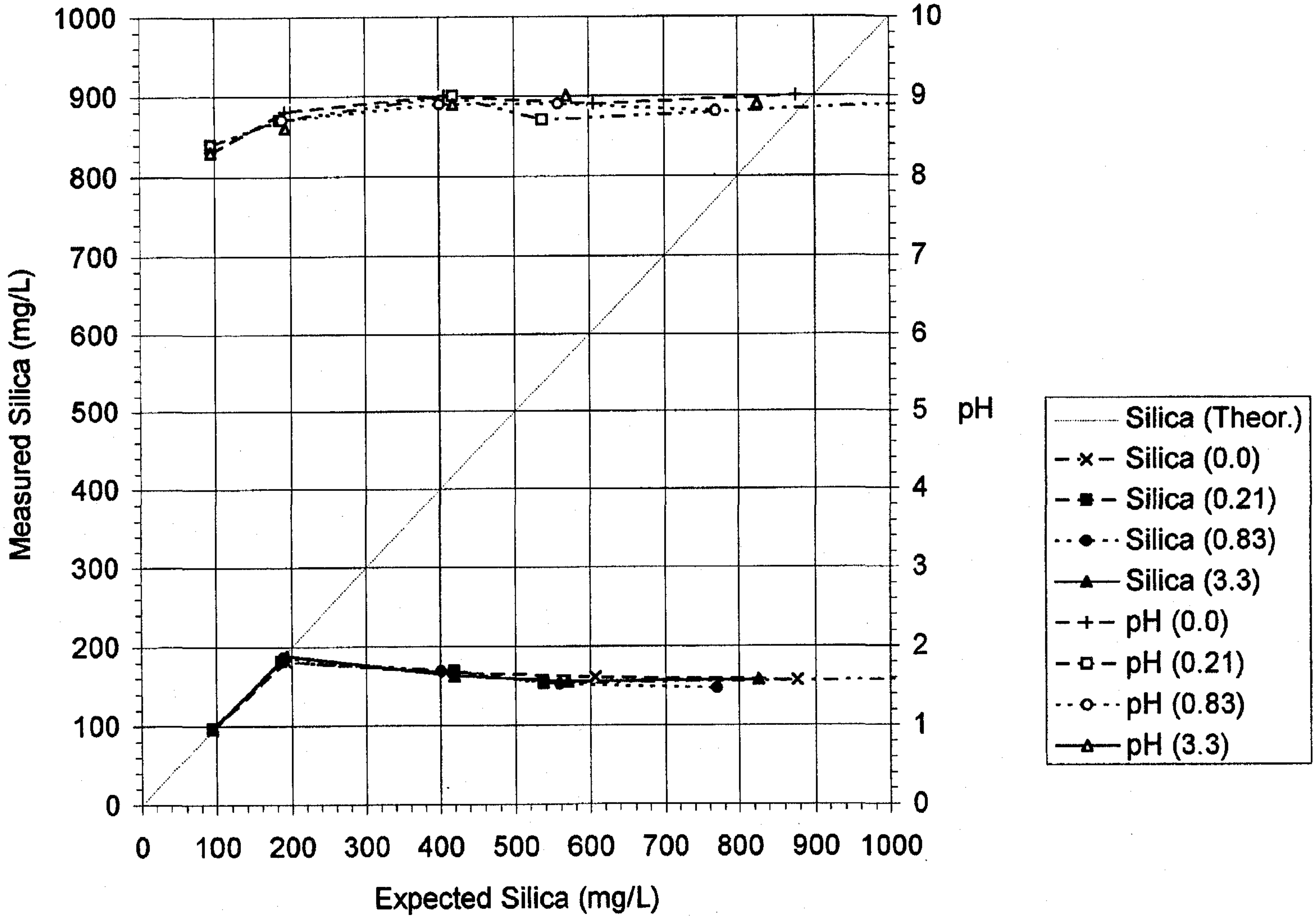

Figure 8. Effect of Bromide on the Solubility of Silica in Water.
Bromide: Silica MRs = (0), (0.21), (0.83), (3.3).

Table 5
Slope and Maximum SiO_2 Solubility Data for Sodium Bromide Evaporation Experiments Shown in Figure 8

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility**
	S_a	S_b	S_c	(expected SiO_2)
0.0	**0** (192-877)	-----	-----	**181** (192)
0.21	**0** (186-1295)	-----	-----	**181** (186)
0.83	**-0.1** (189-770)	-----	-----	**186** (189)
3.3	**-0.1** (193-826)	-----	-----	**188** (193)

Effect of Sodium Iodide on Silica Solubility in Water[1]

Figure 9 shows the effect of various MRs of added iodide ion I^- on the solubility of silica in the tap water. MRs of iodide to silica added were 0.21, 0.83, and 3.3.

The addition of iodide showed no effect on silica solubility significantly different from the control.

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[1] See Appendix N, Tables 13N–16N for data.

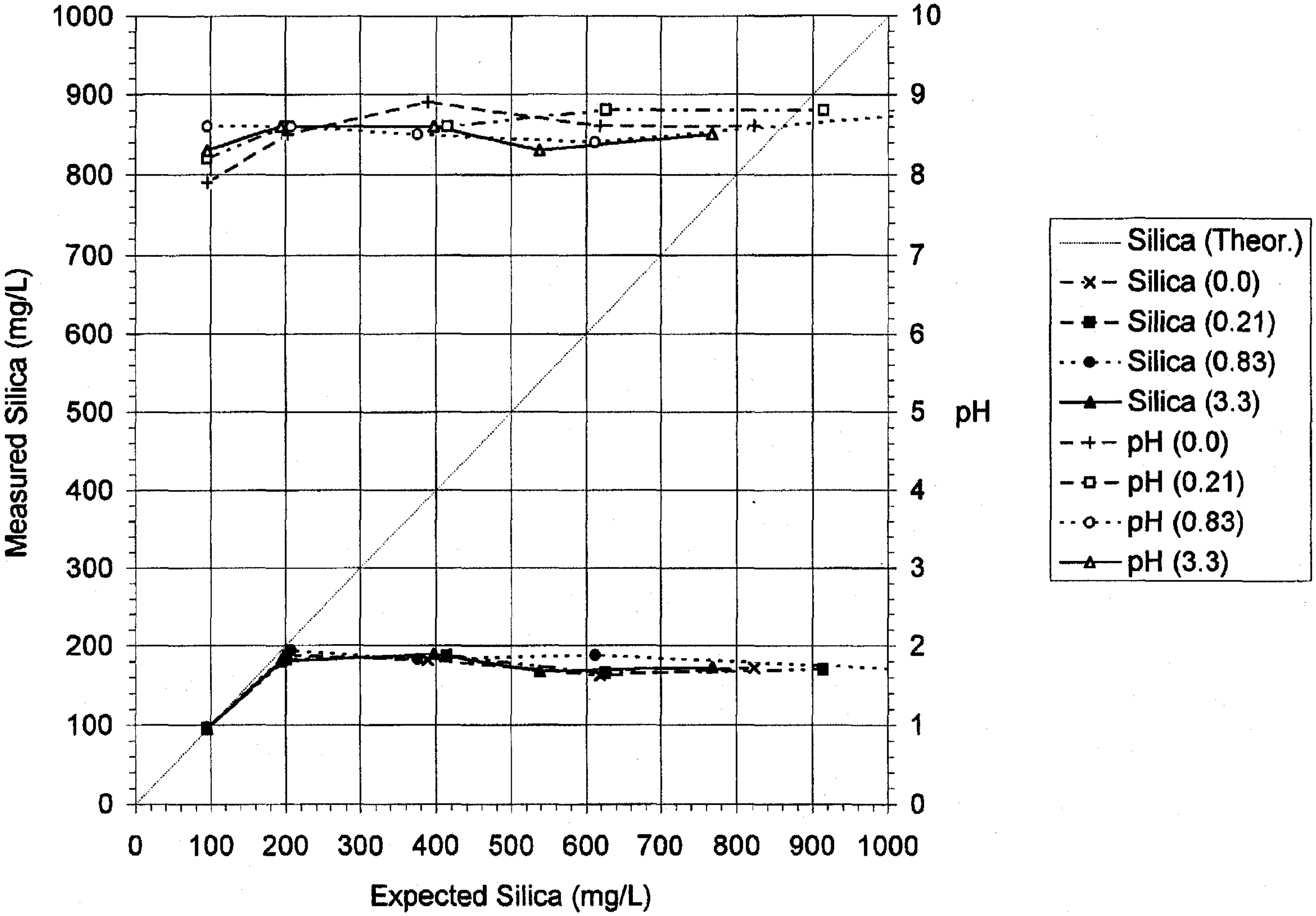

Figure 9. Effect of Iodide on the Solubility of Silica in Water.
Iodide:Silica MRs = (0), (0.21), (0.83), (3.3).

Table 6
Slope and Maximum SiO_2 Solubility Data for Sodium Iodide Evaporation Experiments Shown in Figure 9

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility, mg/L** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (203-823)	-----	-----	**188** (203)
0.21	**0** (201-914)	-----	-----	**187** (414)
0.83	**0** (207-1087)	-----	-----	**194** (207)
3.3	**0** (194-768)	-----	-----	**189** (397)

Effect of Sodium Thiocyanate on Silica Solubility in Water[1]

Thiocyanate ion is a pseudo-halide; hence, is included here. Figure 10 shows the effect of various MRs of added thiocyanate ion SCN^- on the solubility of silica in the tap water. MRs of thiocyanate to silica added were 0.22, 0.86, and 3.44.

Two very high measured silica concentrations occurred in the MR 0.86 and 3.44 runs at expected silica concentrations between 550 and 600 mg/L. In both of these runs, the curves had followed the control (MR 0.0) curve up to expected silica values of 420 mg/L. This was an apparent supersaturation.

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[1] See Appendix N, Tables 17N–20N for data.

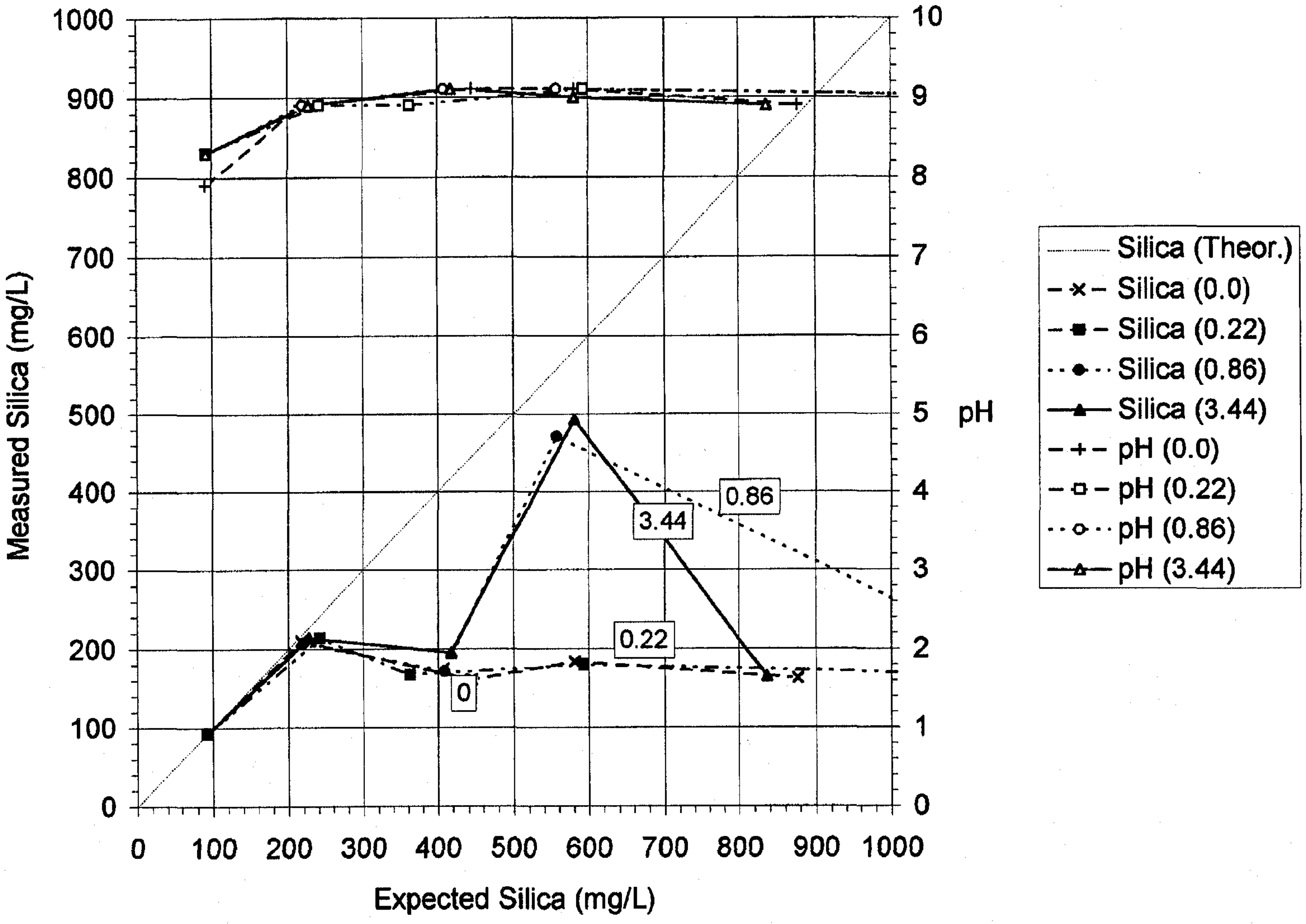

Figure 10. Effect of Thiocyanate on the Solubility of Silica in Water.
Thiocyanate:Silica MRs = (0), (0.22), (0.86), (3.44).

Table 7
Slope and Maximum SiO_2 Solubility Data for Sodium Thiocyanate Evaporation Experiments Shown in Figure 10

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility mg/L** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.2** (217-445)	**0** (445-876)	-----	**210** (217)
0.22	**-0.4** (242-363)	**0** (363-1200)	-----	**214** (242)
0.86	**-0.2** (221-409)	**+2** (409-558)	**-0.5** (558-1227)	**471** (558)
3.44	**-0.1** (228-418)	**+1.8** (418-581)	**-1.3** (581-837)	**492** (581)

Mole Ratio Effect of Halide Ions on the Solubility of Silica

In these graphs halide anions have been compared for effectiveness as solubilizers for silica on the basis of mole ratio of additive to silica at an Expected Silica concentration of 600 mg/L.

The halides, with the exception of fluoride, show similar low effectiveness as solubilizers. Surprisingly, thiocyanate, on the basis of very limited work, shows a rather high solubilizing effect or supersaturation.

Figure 11 shows chloride, bromide, and iodide have "control-like" behavior. Fluoride, as might be expected, shows that increasing the mole ratio increases its solvent power.

The pseudo halogen, thiocyanate (Figure 11), shows a somewhat similar effect: a steep slope, then an almost constant level, showing no further reaction as the mole ratio to silica is increased.

Bromide seems to show a depressing effect on solubility. The bromide ion shows no "hump" as the mole ratio increases, unlike the curves for chloride and iodide.

The results shown for the effect of additive mole ratio at the Expected Silica concentration of 600 mg/L are applicable only at this concentration factor.

The order of effectiveness for the halide ions seems to be as follows:

$$F^{-1} > SCN^{-1} > Cl^{-1} = Br^{-1} = I^{-1}$$

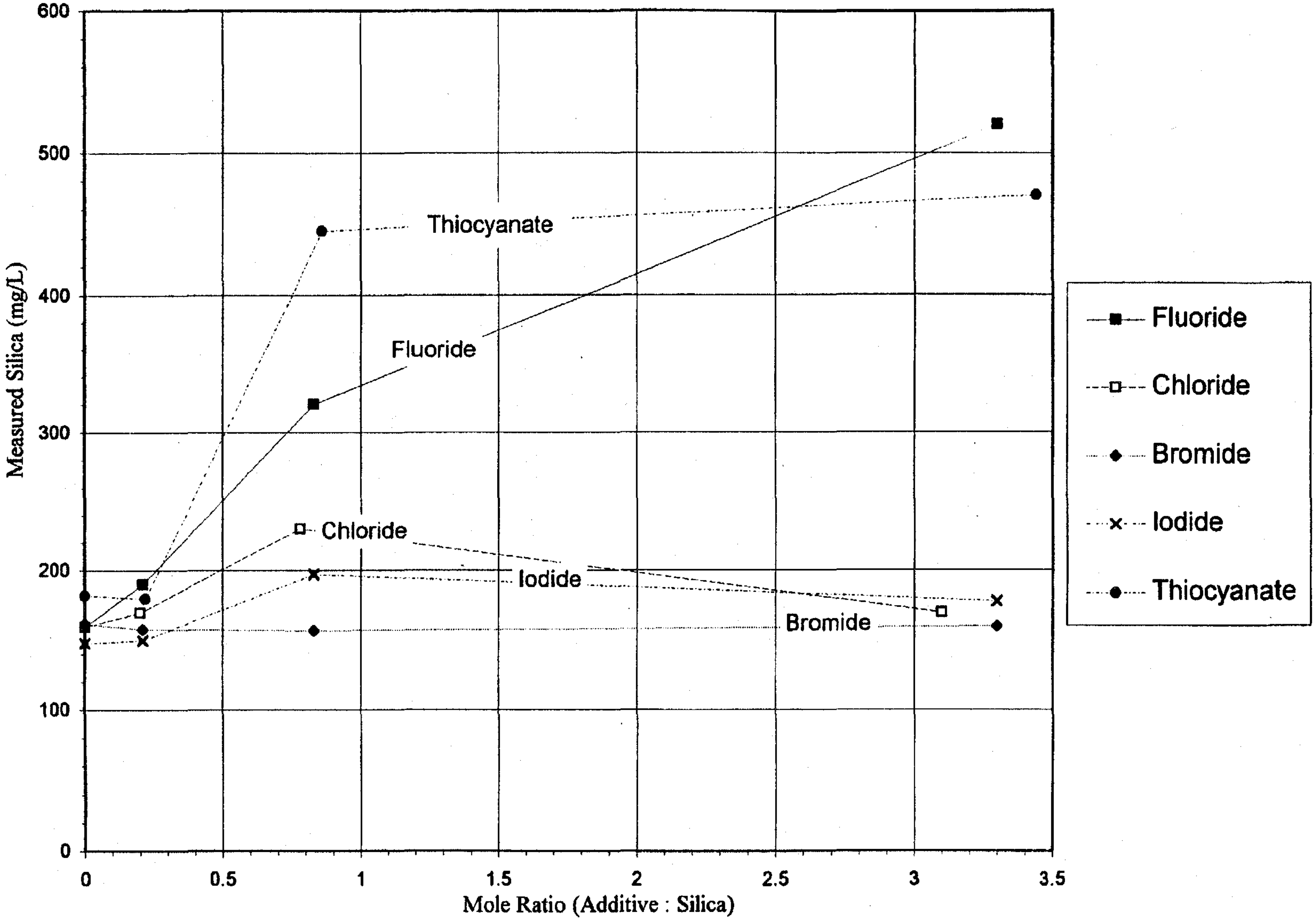

Figure 11. Effect of Additive Mole Ratio to SiO_2 on Silica Solubility.
Expected Silica Concentration is 600 mg/L SiO_2. Additives: F^-, Cl^-, Br^-, I^-, SCN^-.

c. Oxygen-Containing Anions

Effect of Sodium Nitrate on Silica Solubility in Water[1]

The curves of silica solubility in the presence of nitrate, NO_3^-, are shown in Figure 12. Mole ratios of nitrate to silica added were 0.2, 0.8, and 3.23. About 1 mg/L of nitrate naturally occurs in the LANL tap water.

The nitrate ion was used in this work as the pH adjusting ion, as nitric acid. It was selected as an ion that has a low complexing effect on metals, and also a less corrosive effect on stainless steel, than the halides.

In Figure 12 the MR 0.2 and 0.81 solutions of sodium nitrate show an anomalously high solubility, or, more correctly, a supersaturation effect. The MR 3.23 solution seems to show a solubility limit of 325 mg/L at 450 mg/L expected. In the compilation of the results of the control runs, Figure 1, it may be seen that a similar effect occurs in a number of experiments.

Since all of the previous work had been done with nitric acid, it was decided to continue the use of nitric acid for pH adjustments. In subsequent work it will be seen that the effects or lack of effects of various ions are so characteristic that any nitrate effect is not apparent.

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[1] See Appendix N, Tables 21N–24N for data.

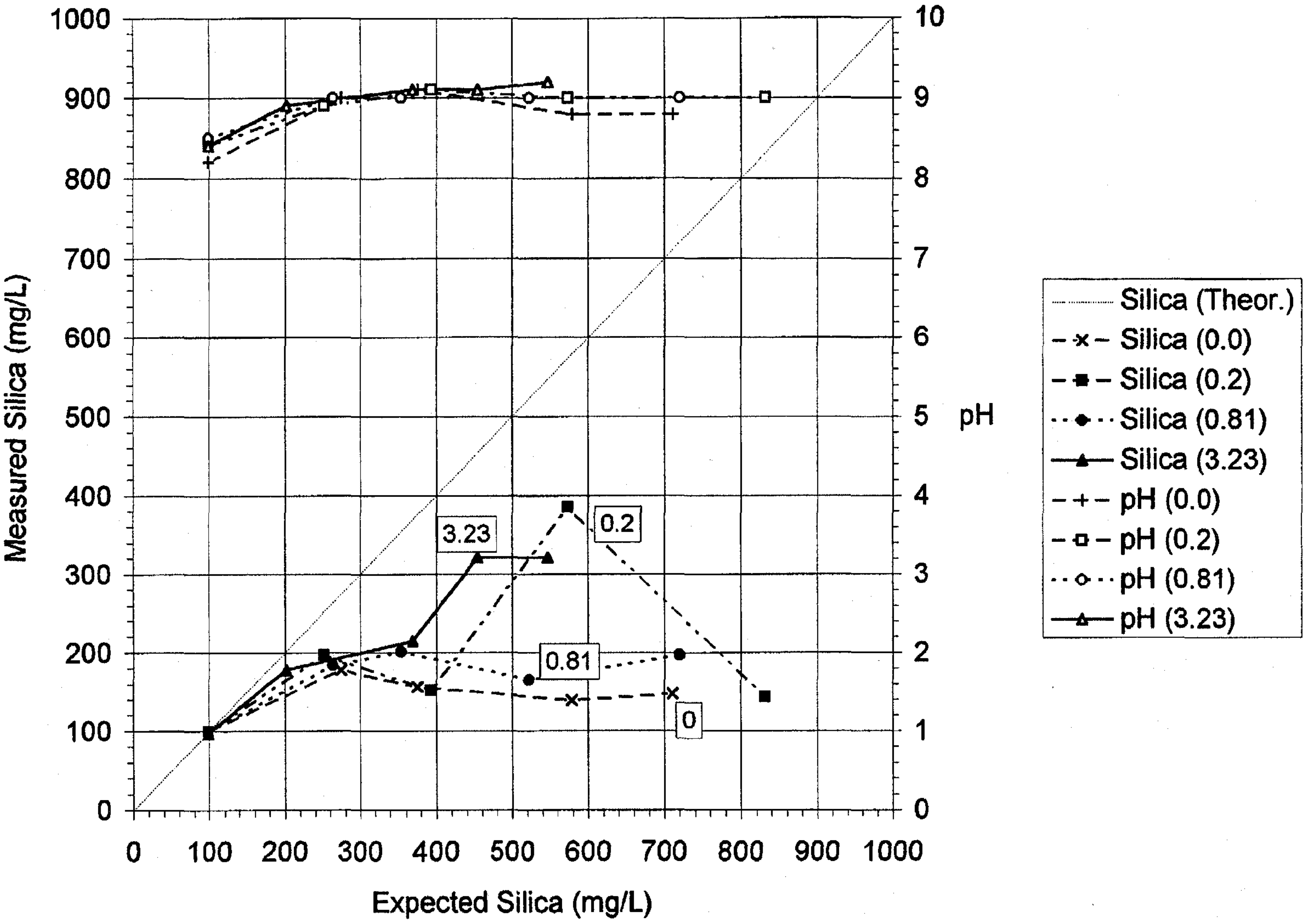

Figure 12. Effect of Nitrate on the Solubility of Silica in Water.
Nitrate:Silica MRs = (0), (0.2), (0.81), (3.23).

Table 8
Slope and Maximum SiO_2 Solubility Data for Sodium Nitrate Evaporation Experiments Shown in Figure 12

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility mg/L** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.2** (275-376)	**0** (376-712)	-----	**178** (275)
0.2	**-0.3** (251-394)	**+1.3** (394-573)	**-0.9** (573-832)	**385** (573)
0.81	**0** (264-720)	-----	-----	**201** (354)
3.23	**+0.2** (202-369)	**+1.3** (369-454)	**0** (454-547)	**321** (547)

Effect of Sodium Nitrite on Silica Solubility in Water[1]

The silica solubility curves in the presence of nitrite, NO_2^-, are shown in Figure 13. Mole ratios of nitrite to silica added were 0.21, 0.83, and 3.3.

The 0.21 and 0.83 MR runs exhibit silica solubilities similar to those of control solutions. The 3.3 MR solution shows a slight silica solubility up to 226 mg/L, still within the control range.

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[1] See Appendix N, Tables 25N–28N for data.

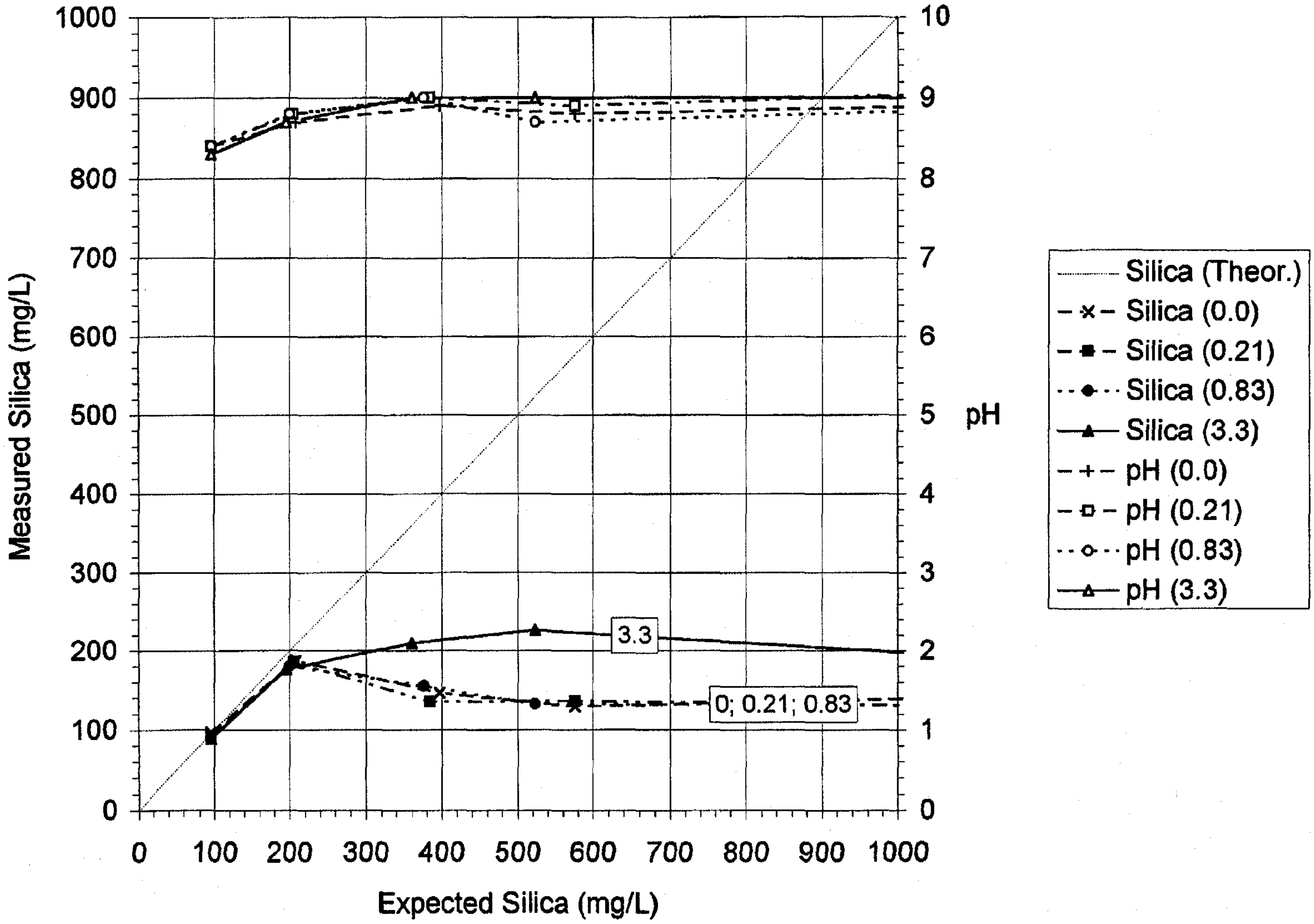

Figure 13. Effect of Nitrite on the Solubility of Silica in Water.
Nitrite:Silica MRs = (0), (0.21), (0.83), (3.3).

Table 9
Slope and Maximum SiO_2 Solubility Data for Sodium Nitrite Evaporation Experiments Shown in Figure 13

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.2** (208-397)	**0** (397-1087)	-----	**187** (208)
0.21	**-0.3** (206-384)	**0** (384-576)	-----	**185** (206)
0.83	**-0.2** (201-524)	**0** (524-1646)	-----	**180** (201)
3.3	**+0.2** (195-524)	**-0.1** (524-2057)	-----	**226** (524)

Effect of Sodium Sulfate on Silica Solubility in Water[1]

The effect of sulfate ion, SO_4^{-2}, on silica solubility may be seen in Figure 14. The MRs of sulfate to silica added were 0.21, 0.83, and 3.33. The natural sulfate concentration in LANL tap water is around 3 mg/L.

Sulfate seems to show a supersaturating effect on silica in the MR 0.83 and 3.33 evaporation experiments. The MR 0.21 run follows the control run up to an expected silica concentration of 400 mg/L. At expected silica concentrations greater than 400 mg/L some solubilizing effect of sulfate appears in the MR 0.21 run.

It should be noted in the MR 3.33 run data tables (see Appendix N) that the measured calcium and magnesium concentrations are nearly equal to their expected concentrations up to the point at which the measured silica is 550 and the expected silica is 606 mg/L.

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[1] See Appendix N, Tables 29N–32N for data.

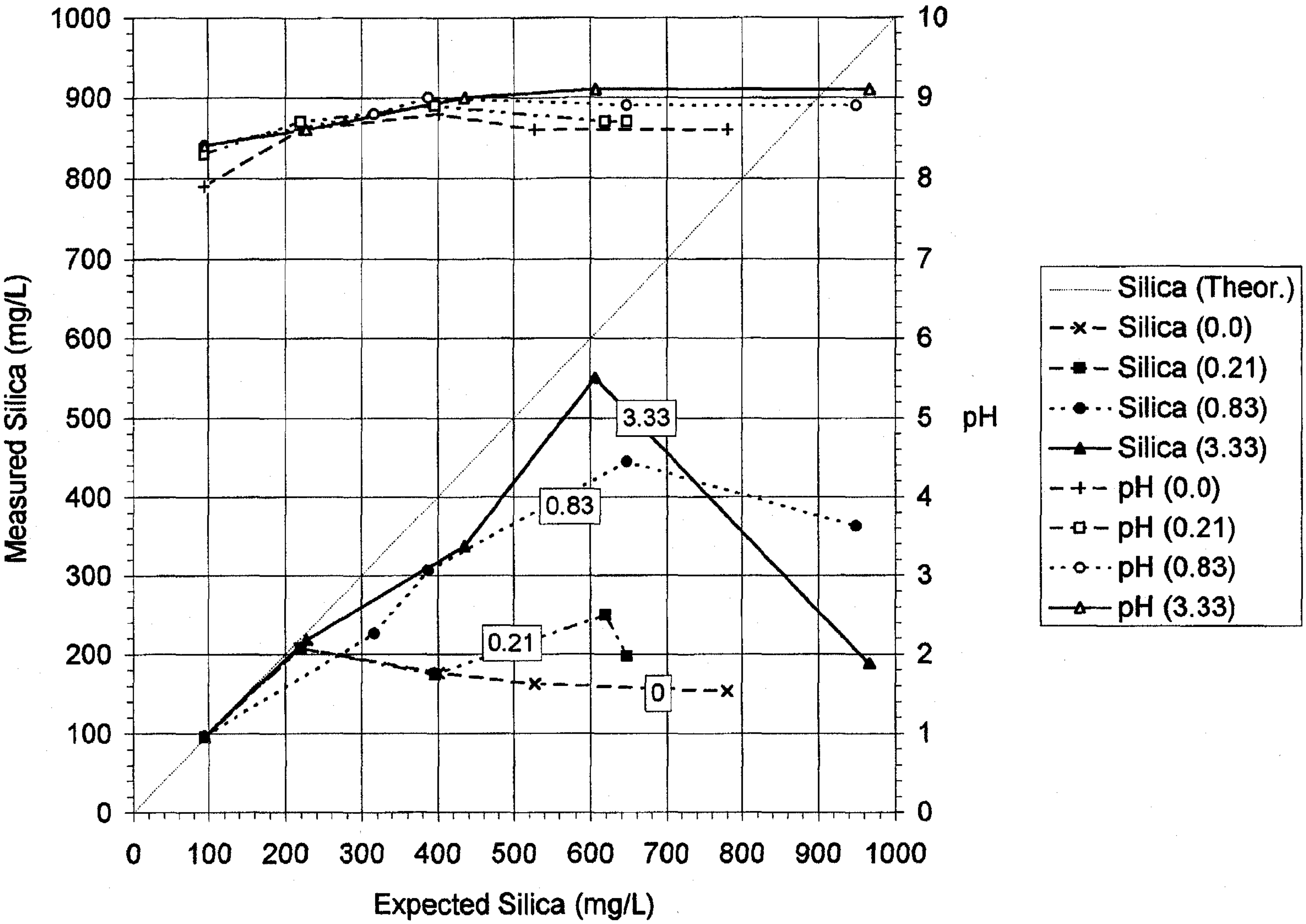

Figure 14. Effect of Sulfate on the Solubility of Silica in LANL Water.
Sulfate:Silica MRs = (0), (0.21), (0.83), (3.33).

Table 10
Slope and Maximum SiO_2 Solubility Data for Sodium Sulfate Evaporation Experiments Shown in Figure 14

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (219-781)	-----	-----	**207** (219)
0.21	**-0.2** (221-396)	**+0.3** (396-620)	**-1.9** (620-648)	**249** (620)
0.83	**+0.2** (200-317)	**+0.7** (317-648)	**-0.3** (648-950)	**444** (648)
3.33	**+0.6** (228-435)	**+1.3** (435-606)	**-1** (606-966)	**550** (606)

Effect of Ammonium Sulfamate on Silica Solubility in Water[1]

Ammonium sulfamate, $NH_4SO_3NH_2$, shows a marked increase in silica solubility as a function of mole ratio. The possibility of a pH effect is also noted in this experiment. The silica solubility curves in the presence of ammonium sulfamate are shown in Figure 15. The MRs of sulfamate to silica added were 0.2, 0.78, and 3.14. Sulfamic acid is a fairly strong acid, its ionization constant being 10^{-1}.

The MR 0.2 run showed no difference from the control run. A quite notable increase in silica solubility is present in the MR 0.78 and 3.14 runs. The curves show a definite solubilizing effect, but further work would be needed to confirm this.

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[1] See Appendix N, Tables 33N–36N for data.

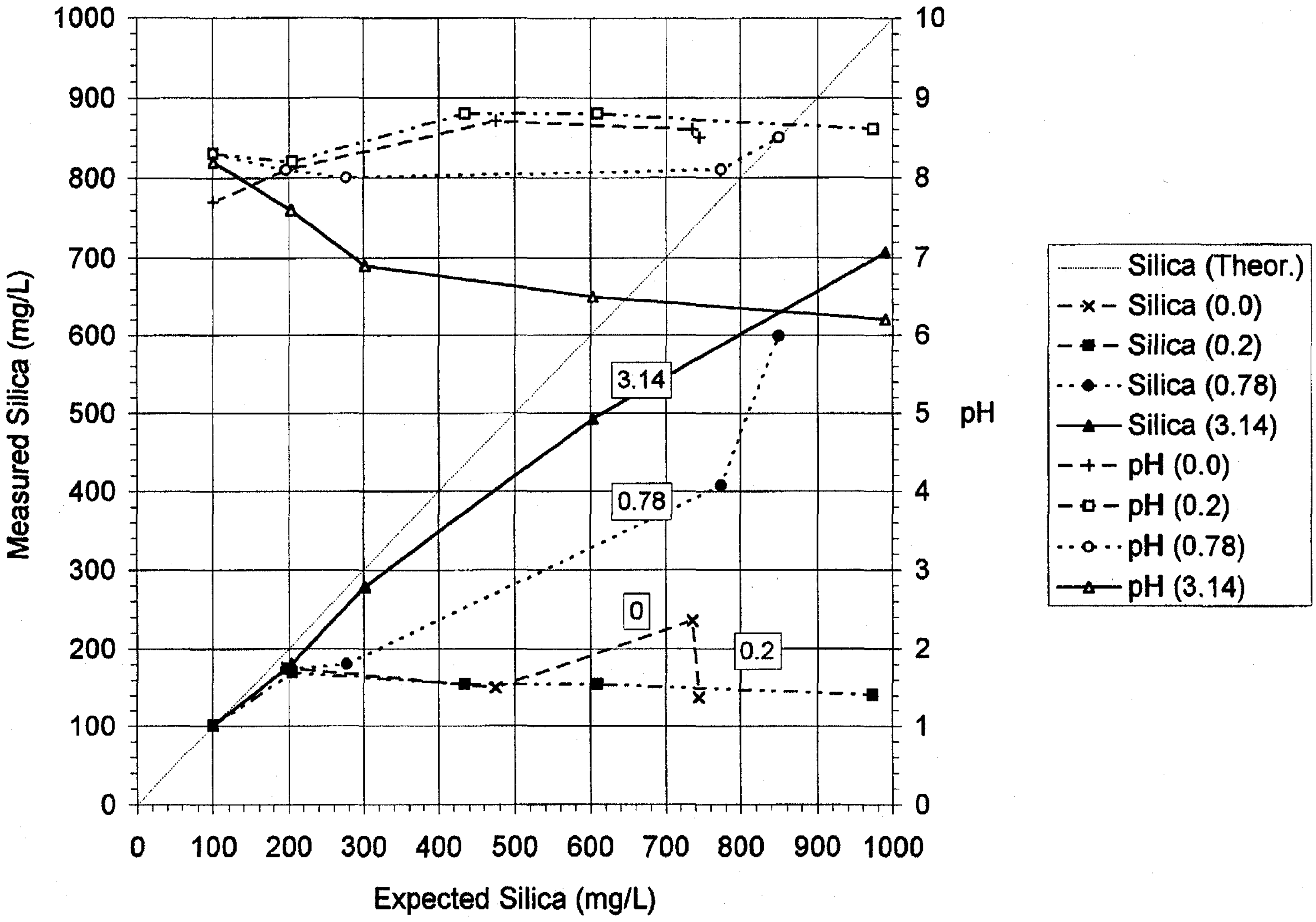

Figure 15. Effect of Ammonium Sulfamate on the Solubility of Silica in Water.
Ammonium Sulfamate:Silica MRs = (0), (0.2), (0.78), (3.14).

Table 11
Slope and Maximum SiO_2 Solubility Data for Ammonium Sulfamate Evaporation Experiments Shown in Figure 15

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (198-745)	-----	-----	**176** (198)
0.2	**0** (205-973)	-----	-----	**169** (205)
0.78	**+0.1** (197-277)	**+0.5** (277-774)	**+2.5** (774-850)	**599** (850)
3.14	+1 (203-302)	**+0.6** (302-989)	-----	**706** (989)

Effect of Sodium Bisulfite on Silica Solubility in Water[1]

The bisulfite ion, HSO_3^-, shows in Figure 16 some supersaturation effect on silica. Mole ratios of bisulfite to silica added were 0.2, 0.79, and 3.2.

The MR 0.2 run had no effect on silica solubility. The MR 0.79 and 3.2 runs exhibit supersaturation of silica up to measured concentrations of 480-500 mg/L. Nearly all of the calcium and magnesium were in solution in the highest measured silica solutions for both the MR 0.79 and 3.2 runs (See Appendix N). Bisulfite is known for its solubilizing effect on magnesium and calcium.

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[1] See Appendix N, Tables 37N–40N for data.

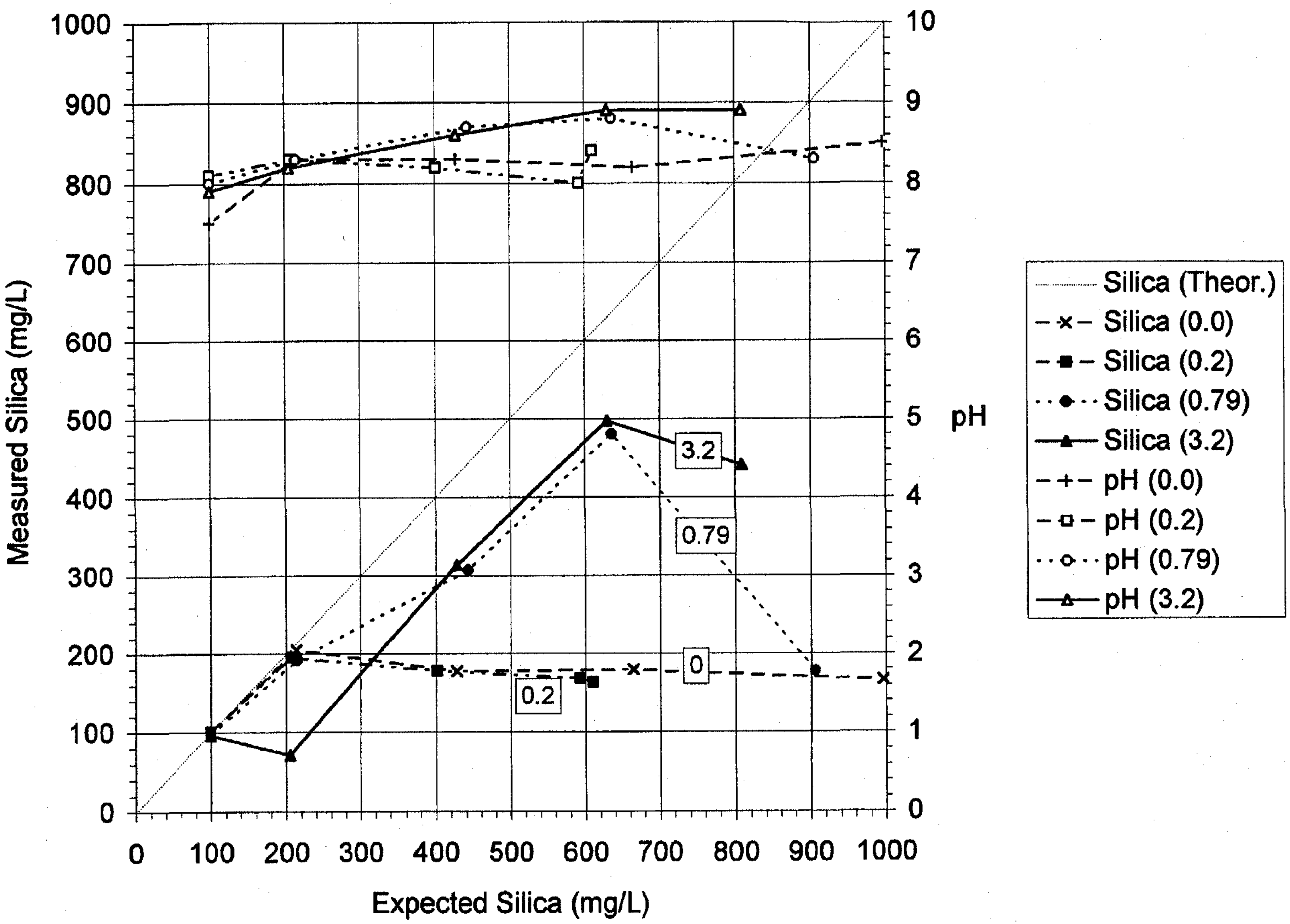

Figure 16. Effect of Bisulfite on the Solubility of Silica in Water.
Bisulfite:Silica MRs = (0), (0.2), (0.79), (3.2).

Table 12
Slope and Maximum SiO_2 Solubility Data for Sodium Bisulfite Evaporation Experiments Shown in Figure 16

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (214-997)	-----	-----	**205** (214)
0.2	**-0.1** (206-610)	-----	-----	**195** (206)
0.79	**+0.7** (214-636)	**-1.1** (636-906)	-----	**480** (636)
3.2	**+0.7** (200-630)	**-0.3** (630-808)	-----	**497** (630)

Effect of Disodium Phosphate on Silica Solubility in Water[1]

The effect of PO_4^{-3}, added as disodium phosphate, Na_2HPO_4, on silica solubility may be seen in Figure 17. The MRs of phosphate to silica added were 0.23, 0.9, and 3.7. The natural phosphate concentration in LANL tap water is less than 1 mg/L.

All three MRs of phosphate additions resulted in increased solubilization of silica as compared to the control. The MR 0.23 curve rose to nearly theoretical silica concentration up to 500 mg/L of expected silica. None of the solutions, except the control, showed a solubility limit within the limits of the experiment. The control curve shows an anamolous high point at around 600 mg/L expected silica (see Appendix N). Phosphate showed a strong solubilizing effect as indicated by the high slope values of 0.9 or higher in Table 13. The MR 0.9 and 3.7 curves show near theoretical silica concentrations up to 600 mg/L measured and 695 mg/L of expected silica.

The pHs of the solutions with the phosphate additions varied from about pH 8.8 to 9.4. Perhaps these high measured silica values could be a function of the high pH in the solutions, as evidenced by the results of the pH work (see Experimental Results, Effect of pH, Figure 5).

Calcium is substantially removed from all the solutions with phosphate additions. Magnesium concentrations were essentially the same as in the control in all of the phosphate solutions. (See Appendix N). Further work in the use of phosphates is justified.

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[1] See Appendix N, Tables 41N–44N for data.

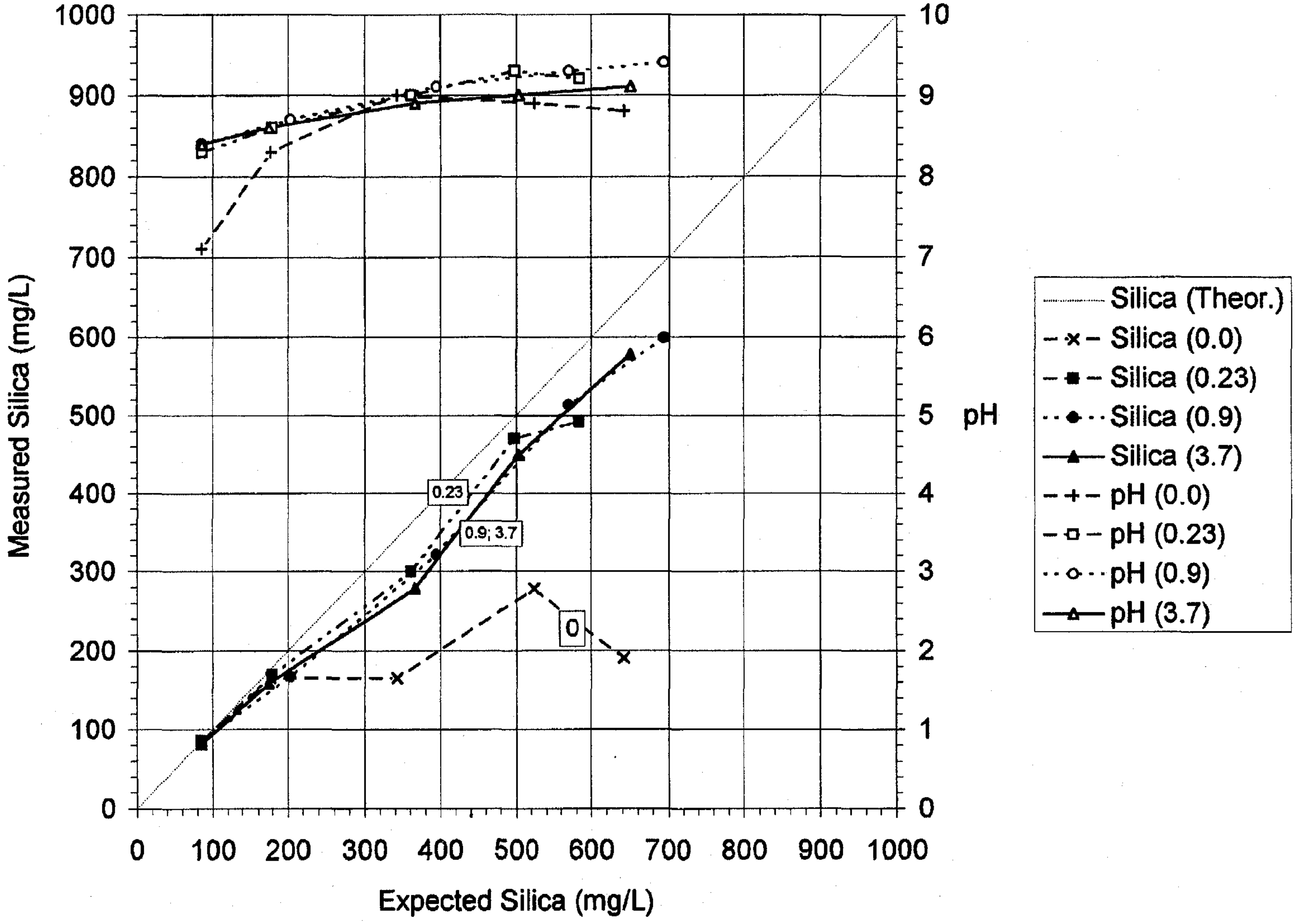

Figure 17. Effect of Phosphate on the Solubility of Silica in Water.
Phosphate:Silica MRs = (0), (0.23), (0.9), (3.7).

Table 13
Slope and Maximum SiO_2 Solubility Data for Disodium Phosphate Evaporation Experiments Shown in Figure 17

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (177-342)	**+0.6** (342-524)	**-0.7** (524-642)	**278** (524)
0.23	**+0.7** (179-362)	**+0.9** (362-584)	-----	**492** (584)
0.9	**+0.8** (203-395)	**+0.9** (395-694)	-----	**599** (694)
3.7	**+0.6** (175-367)	**+1.1** (367-650)	-----	**578** (650)

Mole Ratio Effect of Oxygenated Inorganic Anions on the Solubility of SiO_2

Figure 18 shows the effects of varying the mole ratios of the anions nitrite, nitrate, sulfate, sulfamate, bisulfite, and phosphate on silica solubility at an Expected Silica concentration of 600 mg/L.

Sulfate has marked solubilizing effect, as previously discussed. Sulfamate has a somewhat similar effect, but less than sulfate, although the curves look similar. The effectiveness of bisulfite on silica solubilization lies between the effectiveness of sulfate and sulfamate.

Phosphate shows a marked solubilizing effect compared to the sulfur-containing compounds. The anions that solubilize calcium and magnesium are rather good solubilizers for silica.

Nitrate shows a rather ambiguous effect that needs further evaluation. Nitrite shows little solubilization as a function of mole ratio.

The order of the effectiveness of the oxygenated anions on silica solubility at the Expected Silica concentration of 600 mg/L are shown below:

$$PO_4^{-3} > SO_4^{-2} > HSO_3^{-1} > NH_2SO_3^{-1} > NO_3^{-1} > NO_2^{-1}$$

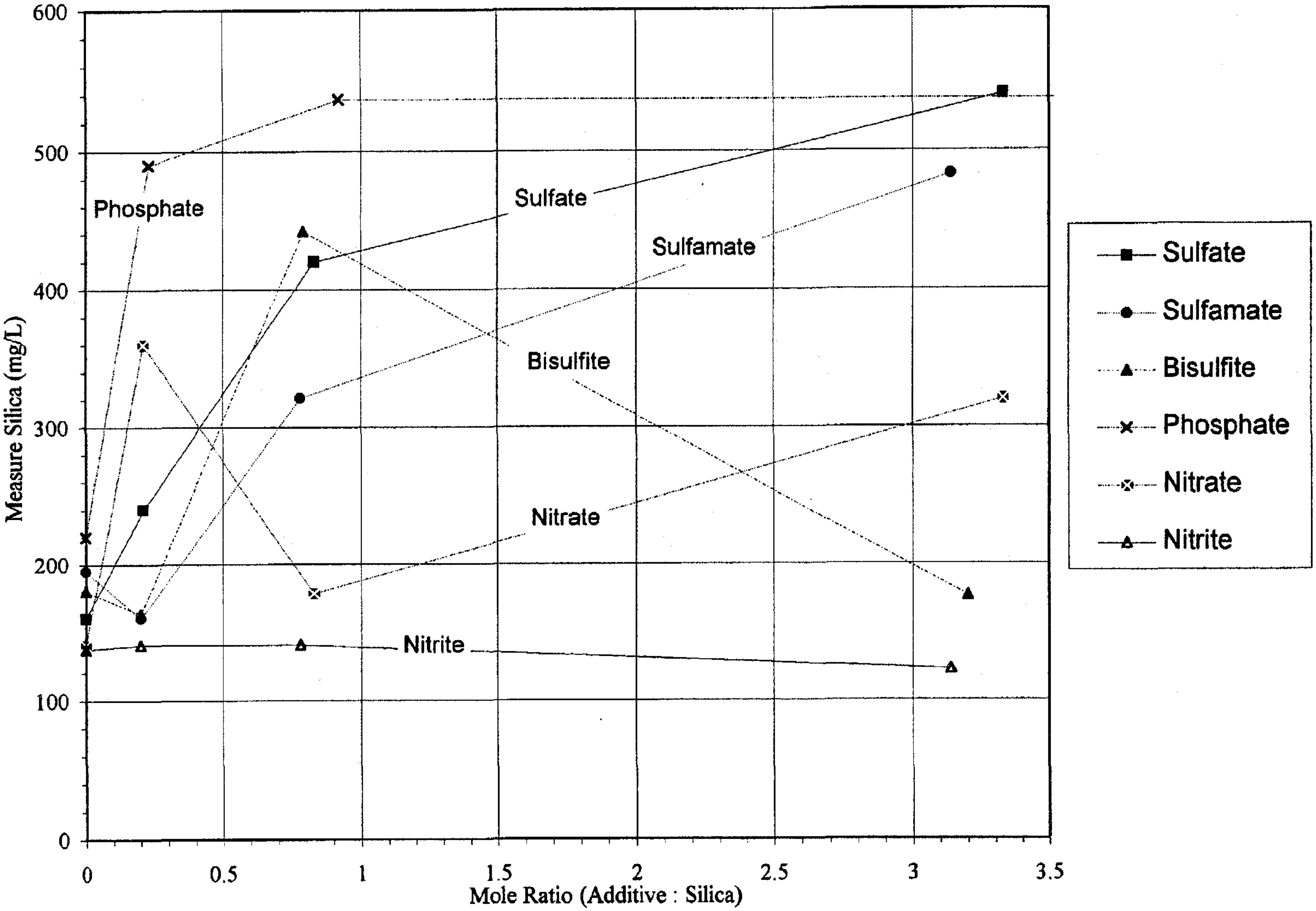

Figure 18. Effect of Additive Mole Ratio to SiO_2 on Silica Solubility.
Expected Silica Concentration Is 600 mg/L SiO_2. Additives: SiO_4^{2-}, $NH_2SO_3^-$, HSO_3^-, PO_4^{3-}, NO^-_3, NO^-_2.

Silica Solubility in Evaporated Sodium Metasilicate Solutions[1]

Since so much work has been done in the literature on sodium silicate based solutions as prototypes or "stand-ins" for natural solutions, it was deemed desirable to run a series of experiments for comparison with our work on LANL tap water. These experiments were done by adding silicate to deionized water; they do not contain any other cations such as calcium, magnesium, etc.

Figures 19, 20, and 21 show the effect of evaporation on silica solubility in sodium metasilicate solutions. These experiments were performed using a silica solution prepared by dissolving sodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$, in deionized water. The curves in Figure 19 show four duplicate evaporation runs with initial silica concentrations of 113 mg/L. The measured silica concentrations in all four evaporation runs in Figure 19 retain near theoretical silica concentrations up to 1000 mg/L expected silica. The solubility of silica in LANL water is usually in the 150-220 mg/L range. Comparison of the total silica solubility curves with the reactive silica curve, which behaves similarly to blanks run with LANL tap water, would suggest that the silica in silicate solutions is really polymeric (a thought attributed to Peter Debye).

Figure 20 shows the effect of pH on silica solubility in these solutions. The effect is a moderate reduction of the silica solubility in the pH 6.0 and pH 9.0 solutions. The straight line slopes are lower. The solubilities in the pH 6.0 solution are somewhat less than in the pH 3.0 or pH 10.5 solutions. The solubility curves for the pH 3.0 and pH 10.5 conditions are virtually identical.

Figure 21 shows the reactive silica content in a silica solution. The lowest reactive silica contents are found at pH 6.0 with the highest at pH 3.0.

It would seem that the high levels of silica remaining in solution at the high Expected Silica levels is not a function of high pH in these experiments.

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[1] See Appendix N, Tables 45N–52N for data.

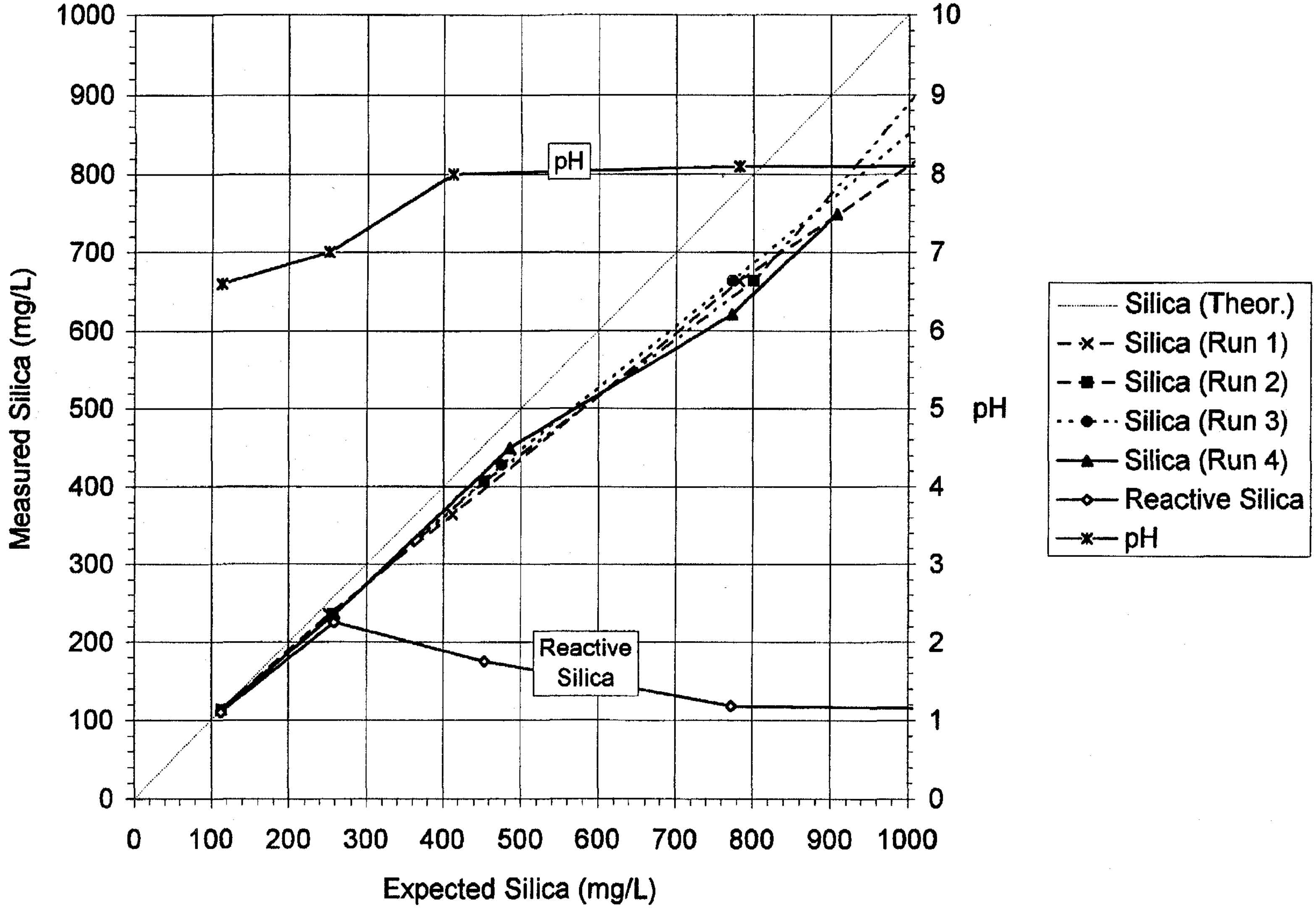

Figure 19. The Solubility of Silica in a 113 mg/L Silica Solution
Made from Sodium Metasilicate and Deionized Water.

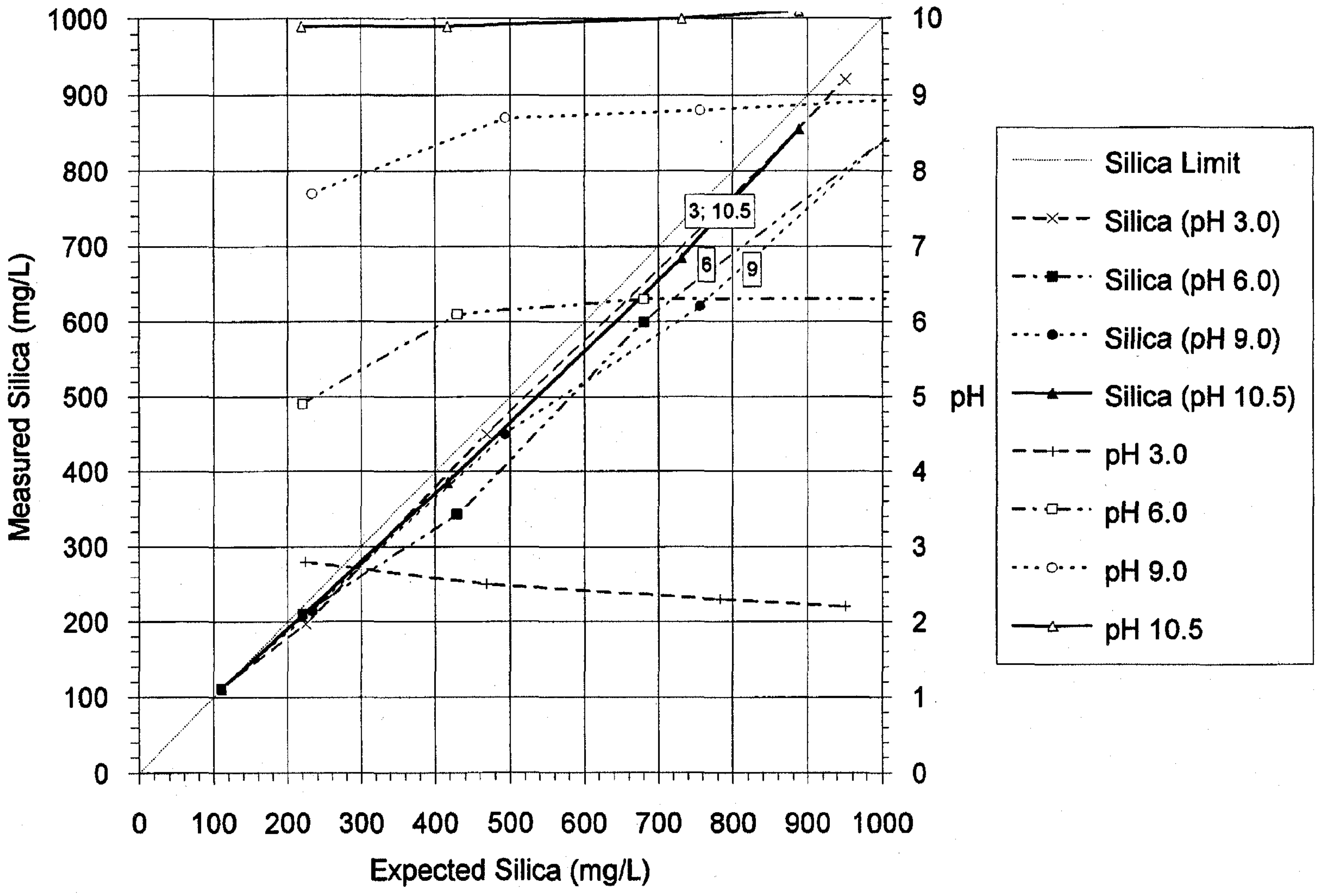

Figure 20. The Solubility of Silica in a 111 mg/L Silica Solution Made from Sodium Metasilicate and Deionized Water. Initial pHs Adjusted to (3.0), (6.0), (9.0), and (10.5).

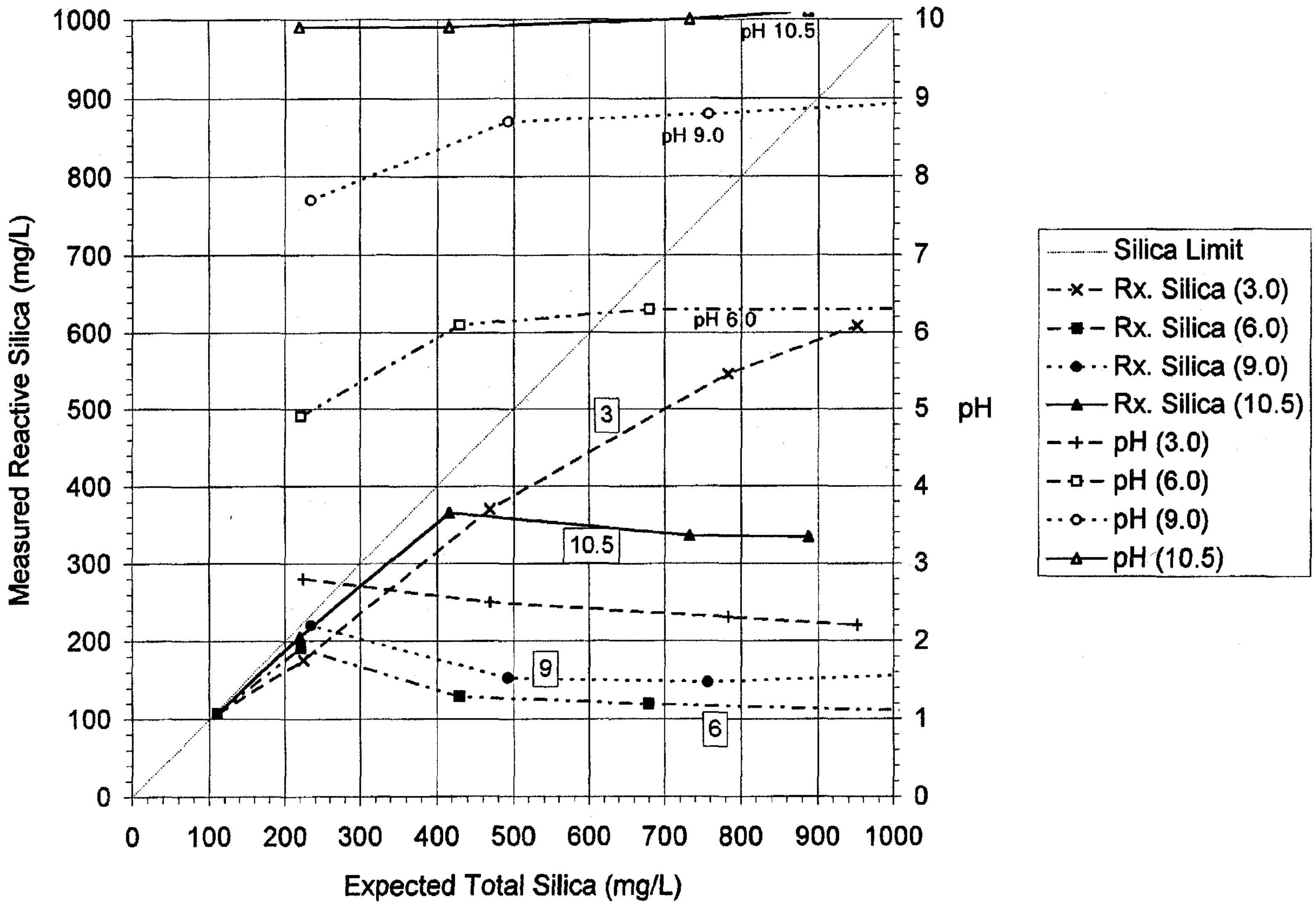

Figure 21. The Reactive Silica Contents in a 111 mg/L Silica Solution Made from Sodium Metasilicate and Deionized Water. Initial pHs Adjusted to (3.0), (6.0), (9.0), and (10.5).

d. Conclusions – Inorganic Anion Addition Work

Preliminary work showed that pH has a marked effect on the solubility of silica in the original water. Minimum solubility was found to be around 8.2, the natural pH of the LANL water.

Fluoride is one of the best of the inorganic anions as a solubilizer, but it also represents known compound formation (such as fluosilicates). The presence of magnesium may be a necessary factor in the ultimate insolubilization of SiO_2 by evaporation.

Halides other than fluoride had no solubilizing effect. However, the pseudo-halide, thiocyanate, shows a surprising supersaturating effect. Nitrate does not seem to be as innocuous or nonsolubilizing as had been assumed. Sulfate, bisulfite, and sulfamate show very marked solubilizing effects on silica. Possibly, this may be due to some type of complex formation with magnesium and calcium. It should be noted that the sulfate and other oxygen-containing anions (with the possible exception of sulfamate and phosphate) do not appear to be true solubilizers; they are probably supersaturators. As previously mentioned, the distinction between supersaturation and solubility is that the supersaturation curve may reach a maximum at some concentration factor, then fall abruptly to the "control" value.

The effects of inorganic anions may be summarized in the solubility series below (which indicate approximate ranking as to solubilization at the Expected Silica content of 600 mg/L):

<u>Halides</u>

$F^{-1} > SCN^{-1} > Cl^{-1} = Br^{-1} = I^{-1}$

<u>Oxygenated</u>

$PO_4^{-3} > SO_4^{-2} > HSO_3^{-1} > NH_2SO_3^{-1} > NO_3^{-1} > NO_2^{-1}$

Overall, fluoride and phosphate and possibly sulfamate seem to have solubilizing properties in the range of mole ratios and concentration factors used in this work. The others have at best only supersaturating effects.

2. Organic Anions

The solubilizing effects on silica of various types of anionic organic chemicals were evaluated. Several classes of organic compounds with different functional groups and configurations were used. Table 14 below lists the specific chemicals in each chemical class that were used in the evaporation experiments.

Table 14
Organic Chemicals Studied for Their Effect on Silica Solubilities in LANL Tap Water

Organic Compounds and Anions			
Figure	**Chemical Additive**	**Mole Ratio of Additive to Silica**	**Initial pH of Solutions**
	Monobasic:		
22	Sodium Formate HCOONa	0, 0.2, 0.81, 2.43	8.2
23	Sodium Acetate CH_3COONa	0, 0.2, 0.78, 2.35	8.2
	Dibasic:		
24	Sodium Oxalate NaOOCCOONa	0, 0.11, 0.43, 1.7	8.2
25	Sodium Oxalate	0.44	3.5, 4.5, 5.5, 6.5
26	Sodium Oxalate	0.44	7.2, 8.2, 9.0, 10.0
27	Sodium Oxalate + Calcium	0, 0.19, 0.38, 0.77	8.2
28	Sebacic Acid 1,8-octanedicarboxylic acid	0, 0.21, 0.82, 2.45	8.2
29	Maleic Acid cis-1,2-ethylenedicarboxylic acid	0, 0.1, 0.4, 1.6	8.2
	Hydroxy:		
30	Citric Acid 2-Hydroxy-1,2,3-propane tricarboxylic acid	0, 0.21, 0.83, 2.48	8.2
	Tetrabasic:		
31	EDTA Ethylenediaminetetra-acetic acid	0, 0.08, 0.4, 0.8	8.2

Organic Compounds and Acids

Figure	Chemical Additive	Mole Ratio of Additive to Silica	Initial pH of Solutions
	Benzene Carboxylic Acids:		
32	o - Phthalic Acid 1,2-benzenedicarboxylic acid	0, 0.1, 0.4, 1.6	8.2
33	p-Phthalic Acid 1,4-benzenedicarboxylic acid	0, 0.22, 0.88, 2.64	8.4
	Poly Hydroxy Phenols:		
34	Catechol 1,2-dihydroxybenzene	0, 0.09, 0.46, 1.84	7.9
35	Pyrogallol 1,2,3-trihydroxybenzene	0, 0.09, 0.46, 1.84	8.2
36	Phloroglucinol 1,3,5-trihydroxybenzene	0, 0.08, 0.42, 1.7	7.9
	Phenol Carboxylic Acid:		
37	Sodium Salicylate 2-hydroxybenzoic monosodium salt	0, 0.2, 0.81, 3.23	7.8
	Sulfonates		
38	p - Toluene Sulfonic Acid 4-methylbenzene sulfonic acid	0, 0.09, 0.45, 1.8	8.0
39	Alkyl Naphthalene Sulfonic Acid	0, 0.03, 0.16, 0.62	8.2
40	Tiron 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt	0, 0.017, 0.09, 0.17	8.2
41	Tiron	0, 0.13, 0.17, 0.43	8.2
	Lignin Sulfonates		
43	Kelig 32	0, 0.03, 0.06, 0.11	8.1
44	Marasperse N-22	0, 0.017, 0.034, 0.068	8.1
45	Maracell XE	0, 0.11, 0.21, 0.43	8.2

Effect of Sodium Formate on Silica Solubility in Water[1]

Figure 22 shows the effects of various mole ratios of additions of formate ion, $HCOO^-$, on the solubility of silica in LANL tap water. The mole ratios of formate to silica added were 0.2, 0.81, and 2.43.

The MR 2.43 has a substantial solubilizing effect on silica up to expected silica concentrations of 600 mg/L. All three mole ratios of formate added resulted in nearly identical slopes of their solubility curves, each solubility curve shown in Figure 22 reaches a limiting value instead of continuing to higher concentrations. The curves then fall rapidly down to the values on the control curve, indicating a supersaturation effect.

It is interesting to note that at the high points of the three curves with sodium formate additions, the measured magnesium is close to the expected values (see Appendix N). When the silica concentration falls, the magnesium concentration also falls, indicating removal with the silica.

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[1] See Appendix N, Tables 53N–56N for data.

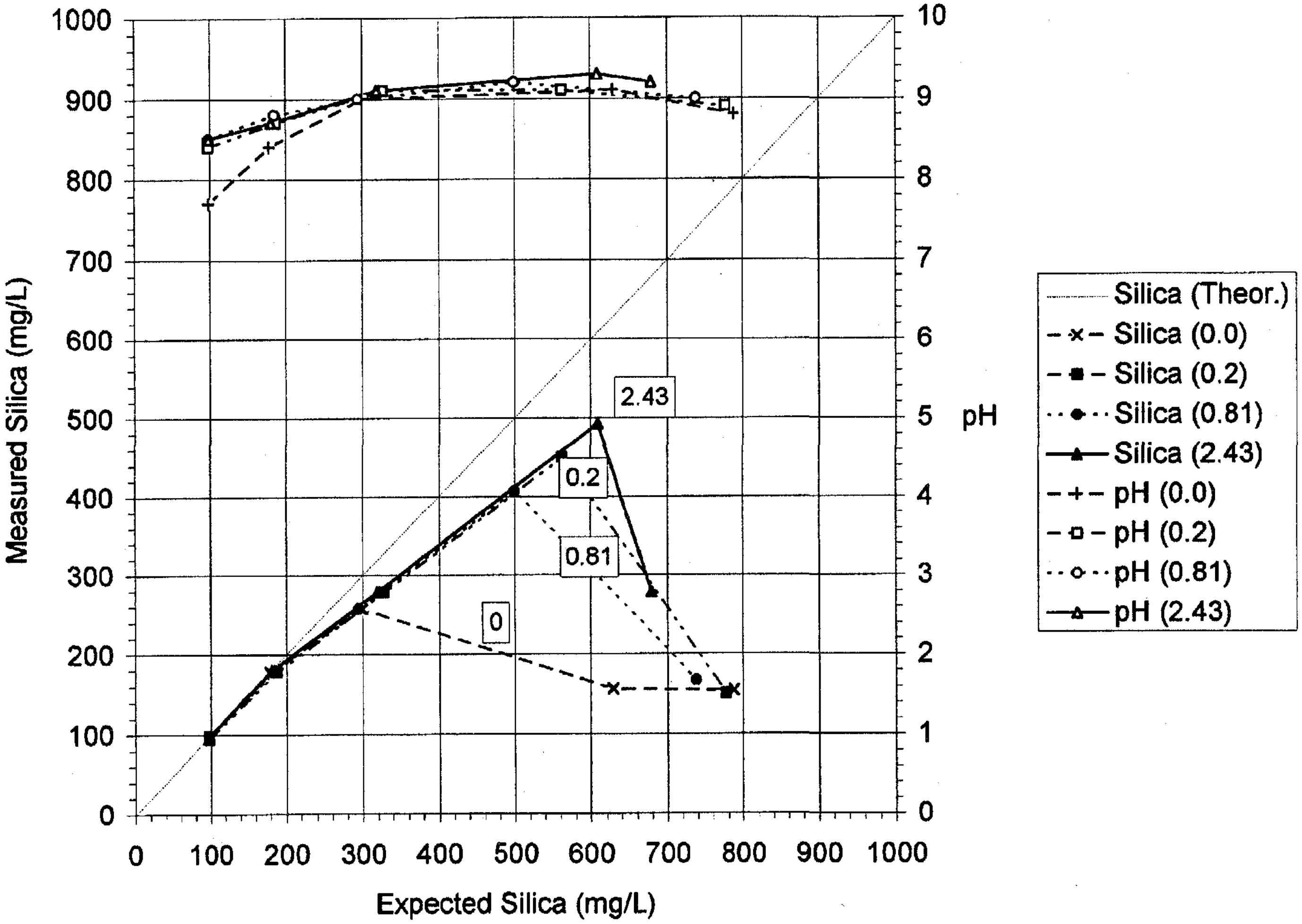

Figure 22. Effect of Formate on the Solubility of Silica in Water.
Formate:Silica MRs = (0), (0.2), (0.81), (2.43).

Table 15
Slope and Maximum SiO_2 Solubility Data for Sodium Formate in Water Evaporation Experiments Shown in Figure 22

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**+0.7** (179-300)	**-0.3** (300-628)	**0** (628-788)	**257** (300)
0.2	**+0.7** (188-563)	**-1.4** (563-777)	-----	**449** (563)
0.81	**+0.7** (186-501)	**-1** (501-738)	-----	**407** (501)
2.43	**+0.7** (182-609)	**-3.1** (609-679)	-----	**492** (609)

Effect of Sodium Acetate on Silica Solubility in Water[1]

Acetic acid, CH_3COOH, is the second member of the alkanoic acid series. Figure 23 shows the effect of various mole ratios of added acetate ion, CH_3COO^-, on the solubility of silica in LANL tap water. The MRs of acetate to silica added were 0.2, 0.78, and 2.35.

The effect of acetate ion on solubility is seemingly nil. The curves at increasing MRs of acetate ion cannot be distinguished from those of the control. Only these first two alkanoic acid compounds have been investigated.

The measured magnesium values in these experiments with acetate additions were lower than expected indicating removal by silica (see Appendix N).

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[1] See Appendix N, Tables 57N–60N for data.

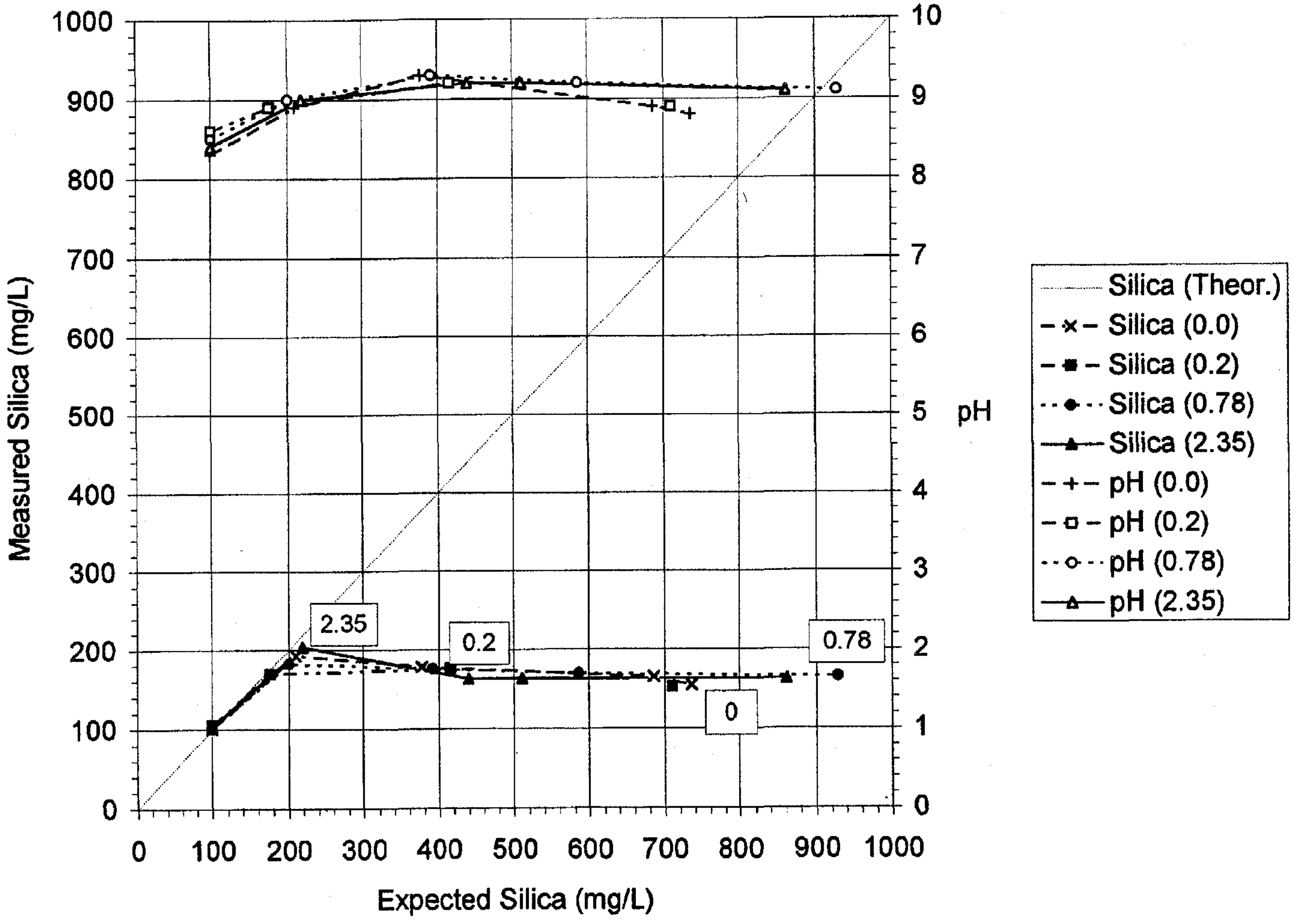

Figure 23. Effect of Acetate on the Solubility of Silica in Water.
Acetate:Silica MRs = (0), (0.2), (0.78), (2.35).

Table 16
Slope and Maximum SiO_2 Solubility Data for Sodium Acetate in Water Evaporation Experiments Shown in Figure 23

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (210-686)	-----	-----	**193** (210)
0.2	**0** (176-710)	-----	-----	**175** (416)
0.78	**0** (201-928)	-----	-----	**182** (201)
2.35	**-0.2** (219-440)	**0** (440-862)	-----	**203** (219)

Effect of Sodium Oxalate on Silica Solubility in Water[1]

The effect of sodium oxalate, NaOOCCOONa, on silica solubility is seen in Figure 24. The MRs of oxalate to silica added were 0.11, 0.43, and 1.7.

The results show that the oxalate ion is a very effective solubilizer of silica. No evidence of supersaturation was found within the range of this series.

Measured calcium concentrations in the MR 0.43 and 1.7 oxalate to silica experiments were less than 2 mg/L in all solutions (see Appendix N). Calcium was noticeably precipitated in the two high oxalate MR evaporation runs. Calcium concentrations in the MR 0.11 experiment did not differ appreciably from the calcium content in the control evaporation run. The magnesium showed high solubility when silica solubility was high (see Appendix N).

The effect of pH on the solubility of silica in oxalate solutions is shown in Figure 25 for the initial pH range 3.5 to 6.5. The evaporations were done on solutions containing MR 0.44 oxalate:silica.

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[1] See Appendix N, Tables 61N–72N for data.

The solubility results in the initial pH range of 7.2 to 10.0 are shown in Figure 26. The slopes of the curves vary little over the range of pH values. This indicates that even at the highest concentration factors, a solubility of 1049 mg/L, the pH had no substantial effect on solubility. No limit on solubility (break in the curves) was reached in these solubility experiments.

The final pH curves show the usual type of buffering effect: higher at high initial pHs and lower at the low initial pH values. Calcium was substantially precipitated in all the experiments. Oxalate shows marked solubilizing effects on silica. No supersaturation of silica is shown. Magnesium seems to be inactivated and remains in solution (see Appendix N).

The Result of Excess Calcium on Oxalate's Effect on Silica Solubility[1]

The effect of added calcium on silica solubility in the presence of oxalate is shown in Figure 27. The MRs of oxalate:silica added were 0.19, 0.38, and 0.77; while the MRs of calcium: silica added were 0.24, 0.48, and 0.96. These additions yield a calcium:oxalate MR = 1.25. Apparently, the oxalate is effectively removed as calcium oxalate from solution and does not keep silica in solution. The resulting curves of Measured Silica vs. Expected Silica in Figure 27 approximate the control curve (see Appendix N).

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[1] See Appendix N, Tables 73N–76N for data.

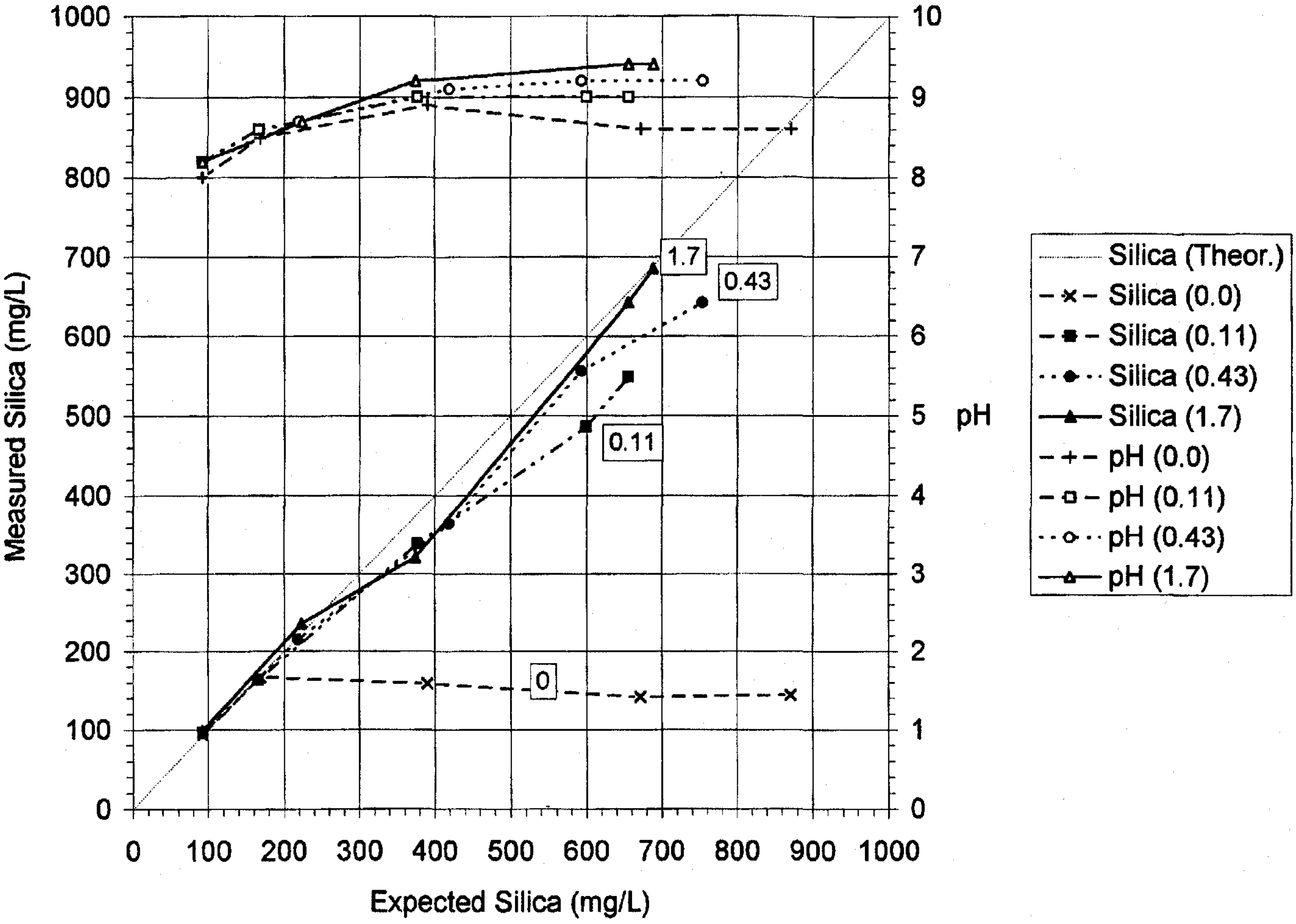

Figure 24. Effect of Oxalate on the Solubility of Silica in Water.
Oxalate:Silica MRs = (0), (0.11), (0.43), (1.7).

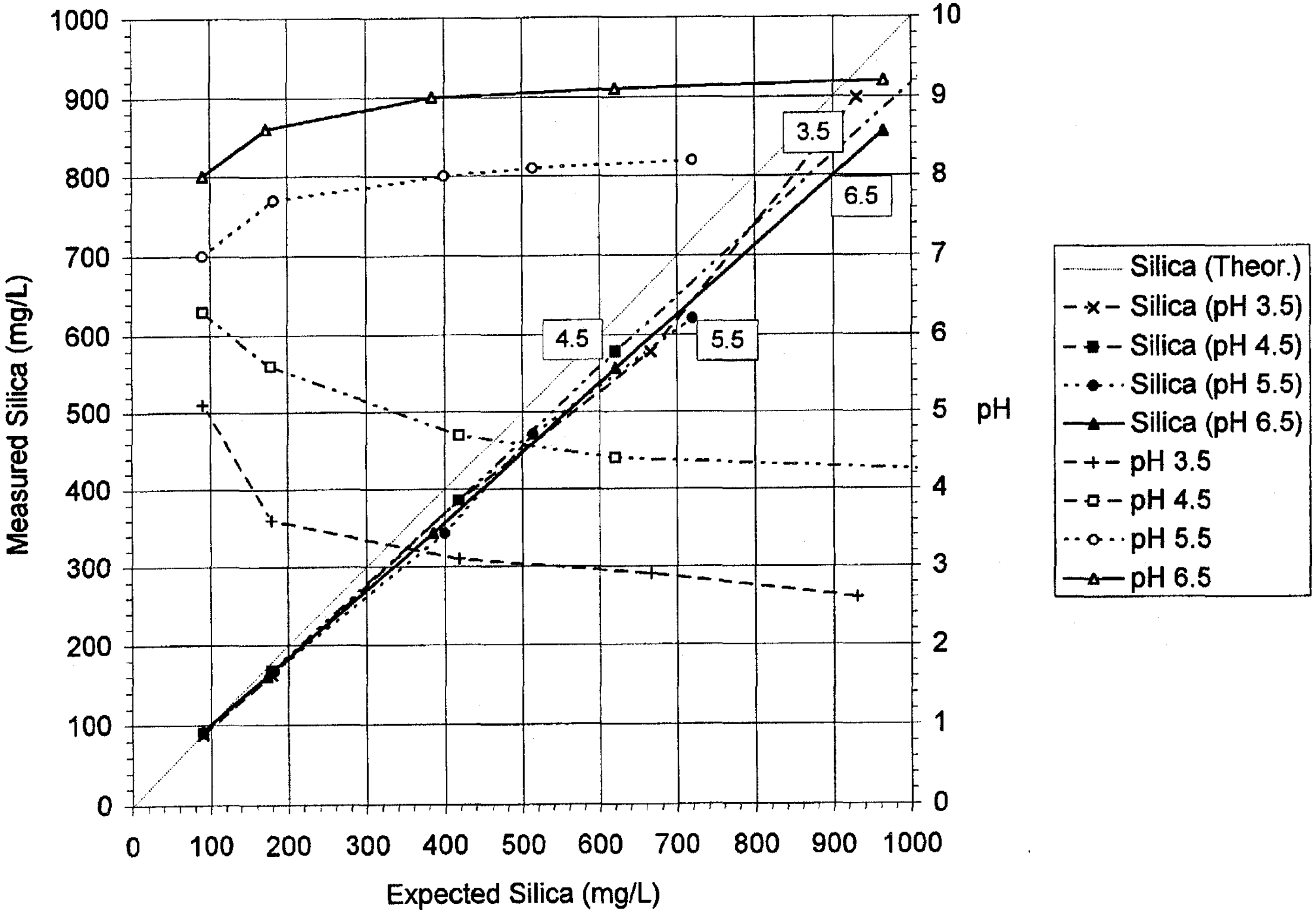

Figure 25. Effect of Oxalate on the Solubility of Silica in Water.
Oxalate:Silica MR = 0.44. Initial pHs (3.5), (4.5), (5.5), (6.5).

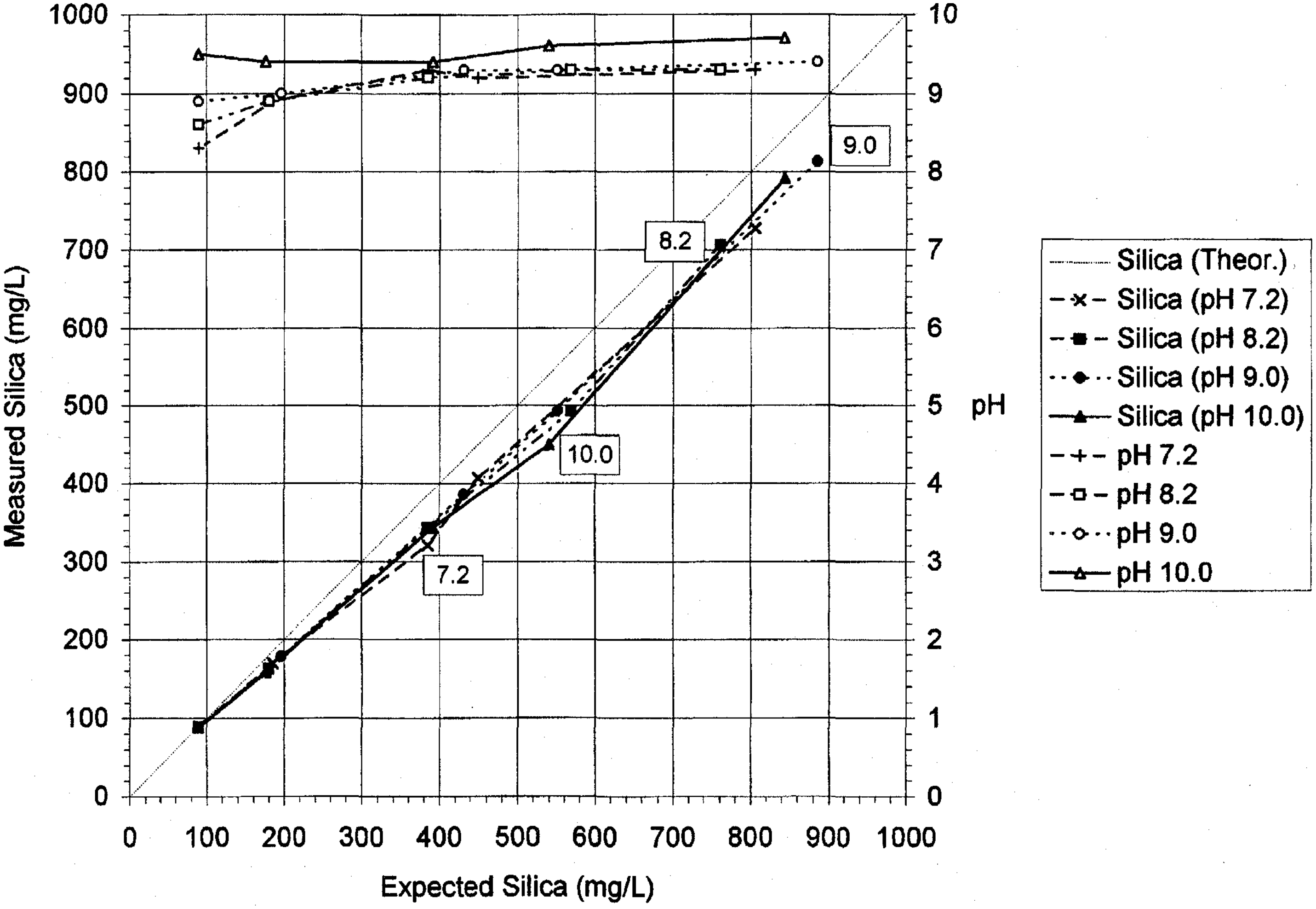

Figure 26. Effect of Oxalate on the Solubility of Silica in Water. Oxalate:Silica MR = 0.44. Initial pHs (7.2), (8.2), (9.0), (10.0).

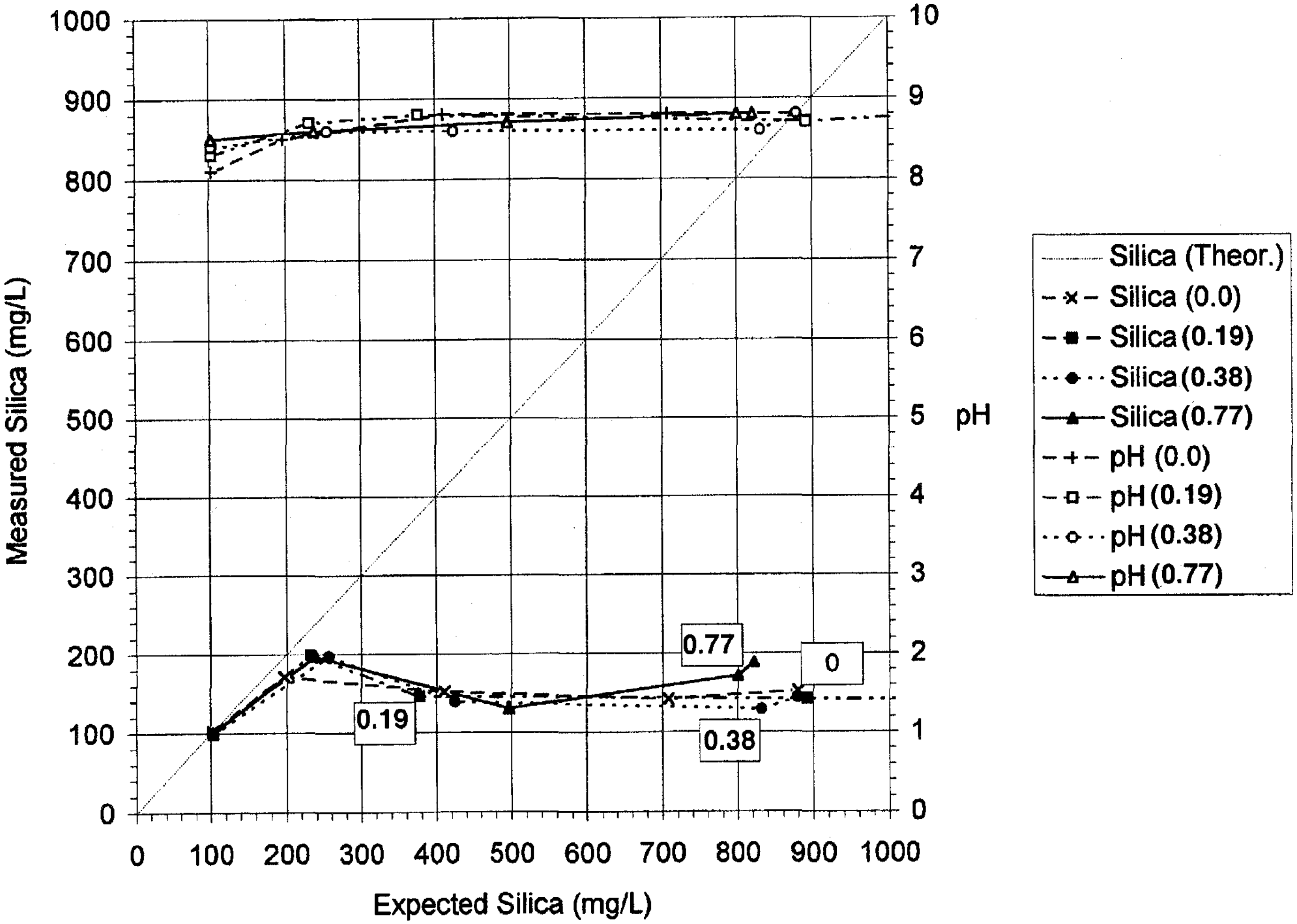

Figure 27. Effect of Oxalate on the Solubility of Silica in Water.
Calcium:Oxalate MR = 1.25. Oxalate:Silica MRs = (0), (0.19), (0.38), (0.77).

Table 17

Slope and Maximum SiO_2 Solubility Data for Sodium Oxalate in Water Evaporation Experiments Shown in Figure 24

Additive:SiO_2 Mole Ratio	**Slopes** (maximum expected SiO_2)			**Maximum Solubility** (maximum expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (169-871)	-----	-----	**167** (169)
0.11	**+0.8** (166-656)	-----	-----	**549** (656)
0.43	**+0.8** (219-753)	-----	-----	**642** (753)
1.7	**+1** (223-688)	-----	-----	**685** (688)

Table 18

Slope and Maximum SiO_2 Solubility Data for Sodium Oxalate in Water Evaporation Experiments Shown in Figures 25 and 26

Additive:SiO_2 Mole Ratio 0.44	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
pH 3.5	**+1** (179-931)	-----	-----	**899** (931)
pH 4.5	**+0.9** (178-1149)	-----	-----	**1049** (1149)
pH 5.5	**+0.8** (182-720)	-----	-----	**621** (720)
pH 6.5	**+0.9** (173-964)	-----	-----	**856** (964)
pH 7.2	**+0.9** (185-806)	-----	-----	**728** (806)
pH 8.2	**+0.9** (180-761)	-----	-----	**706** (761)
pH 9.0	**+0.9** (196-885)	-----	-----	**813** (885)
pH 10.0	**+1** (176-844)	-----	-----	**792** (844)

Table 19
Slope and Maximum SiO_2 Solubility Data for Sodium Oxalate in Water (with Calcium:Oxalate MR = 1.25) Evaporation Experiments Shown in Figure 27

Additive:SiO_2 Mole Ratio Sodium Oxalate	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (197-708)	-----	-----	**171** (197)
0.19	**-0.4** (233-378)	**0** (378-893)	-----	**199** (233)
0.38	**-0.4** (257-425)	**0** (425-880)	-----	**197** (257)
0.77	**-0.3** (239-497)	**+0.1** (497-800)	-----	**197** (239)

Effect of Sebacic Acid on Silica Solubility in Water[1]

The effect of sebacate ion $COO^-(CH_2)_8COO^-$, a ten-carbon linear dicarboxylic acid, on the solubility of silica in LANL water is shown in Figure 28. The sebacate shows rather small and uncertain effects on solubility. Such effects are typical of supersaturation.

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[1] See Appendix N, Tables 77N–80N for data.

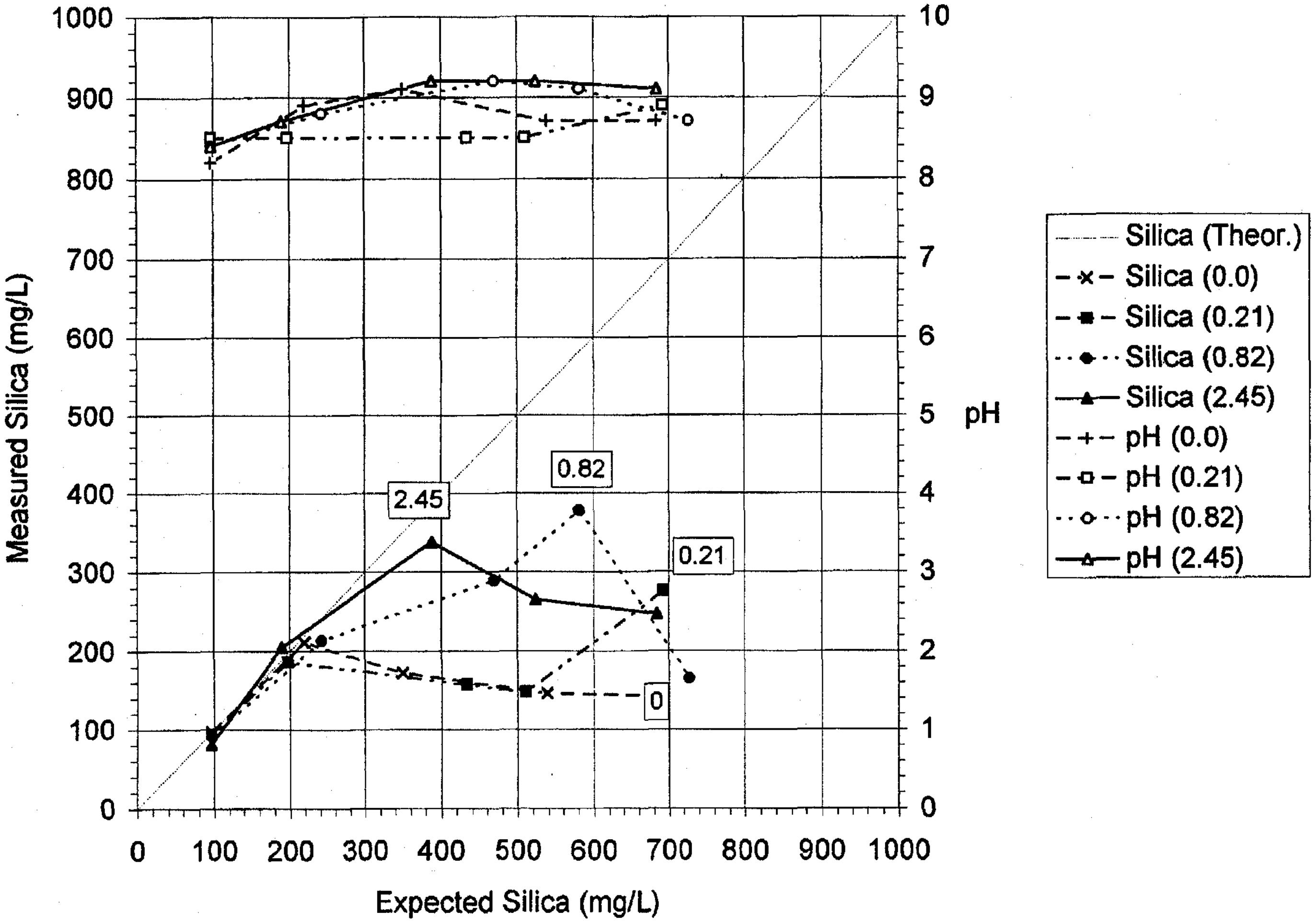

Figure 28. Effect of Sebacic on the Solubility of Silica in Water.
Sebacic:Silica MRs = (0), (0.21), (0.82), (2.45).

Table 20
Slope and Maximum SiO_2 Solubility Data for Sebacic Acid in Water Evaporation Experiments Shown in Figure 28

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.2** (220-539)	-----	-----	**211** (220)
0.21	**-0.1** (198-511)	**+0.7** (511-693)	-----	**276** (693)
0.82	**+0.5** (243-582)	**-1.5** (582-728)	-----	**377** (582)
2.45	**+0.7** (190-388)	**-0.3** (388-685)	-----	**338** (388)

Effect of Maleic Acid on Silica Solubility in Water[1]

The effect of maleate ion, $^{-}HOOCHC{=}CHCOOH^{-}$, on the solubility of silica in LANL water is shown in Figure 29. This acid represents the class of conjugated (unsaturated) linear dicarboxylic acids. The MRs of maleate to silica added were 0.1, 0.4, and 1.6.

The curves representing the MR 0.4 and 1.6 additions show a definite enhancement of supersaturation. Presumably, higher mole ratio additions would have greater effect.

It is surmised that for both of these experiments, MR 0.4 and 1.6, the silica beyond the first inflection point is in a meta-stable or supersaturated condition.

The line representing the MR 0.1 solution shows the behavior of a control run.

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[1] See Appendix N, Tables 81N–84N for data.

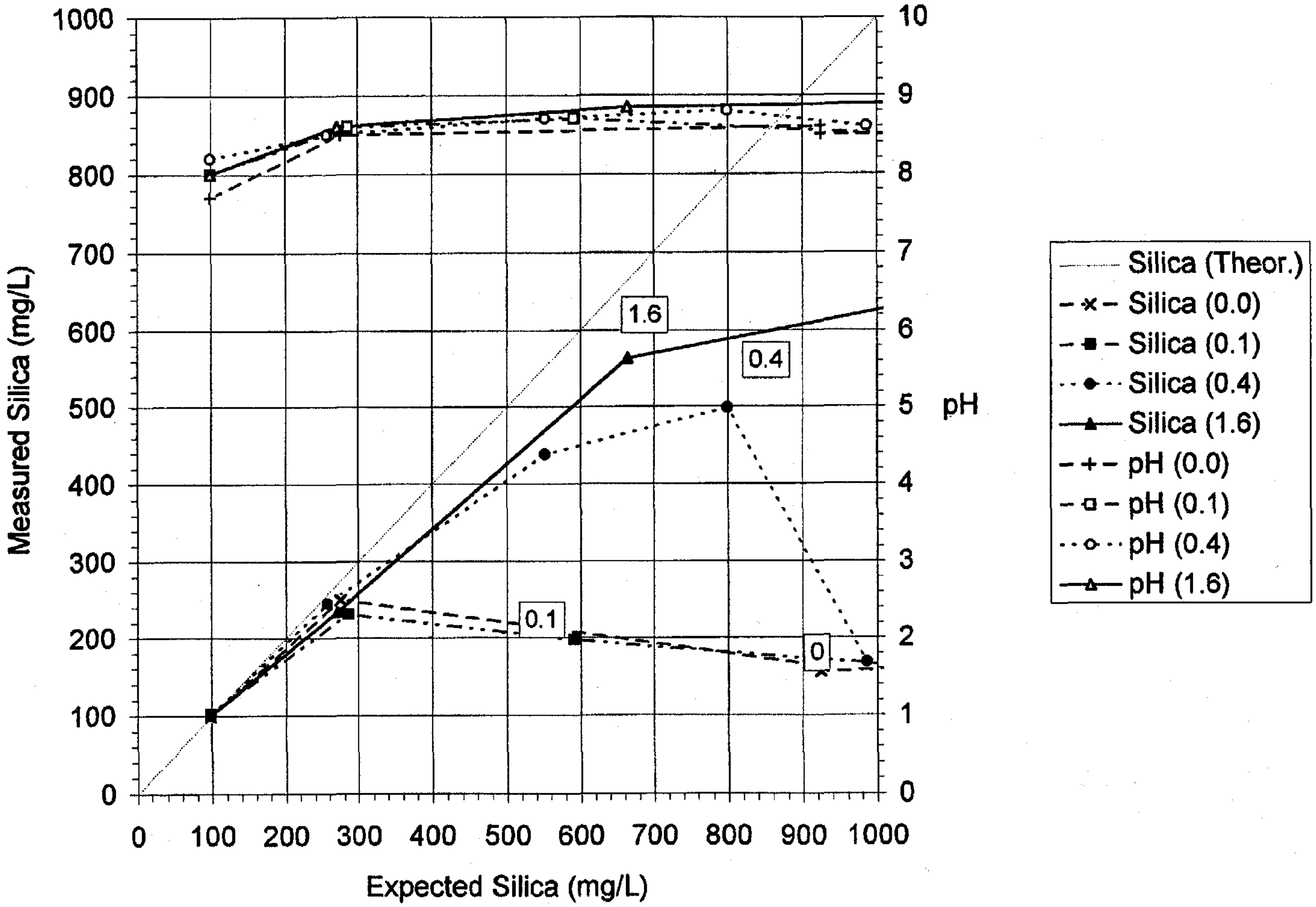

Figure 29. Effect of Maleate on the Solubility of Silica in Water.
Maleic:Silica MRs = (0), (0.1), (0.4), (1.6).

Table 21
Slope and Maximum SiO_2 Solubility Data for Maleic Acid in Water Evaporation Experiments Shown in Figure 29

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.15** (275-924)	-----	-----	**250** (275)
0.1	**-0.11** (286-592)	-----	-----	**231** (286)
0.4	**+0.65** (257-553)	**+0.24** (553-799)	**-1.77** (799-986)	**498** (799)
1.6	**+0.83** (271-665)	**+0.19** (665-1076)	**-6.19** (1076-1138)	**639** (1076)

Effect of Citric Acid on Silica Solubility in Water[1]

Citric acid, 2-hydroxy-1,2,3-propane tricarboxylic acid, is a good complexer of the hydroxy-acid type and may be considered to be typical of its class. Figure 30 shows the solubilities of silica in the presence of citrate. The MRs of citrate to silica added were 0.21, 0.83, and 2.48.

Figure 30 shows all three MR additions of citrate were effective solubilizers of silica. The MR 2.48 run had the least solubilizing effect on silica.

There is an unexpected inflection point in the curves in the 200 to 300 mg/L expected silica range. Essentially all of the calcium and magnesium remained in solution at all concentration factors with citrate addition (see Appendix N).

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[1] See Appendix N, Tables 85N–88N for data.

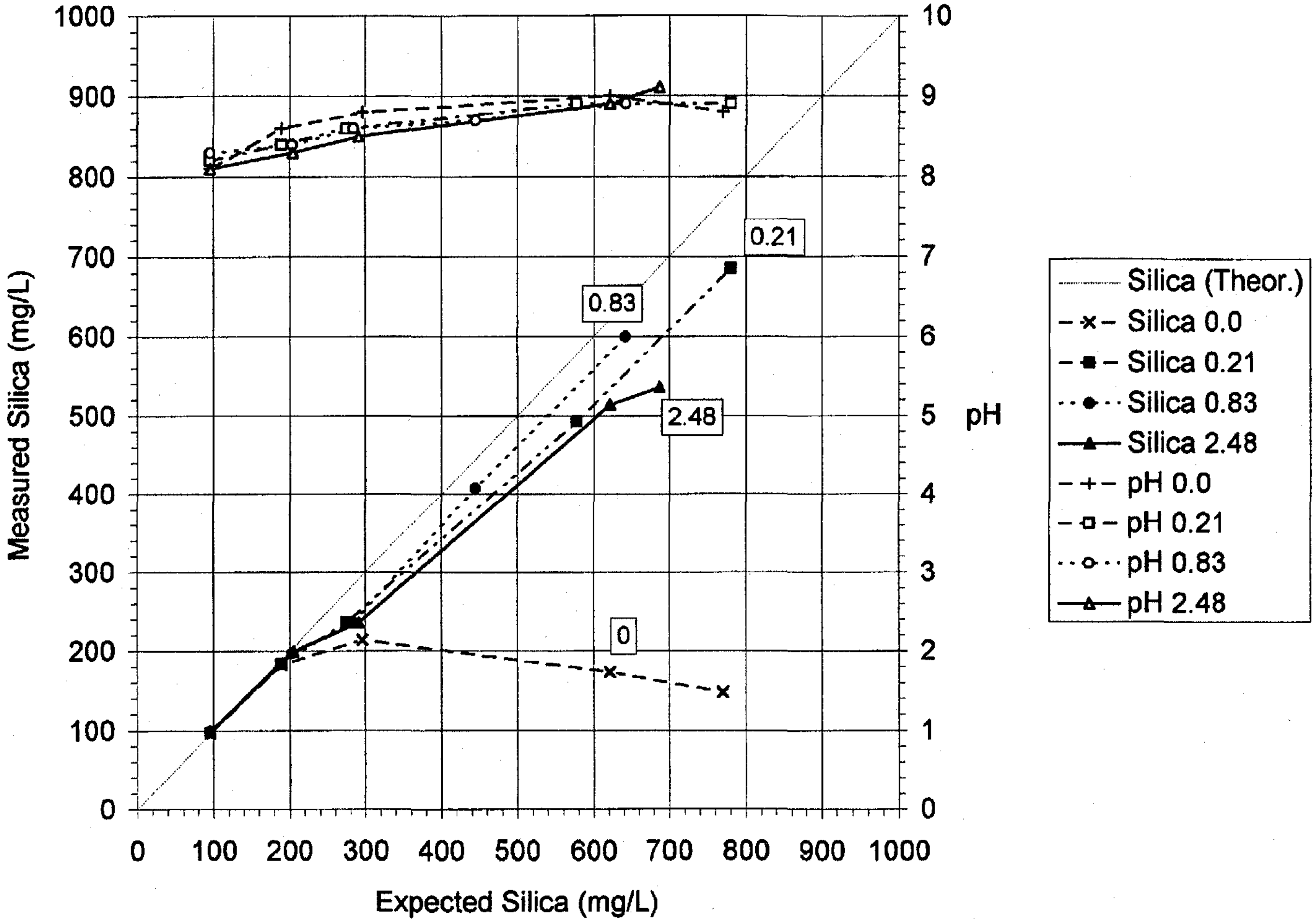

Figure 30. Effect of Citrate on the Solubility of Silica in Water.
Citrate:Silica MRs = (0), (0.21), (0.83), (2.48).

Table 22
Slope and Maximum SiO_2 Solubility Data for Citric Acid in Water Evaporation Experiments Shown in Figure 30

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**+0.3** (189-296)	**-0.1** (296-770)	-----	**214** (296)
0.21	**+0.6** (190-275)	**+0.9** (275-781)	-----	**685** (781)
0.83	**+0.5** (203-285)	**+1** (285-642)	-----	**599** (642)
2.48	**+0.4** (204-292)	**+0.8** (292-688)	-----	**535** (688)

Effect of EDTA on Silica Solubility in Water[1]

Ethylenediaminetetraacetic acid (EDTA) is a tetrabasic acid, also a tertiary amino acid. EDTA is a powerful complexer of alkaline earth and transition metals. Figure 31 shows the solubilities of silica in the presence of EDTA. The MRs of EDTA to silica added were 0.08, 0.4, and 0.8.

All three mole ratios of added EDTA exhibited a limiting effect on solubility between 240-380 mg/L of expected silica, similar to that seen in the citric acid experiment. In this region the slopes of the curves flattened. Above 380 mg/L the slopes of the MR 0.08, 0.4, and 0.8 runs increased to +0.65, +1.05, and +1.00, respectively. Very little difference between the effect of MR 0.4 addition and the MR 0.8 addition of EDTA was evident.

At an expected SiO_2 of 800 mg/L for MR 0.08 a supersaturation effect is evident. The calcium and magnesium analyses show substantial retention of both in the MR 0.08 solution and practically complete retention in the MR 0.4 and 0.8 solutions. A complexing mechanism seems to be operating with the calcium and magnesium and possibly with the silica in both the citric acid and EDTA solutions. The flattening effect

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[1] See Appendix N, Tables 89N–92N for data.

between 240 and 380 mg/L expected might indicate some compound formation, followed by a curve that seems to be the solubility of a new compound or phase.

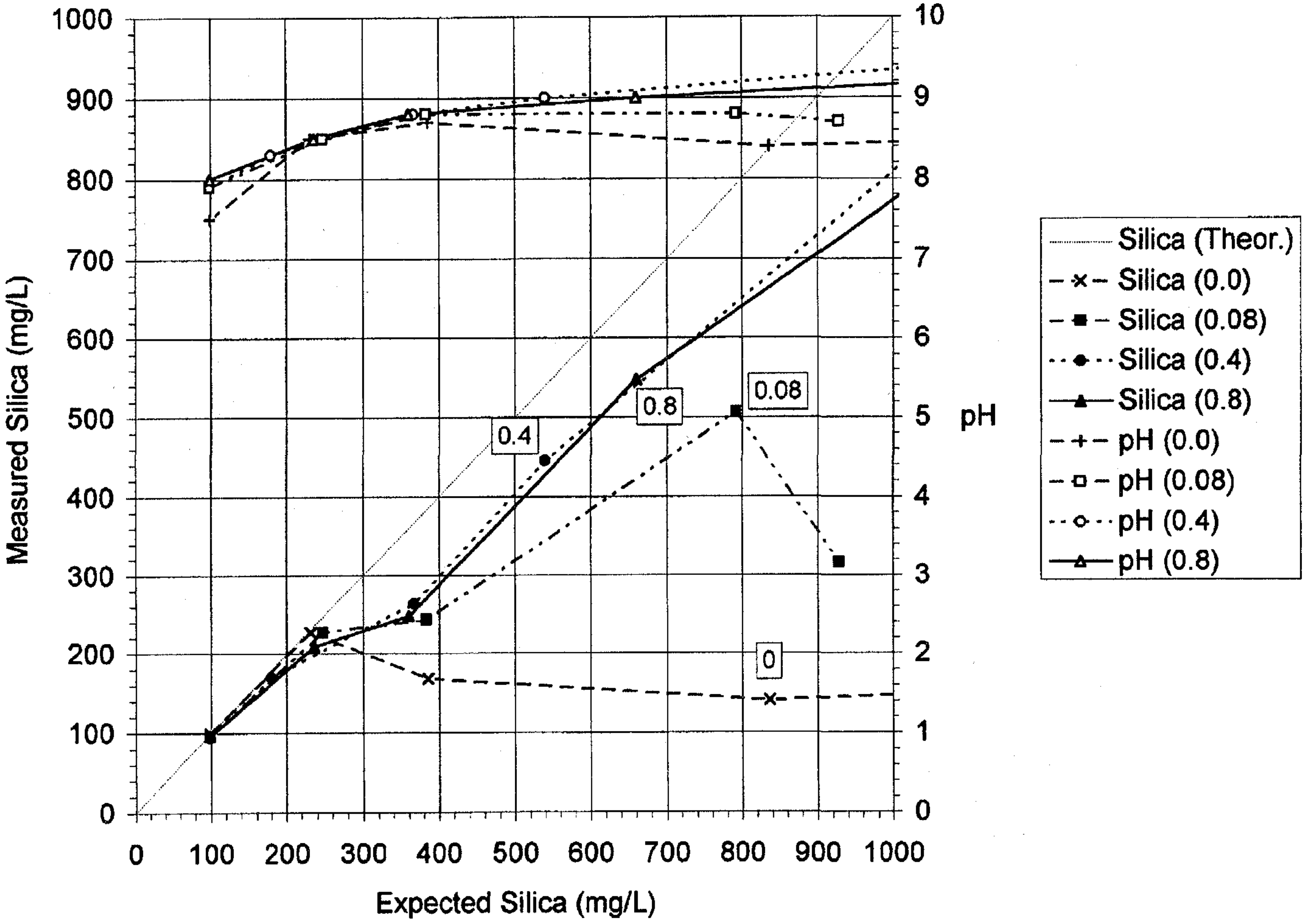

Figure 31. Effect of EDTA on the Solubility of Silica in Water.
EDTA:Silica MRs = (0), (0.08), (0.4), (0.8).

Table 23
Slope and Maximum SiO_2 Solubility Data for EDTA in Water Evaporation Experiments Shown in Figure 31

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.4** (231-386)	**-0.1** (386-837)	-----	**227** (231)
0.08	**+0.1** (248-383)	**+0.7** (383-792)	**-1.4** (792-928)	**507** (792)
0.4	**+0.4** (180-367)	**+1.1** (367-540)	**+0.8** (540-1080)	**871** (1080)
0.8	**+0.3** (236-360)	**+1** (360-660)	**+0.7** (660-1320)	**984** (1320)

Effect of o-Phthalic Acid on Silica Solubility in Water[1]

Figure 32 shows the effect of o-phthalate ion, 1,2-benzenedicarboxlic acid, on the solubility of silica in LANL water. The MRs of ortho-phthalic acid to silica added were 0.1, 0.4, and 1.6.

A commodity chemical, o-phthalate, demonstrated a strong solubilizing effect on silica in the MR 1.6 run. This MR of o-phthalate ion shows a fairly straight-line solubility curve (slope = +0.70) with no maximum limiting concentration up to an expected silica concentration of 750 mg/L.

The MR 0.4 solution closely follows the control line up to 425 mg/L expected silica and then exhibits a strong resolubilization effect up to 418 mg/L of measured silica. The high measured silica solubility in this run occurs at the same expected silica concentrations where other "anomalous" solubilities occurred. These other "anomalous" solubilities and their causes were discussed in the section describing the effect of sodium thiocyanate on silica solubility and will be discussed again later. The MR 0.1 solution shows similar behavior to that of the control run.

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[1] See Appendix N, Tables 93N–96N for data.

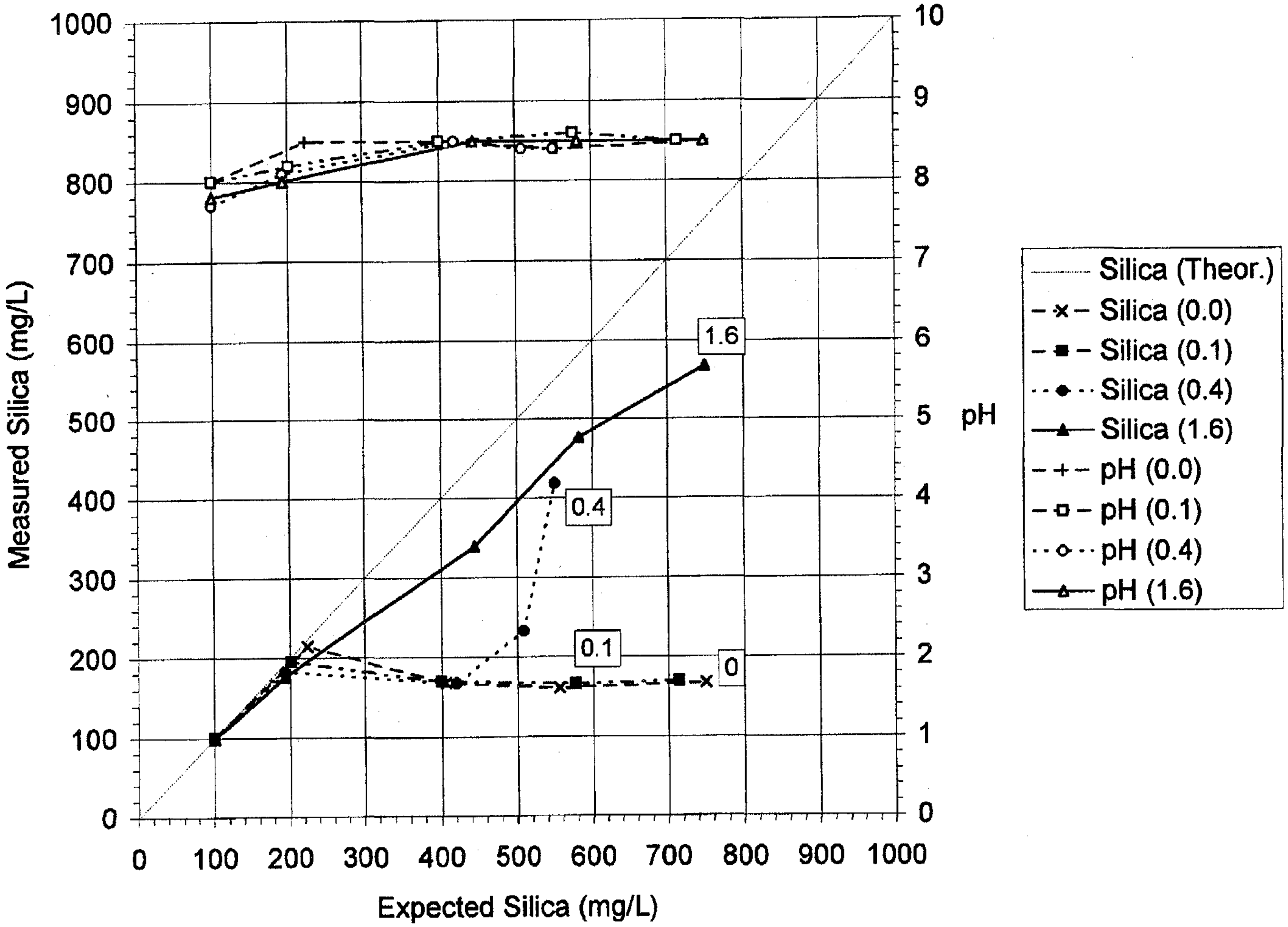

Figure 32. Effect of o-Phthalate on the Solubility of Silica in Water.
o-Phthalate:Silica MRs = (0), (0.1), (0.4), (1.6).

Table 24
Slope and Maximum SiO_2 Solubility Data for o-Phthalic Acid in Water Evaporation Experiments Shown in Figure 32

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.3** (224-405)	**0** (405-750)	-----	**214** (224)
0.1	**-0.1** (201-400)	**0** (400-714)	-----	**195** (201)
0.4	**-0.1** (194-420)	**+0.7** (420-508)	**+4.4** (508-550)	**418** (550)
1.6	**+0.7** (194-750)	-----	-----	**567** (750)

Effect of p-Phthalic Acid on Silica Solubility in Water[1]

Figure 33 shows the effect of p-phthalate ion on the solubility of silica in LANL water. The p-Phthalic acid, para- or 1,4-benzenedicarboxylic acid, has little solubility in water. It was made up as a sodium salt solution and added to the bulk of the tap water for the evaporation runs.

The MR 2.64 solution shows a slope of approximately 1.0 up to 960 mg/L of expected silica. The MR 0.88 curve is also a straight line with a slope of +0.8 and no limit within the limits of the experiment (see Appendix N). The MR 0.22 line follows the control curve to about 385 mg/L expected silica, then shows a high value of 385 mg/L at expected silica concentration of 562 mg/L. This "resolubilization" may be real. This effect may be similar to resolubilization effects noted in other runs at similar expected silica concentrations. This effect is a definite supersaturation and p-phthalate seems to be a good supersaturating agent for silica.

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[1] See Appendix N, Tables 97N–100N for data.

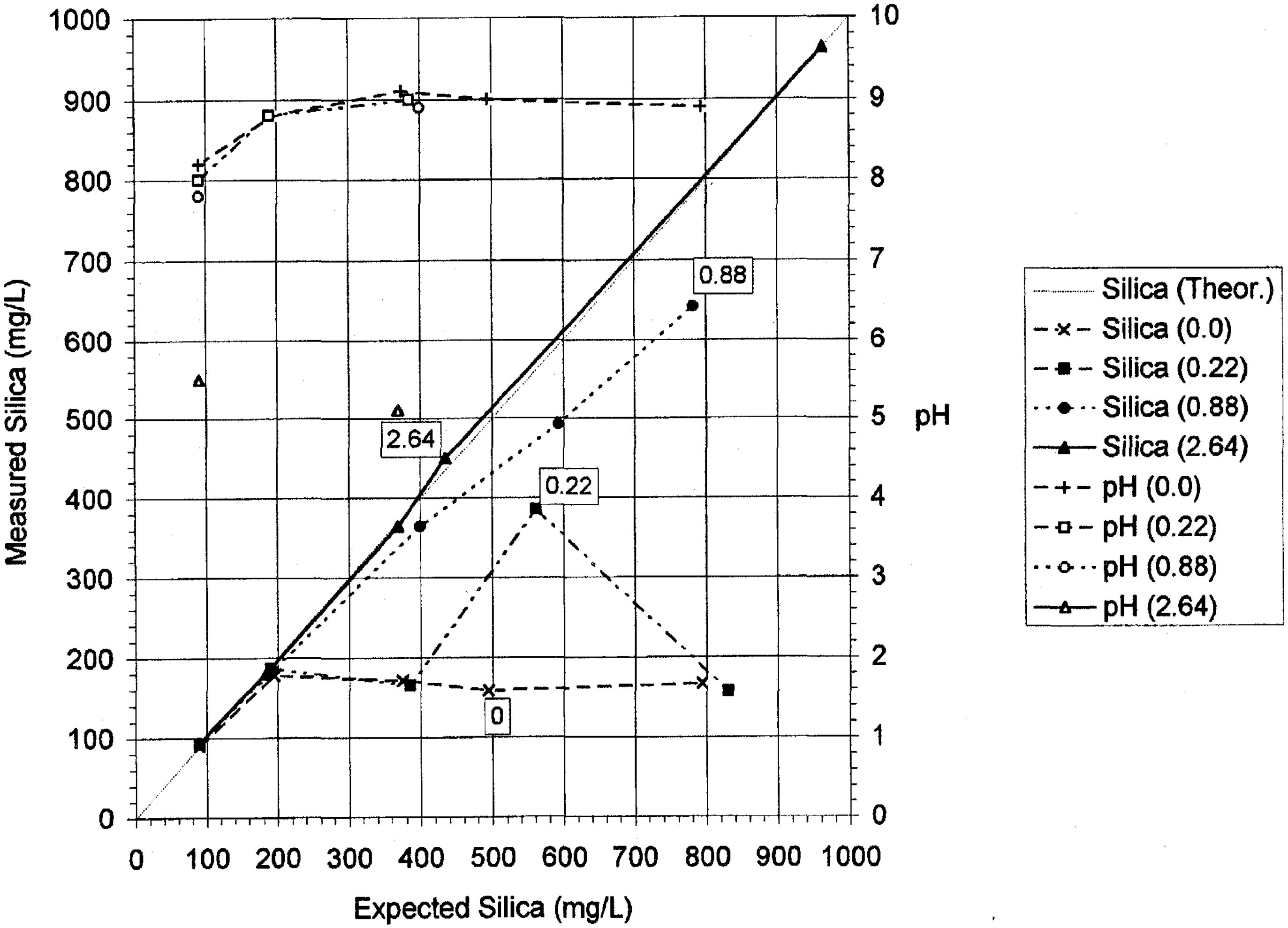

Figure 33. Effect of p-Phthalate on the Solubility of Silica in Water.
p-Phthalate:Silica MRs = (0), (0.22), (0.88), (2.64).

Table 25
Slope and Maximum SiO_2 Solubility Data for p-Phthalic Acid in Water Evaporation Experiments Shown in Figure 33

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (195-793)	-----	-----	**178**
0.22	**-0.1** (190-385)	**+1.2** (385-562)	**-0.9** (562-830)	**385** (562)
0.88	**+0.8** (186-782)	-----	-----	**642** (782)
2.64	**+1** (183-963)	-----	-----	**963** (963)

Effect of Catechol on Silica Solubility in Water[1]

The effect of polyhydroxyphenolic compounds on silica solubility was investigated with additions of catechol (1,2-hydroxybenzene), pyrogallol, and phloroglucinol. Figure 34 shows the effect of various mole ratios of catechol. The MRs of catechol to silica added were 0.09, 0.46, and 1.84.

Figure 34 shows a strong effect of catechol on silica solubility in the MR 0.46 and 1.84 solutions. The slopes of these two curves indicate that nearly all of the silica is remaining in solution up to expected silica concentrations of nearly 800 mg/L. The silica in neither of these evaporation runs had reached a solubility limit. The MR 0.09 solution shows behavior similar to that of a control run, but with slightly higher silica solubilities.

A chelation reaction between silica and catechol is possible. Catechol has long been reputed to be a complexer for aqueous silica.[15] The final pH for the MR 0.46 solution was 8.0 and for the MR 1.84 solution the final pH was 7.5.

---

[1] See Appendix N, Tables 101N–104N for data.

In the two solutions with the highest (MR 0.46 and 1.84) catechol contents, both calcium and magnesium measured concentrations were close to their expected values (see Appendix N). The catechol solutions discolor to a dark brown on exposure to air and light.

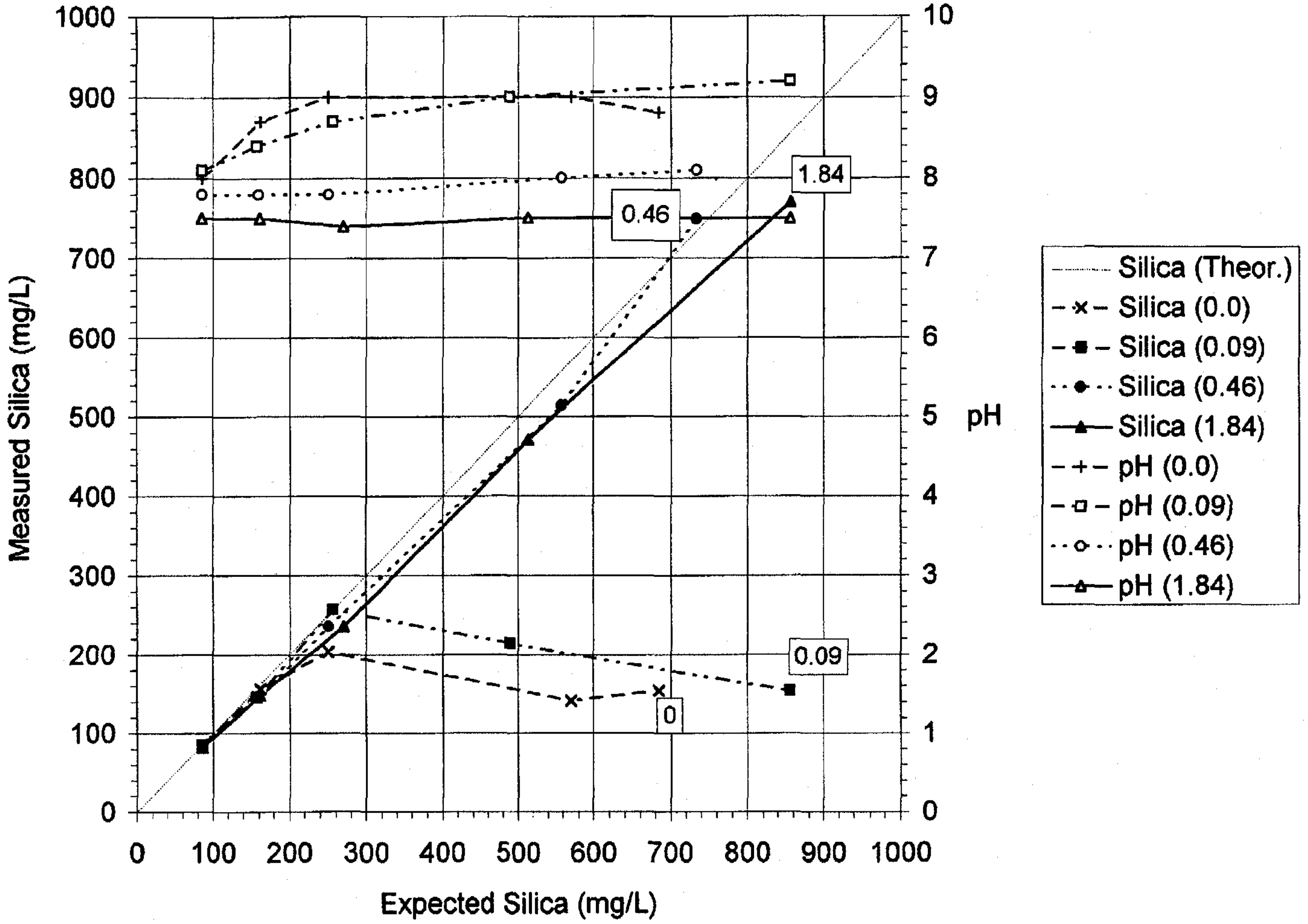

Figure 34. Effect of Catechol on the Solubility of Silica in Water.
Catechol:Silica MRs = (0), (0.09), (0.46), (1.84).

Table 26
Slope and Maximum SiO_2 Solubility Data for Catechol in Water Evaporation Experiments Shown in Figure 34

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.2** (251-571)	-----	-----	**203** (251)
0.09	**-0.2** (257-856)	-----	-----	**257** (257)
0.46	**+1.1** (251-734)	-----	-----	**749** (734)
1.84	**+0.9** (270-856)	-----	-----	**770** (856)

Effect of Pyrogallol on Silica Solubility in Water[1]

The effect of pyrogallol, 1,2,3-trihydroxybenzene, on the solubility of silica in tap water is shown in Figure 35. The MRs of pyrogallol to silica added were 0.09, 0.46, and 1.84.

The solution with MR 0.09 of pyrogallol to silica did not show an effect on silica solubility. The solution with MR 0.46, however, exhibited no limit on silica solubility. The MR 1.84 solution did not show a characteristic solubilizing effect. It is not certain whether this concentration shows a solubility limit for the silica or is a supersaturation effect.

Effect of pH variation was evidently significant. The final pH of the MR 1.84 solution dropped to 7.0. The pH of the other pyrogallol solutions and the control were in the pH 8.5 to 9.0 range.

Like all of the "developer" type phenolics, pyrogallol darkens on exposure to air in alkaline solutions. Some oily films formed on the solution surface, but no filtration difficulties were experienced.

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[1] See Appendix N, Tables 105N–108N for data.

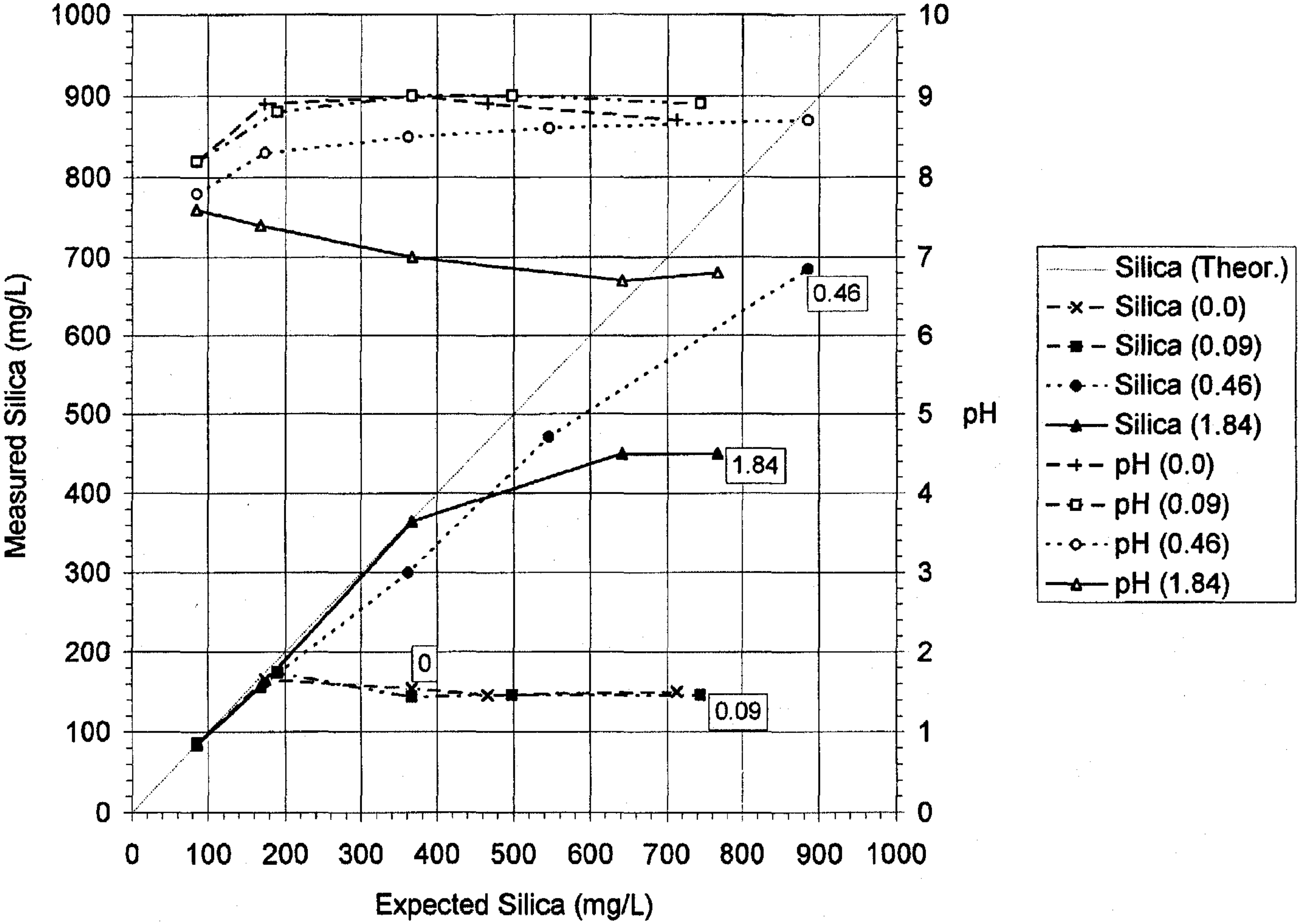

Figure 35. Effect of Pyrogallol on the Solubility of Silica in Water.
Pyrogallol:Silica MRs = (0), (0.09), (0.46), (1.84).

Table 27
Slope and Maximum SiO_2 Solubility Data for Pyrogallol in Water Evaporation Experiments Shown in Figure 35

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (174-713)	-----	-----	**165** (174)
0.09	**-0.1** (190-744)	-----	-----	**173** (190)
0.46	**+0.7** (174-886)	-----	-----	**685** (886)
1.84	**+1.1** (168-367)	**+0.2** (367-767)	-----	**449** (767)

Effect of Phloroglucinol on Silica Solubility in Water[1]

The effect of phloroglucinol, 1,3,5-trihydroxybenzene, on the solubility of silica may be seen in Figure 36. The MRs of phloroglucinol to silica added were 0.08, 0.42, and 1.7.

Phloroglucinol shows a considerable solvent power for silica. The MR 0.42 and 1.7 solutions had slopes of +0.81 and +0.75, respectively. No limit in solubility was found at these mole ratios up to expected silica concentrations of 800 mg/L. The MR 0.08 run also showed some supersaturation effect on silica to a maximum found silica concentration of 385 mg/L at an expected concentration of 595 mg/L.

As with the other phenolic compounds, catechol and pyrogallol, the phloroglucinol solution turned dark brown in appearance. It would be useful to determine the pH effect on these polyhydroxyphenolics on silica solubility. It would also be interesting to determine the effect of the presence of oxygen. We do not know whether it is the phloroglucinol or its oxidation products that exert such an appreciable effect on solubilization.

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[1] See Appendix N, Tables 109N–112N for data.

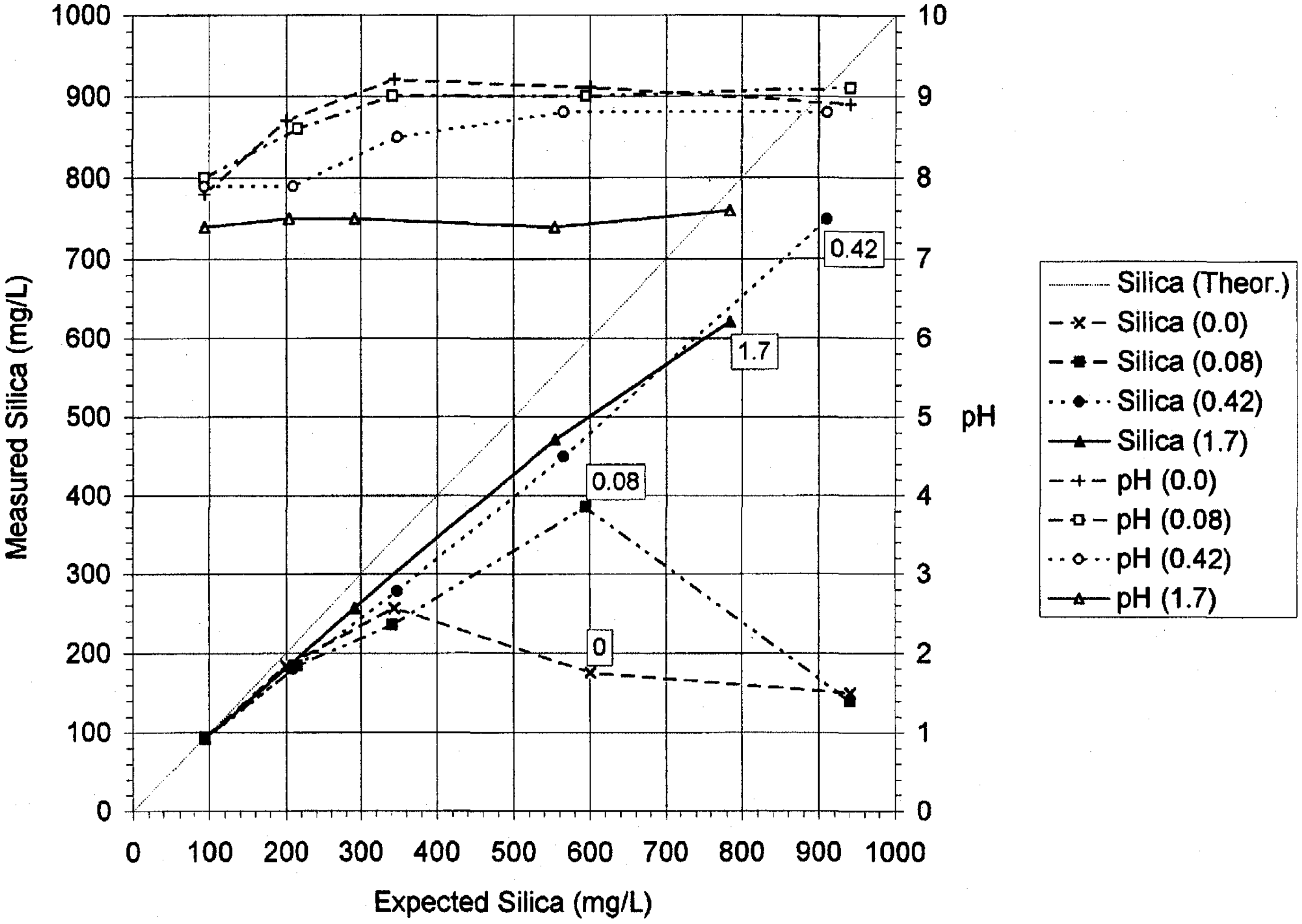

Figure 36. Effect of Phloroglucinol on the Solubility of Silica in Water.
Phloroglucinol:Silica MRs = (0), (0.08), (0.42), (1.7).

Table 28
Slope and Maximum SiO_2 Solubility Data for Phloroglucinol in Water Evaporation Experiments Shown in Figure 36

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**+0.5** (200-344)	**-0.3** (344-601)	**-0.1** (601-942)	**257** (344)
0.08	**+0.5** (216-595)	**-0.7** (595-942)	-----	**385** (595)
0.42	**+0.8** (210-911)	-----	-----	**749** (911)
1.7	**+0.8** (204-785)	-----	-----	**621** (785)

Effect of Sodium Salicylate on Silica Solubility in Water[1]

The effect of various mole ratios of salicylate is seen in Figure 37. This compound is 2-hydroxybenzoic monosodium salt. The MRs of sodium salicylate to silica added were 0.2, 0.81, and 3.23.

Figure 37 clearly indicates that sodium salicylate has no effect on silica solubility in LANL tap water. It duplicates the behavior of the control at all three mole ratio additions. The seemingly favorable structure of salicylate does not seem to chelate silica. Calcium and magnesium also are removed from solution, as in the control runs (see Appendix N).

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[1] See Appendix N, Tables 113N–116N for data.

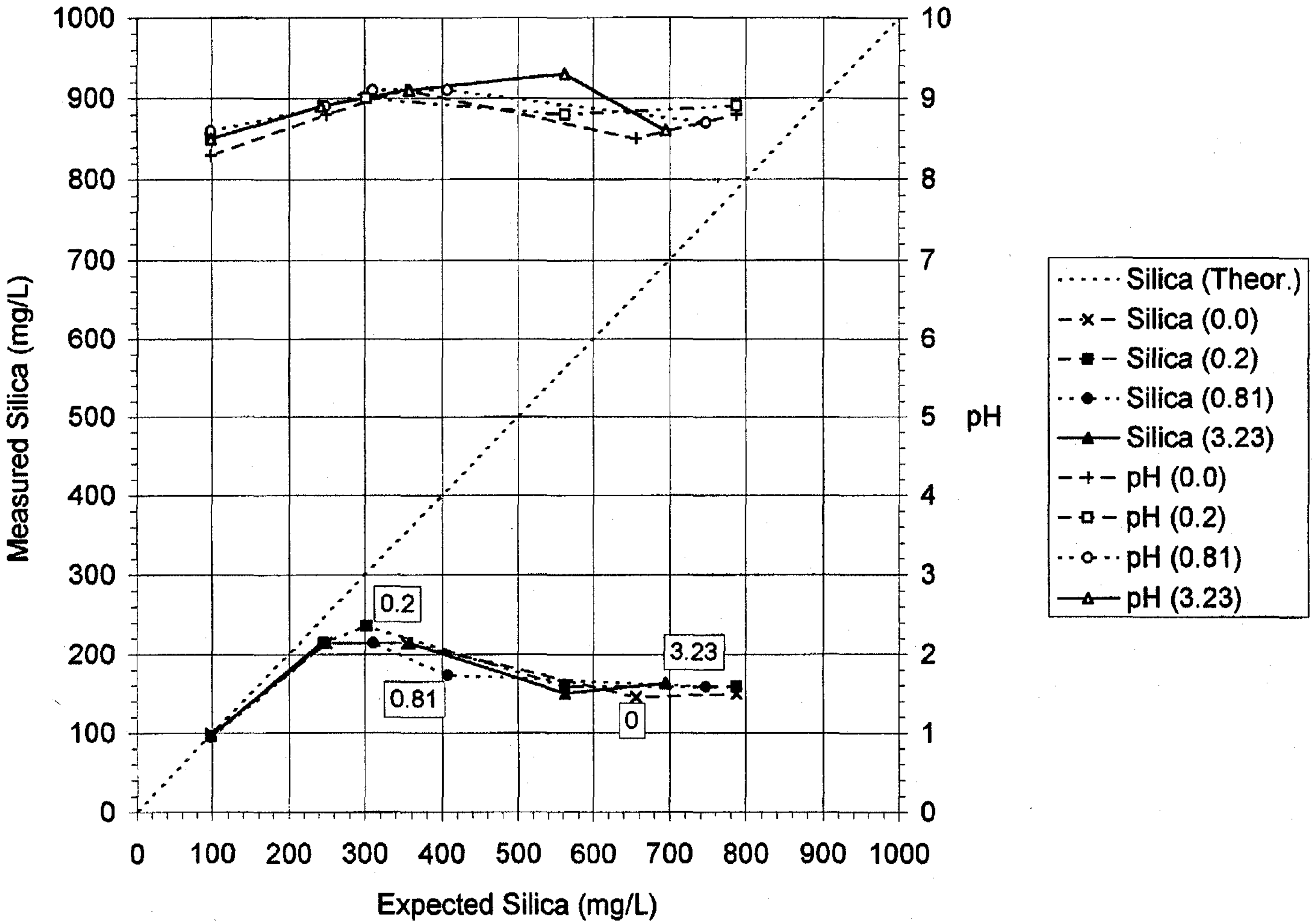

Figure 37. Effect of Salicylate on the Solubility of Silica in Water.
Salicylate:Silica MRs = (0), (0.2), (0.81), (3.23).

Table 29
Slope and Maximum SiO_2 Solubility Data for Sodium Salicylate in Water Evaporation Experiments Shown in Figure 37

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (250-354)	**-0.2** (354-656)	**0** (656-788)	**214** (250-354)
0.2	**+0.4** (246-303)	**-0.3** (303-563)	**0** (563-788)	**235** (303)
0.81	**0** (249-311)	**-0.4** (311-407)	**0** (407-748)	**214** (249-311)
3.23	**0** (243-358)	**-0.3** (358-563)	**+0.1** (563-695)	**214** (243-358)

Effect of p-Toluene Sulfonic Acid on Silica Solubility in Water[1]

The effect of various mole ratios of p-toluene sulfonic acid (p-TSA) is shown in Figure 38. This compound is 4-methylbenzene sulfonic acid. The MRs of p-toluene sulfonic acid to silica added were 0.09, 0.45, and 1.8.

Figure 38 shows that p-TSA, at a MR addition of 1.8, has an effect on silica solubility in LANL tap water. The solubility increases linearly with a slope of +0.71 to a measured silica value of 428 mg/L at an expected silica concentration of 554 mg/L. The MR 0.45 solution closely follows the control line up to 390 mg/L expected silica and then exhibits a supersaturating effect up to 342 mg/L of measured silica. The high measured silica solubility in this run occurs at the same expected silica concentrations where other anomalous solubilities occurred. At both concentrations, p-TSA behaves as a supersaturator. The MR 0.09 solution shows behavior similar to that of the control run.

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[1] See Appendix N, Tables 117N–120N for data.

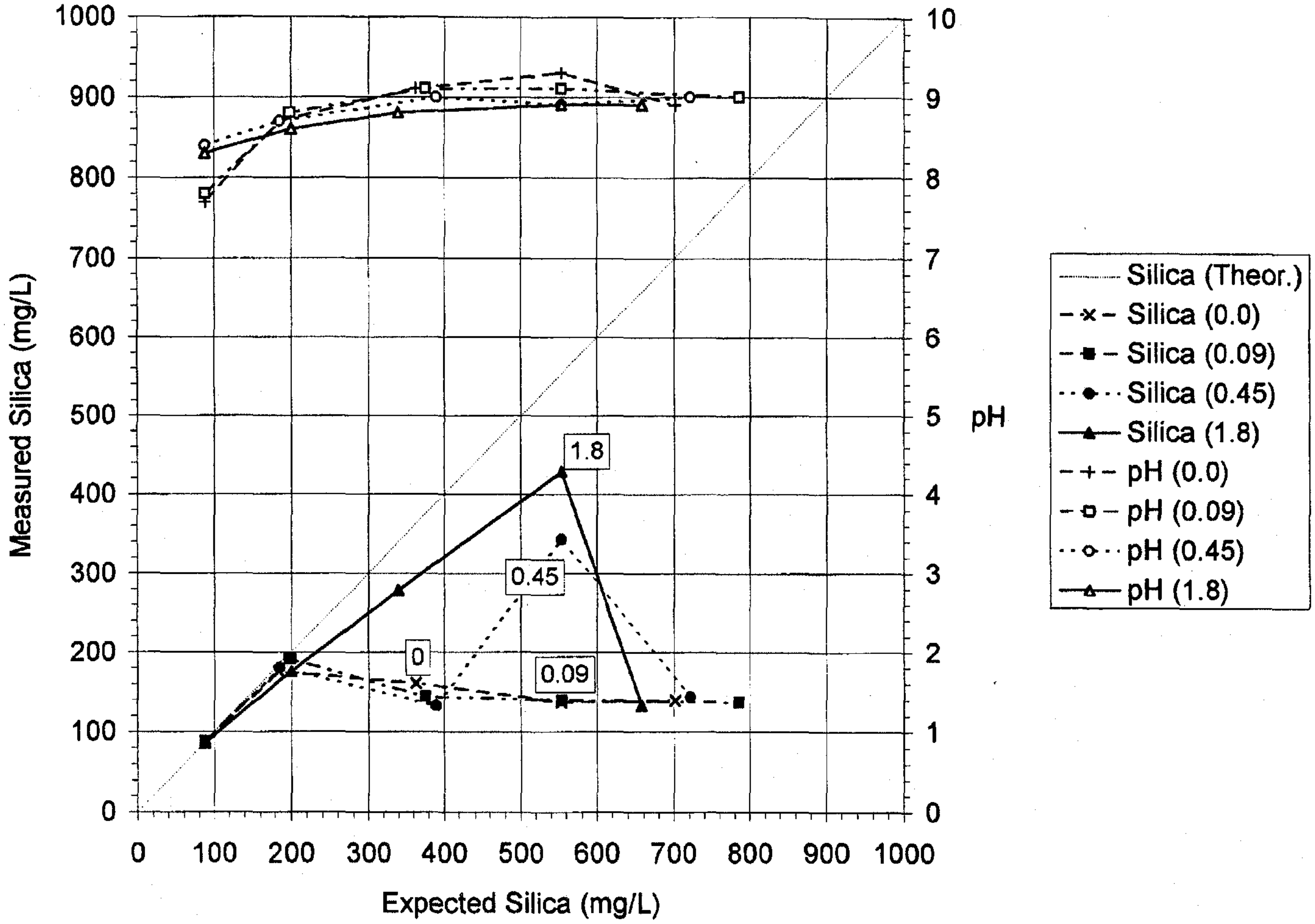

Figure 38. Effect of p -Toluene Sulfonate on the Solubility of Silica in Water.
p-Toluene Sulfonate:Silica MRs = (0), (0.09), (0.45), (1.8).

Table 30
Slope and Maximum SiO_2 Solubility Data for p-Toluene Sulfonic Acid in Water Evaporation Experiments Shown in Figure 38

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (185-554)	**0** (554-702)	-----	**176** (185)
0.09	**-0.3** (199-376)	**0** (376-786)	-----	**191** (199)
0.45	**-0.2** (186-390)	**+1.3** (390-554)	**-1.2** (554-721)	**342** (554)
1.8	**+0.7** (200-554)	**-2.8** (554-658)	-----	**428** (554)

Effect of Alkyl Naphthalene Sulfonic Acid on Silica Solubility in Water[1]

The effect of additions of alkyl naphthalene sulfonic acid (ANSA) on silica solubility in LANL tap water can be seen in Figure 39. This compound is 1,3-diisopropyl-7-naphthalene sulfonic acid. The MRs of ANSA to silica added were 0.03, 0.16, and 0.62.

Figure 39 shows that ANSA has no effect on silica solubility. It duplicates the behavior of the control at all three mole ratio additions. Calcium and magnesium are removed from solution, as in the control runs (see Appendix N, Tables 108N–111N).

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[1] See Appendix N, Tables 121N–124N for data.

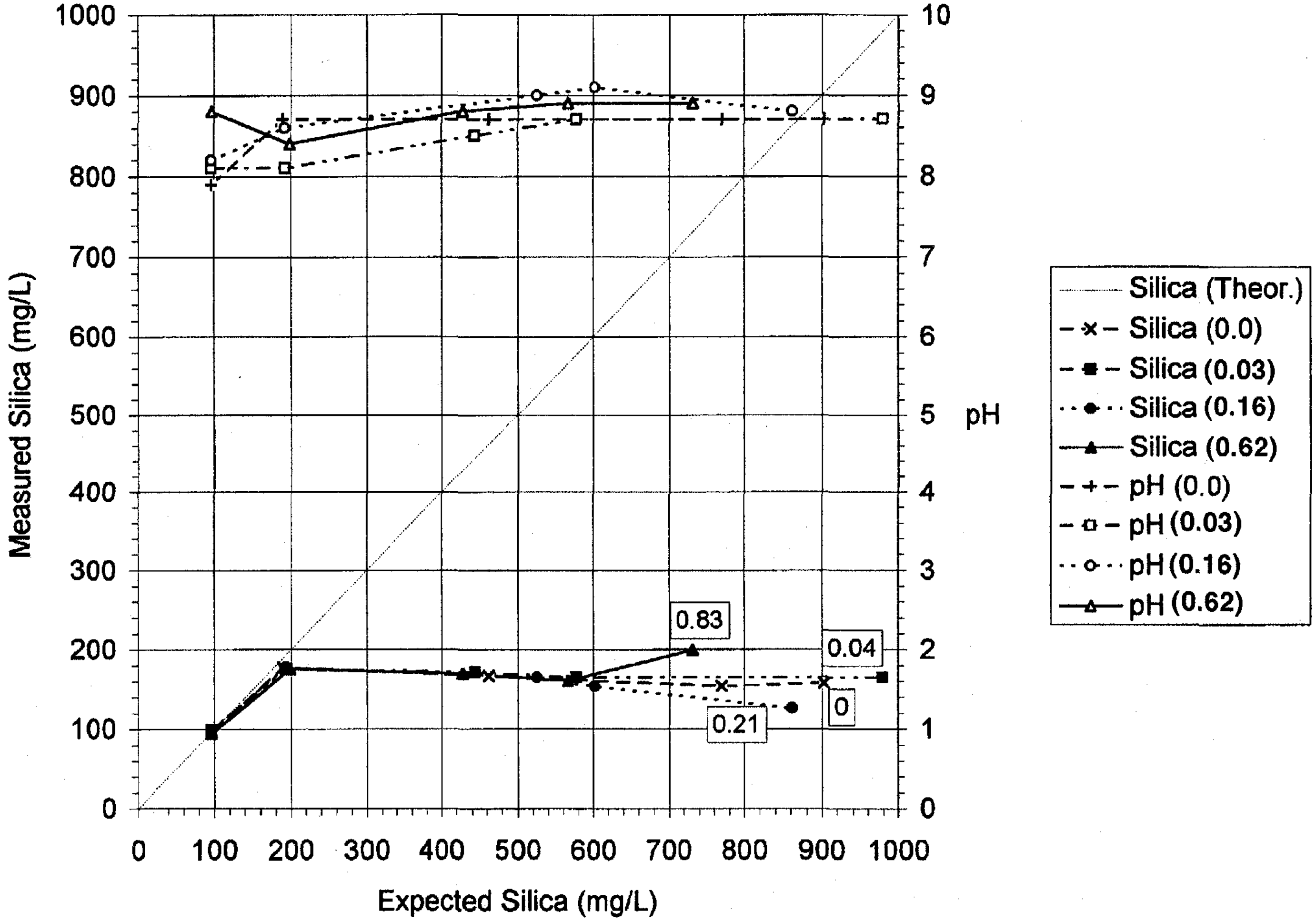

Figure 39. Effect of Alkyl Naphthalene Sulfonate on the Solubility of Silica in Water. Alkyl Naphthalene Sulfonate:Silica MRs = (0), (0.03), (0.16), (0.62).

Table 31
Slope and Maximum SiO_2 Solubility Data for Alkyl Naphthalene Sulfonic Acid in Water Evaporation Experiments Shown in Figure 39

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (189-770)	-----	-----	**178** (189)
0.04	**0** (193-578)	-----	-----	**176** (193)
0.21	**-0.1** (193-602)	-----	-----	**178** (193)
0.83	**0** (199-566)	-----	-----	**176** (199)

Effect of Tiron on Silica Solubility in Water[1]

The effect of addition of Tiron, 4,5-dihydroxy-1,3-benzene disulfonic acid disodium salt on silica solubility in LANL tap water may be seen in Figure 40. The MRs of Tiron to silica added were 0.017, 0.09, and 0.17. A second evaporation series was performed with Tiron to silica MRs equal to 0.13, 0.17, and 0.43. The results are shown in Figure 41.

The MR 0.017 run did not affect silica solubility. The silica solubility closely followed a control run as seen in Figure 40. The run at MR 0.09 showed a solubilizing effect up to 321 mg/L of measured silica at 381 mg/L expected silica, then shows what may be a solubility limit, then supersaturation. The results of an evaporation run with MR 0.13 Tiron to silica, seen in Figure 41, demonstrates this supersaturating effect on silica to continue to a measured silica concentration of 506 mg/L. Good reproducibility of the two MR 0.17 runs in Figures 40 and 41 are shown. The MR 0.17 solutions showed no solubility limit of silica even at expected silica values as high as 876 mg/L. A MR 0.43 solution of Tiron to silica was prepared and was found to be no more effective than the MR 0.17 solutions. Results of the 0.43 MR run are shown in Figure 41. This material seems to be a very good solubilizer for silica; whether it reacts with silica is open to question.

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[1] See Appendix N, Tables 125N–132N for data.

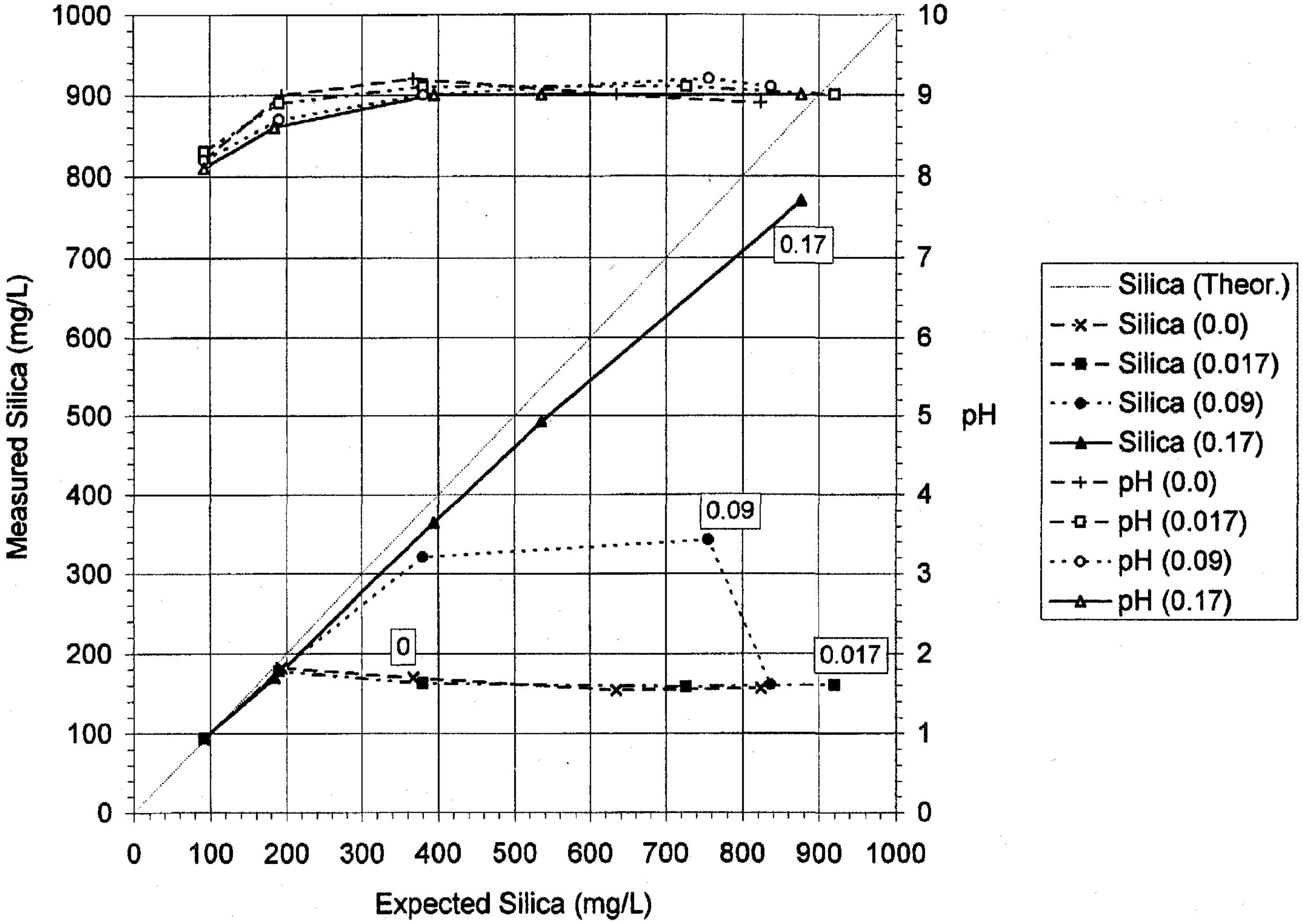

Figure 40. Effect of Tiron on the Solubility of Silica in Water.
Tiron:Silica MRs = (0), (0.017), (0.09), (0.17).

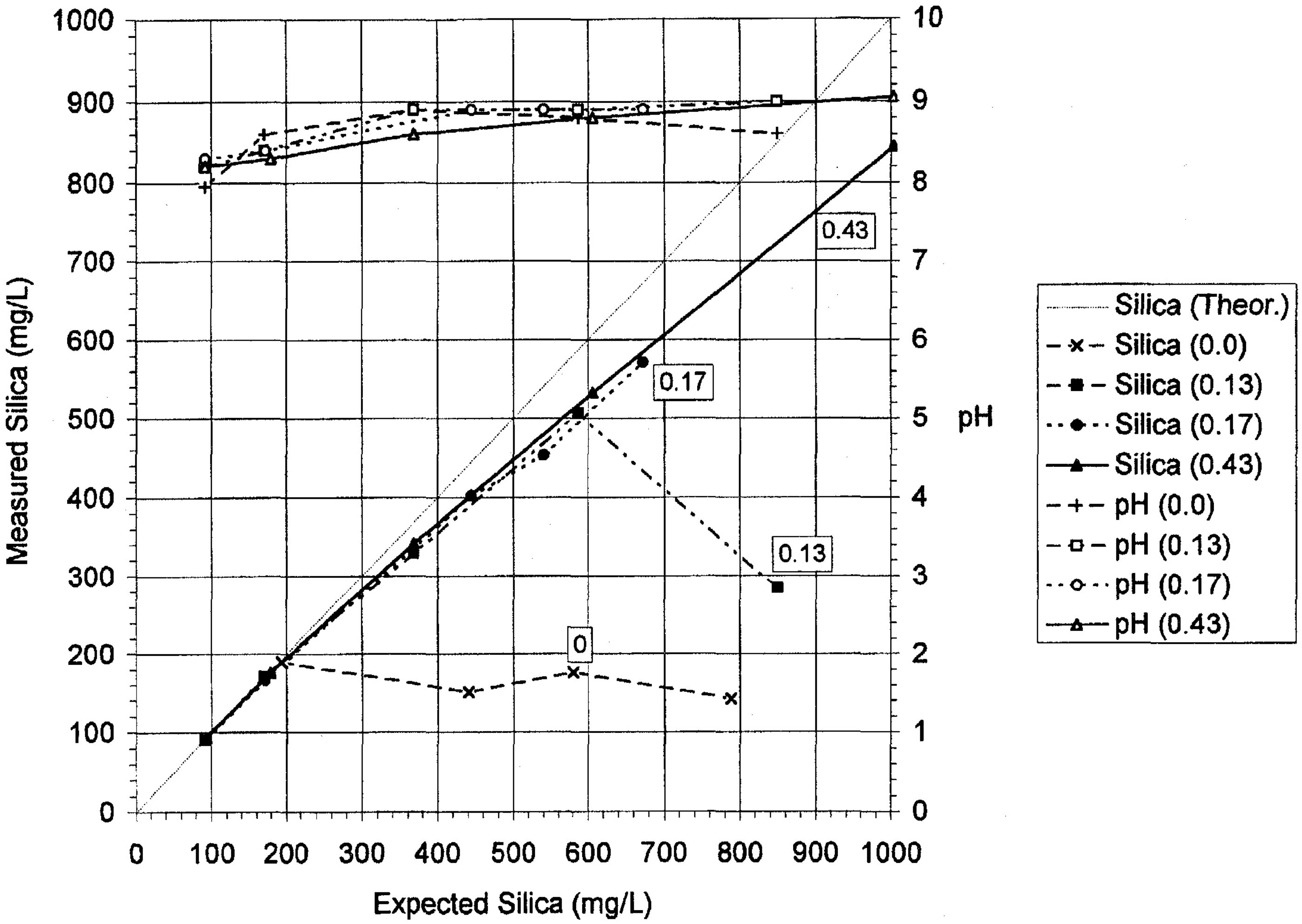

Figure 41. Effect of Tiron on the Solubility of Silica in Water.
Tiron:Silica MRs = (0), (0.13), (0.17), (0.43).

Table 32

Slope and Maximum SiO_2 Solubility Data for Tiron (disodium salt) in Water Evaporation Experiments Shown in Figure 40

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (194-824)	-----	-----	**182** (194)
0.017	**0** (190-920)	-----	-----	**178** (190)
0.09	**+0.8** (190-381)	**+0.1** (381-756)	**-2.2** (756-837)	**342** (756)
0.17	**+0.9** (184-876)	-----	-----	**770** (876)

Table 33

Slope and Maximum SiO_2 Solubility Data for Tiron (disodium salt) in Water Evaporation Experiments Shown in Figure 41

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (194-789)	-----	-----	**190** (194)
0.13	**+0.8** (170-587)	**-0.9** (587-849)	-----	**506** (587)
0.17	**+0.8** (173-673)	-----	-----	**571** (673)
0.43	**+0.8** (179-1004)	-----	-----	**844** (1004)

Effect of Lignosulfonates on Silica Solubility in Water

Lignosulfonates are water-soluble by-products of the sulfite paper industry and are excellent dispersants and, to some degree, complexers, of ions such as calcium and magnesium. Three different lignosulfonates were used in this experimental work: Kelig 32, Marasperse N-22, and Maracell XE. These materials were supplied to us through the courtesy of LignoTech USA, Rothschild, WI. The information given here on the chemistry of the substances was also furnished to us through the courtesy of LignoTech.[16]

The monomer unit for all three of the lignosulfonates is shown in Figure 42. The average molecular weight of the monomer is 185. Table 33 shows for each lignosulfonate material the average number of phenolic, sulfonate, and carboxylic functional groups per monomer unit. The same table also provides each compound's molecular weight and an average number of each functional group per molecule for each of the lignosulfonates.

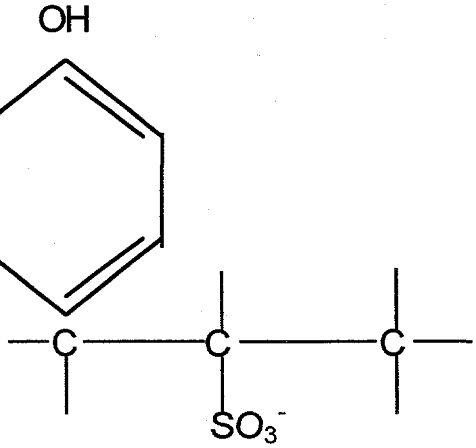

Figure 42. Monomer Unit for the Lignosulfonates:
Kelig 32, Marasperse N-22, and Maracell XE.

Table 34
Chemical Data on the Monomers and Molecules of the Lignosulfonate Materials

Liqnosulfonate	**Per Monomer Unit**		
	Phenol #	**Sulfonate** #	**Carboxyl** #
Kelig 32	1.0	0.8	0.3
Marasperse N-22	1.0	0.8	0.1
Maracell XE	1.0	0.55	0.02

Liqnosulfonate	**MW**	**Per Molecule**			
		Monomer #	**Phenol** #	**Sulfonate** #	**Carboxyl** #
Kelig 32	21,300	115	115	92	35
Marasperse N-22	34,500	186	186	149	19
Maracell XE	6,200	33	33	18	1

Effect of Kelig 32 on Silica Solubility in Water[1]

Figure 43 shows the effect of the lignosulfonate Kelig 32 on the solubility of silica in LANL tap water. Table 35 gives the mass of Kelig 32 added for each of the mole ratio additions, along with the mole ratios of the sulfonate reactive groups (RGR) to silica.

All three mole ratios of Kelig 32 show increased solubility of silica, as may be seen by comparing the curves with the control. The MR 0.03 and Kelig solution shows a solubility limit of the silica and a supersaturation effect. The MR 0.06 Kelig solution demonstrates a silica solubility limit with no supersaturation effect evident within the limits of the experiment. The highest MR 0.11 keeps the SiO_2 in solution to concentrations above 900 mg/L. The concentrations of Kelig 32 in solutions are quite high, due to the high molecular weight of the material. On the basis of mole ratios, Kelig 32 shows that it is a good solubilizer for silica. Magnesium and calcium are almost completely kept in solution when the silica is kept in solution.

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[1] See Appendix N, Tables 133N–136N for data.

In all probability, sulfonate groups in proximity to phenol hydroxyls account for the reactivity of this material. The reactivity of these sulfonated lignin products with silica and silica containing waters merits more detailed investigation.

Table 35
Actual Mole Ratio (MR) and Sulfonate (Reactive Group) Ratio (RGR)
Used with Kelig 32 in Water Experiments

Kelig 32		
Concentration in Solution (mg/L)	**MR**	**RGR (SO_3^-)**
0	0	0
915	0.03	2.6
1830	0.06	5.2
3660	0.11	10.4

MR = molar ratio of additive to silica
RGR (SO_3^-) = molar ratio of reactive sulfonate groups to silica

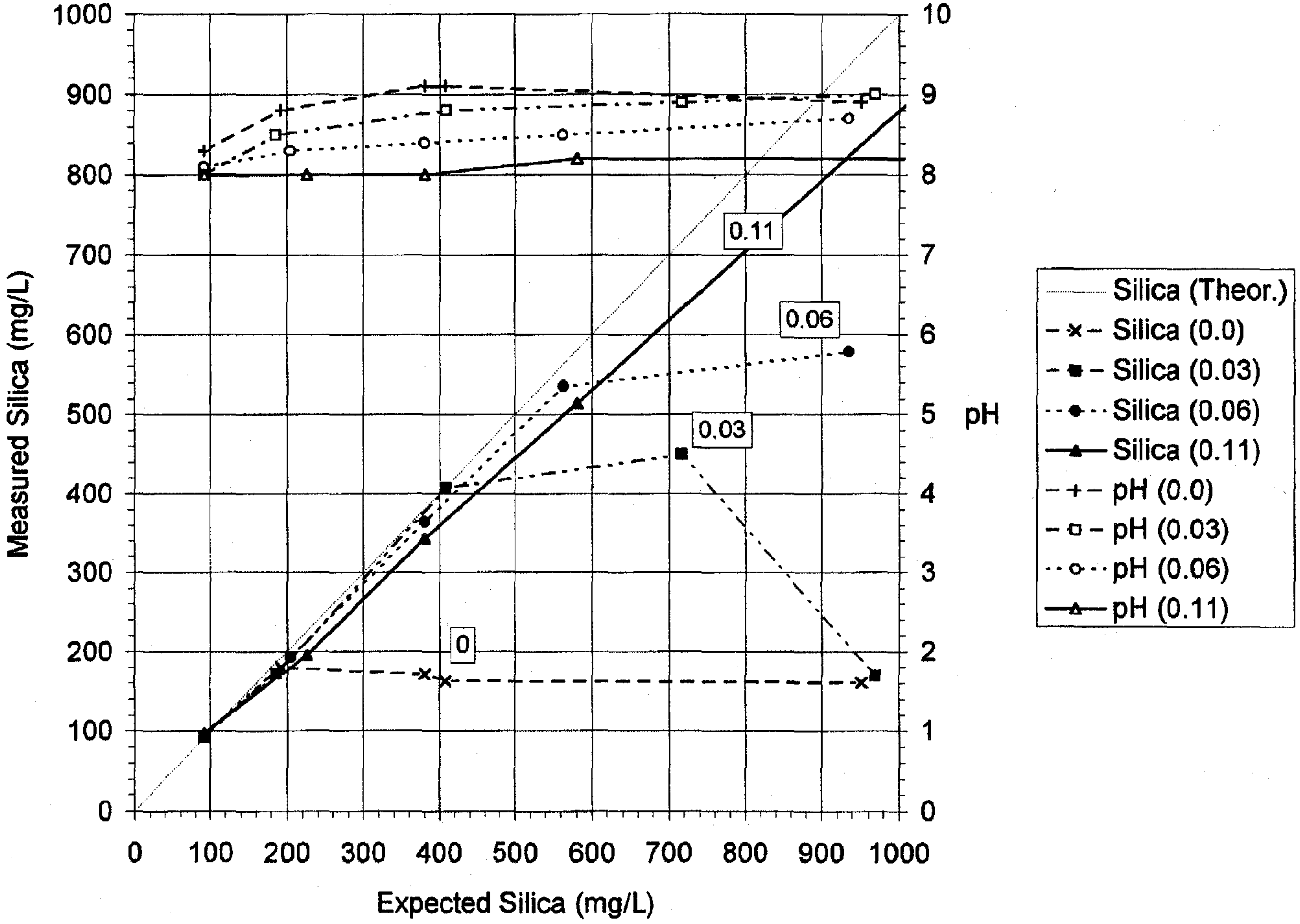

Figure 43. Effect of Kelig 32 on the Solubility of Silica in Water.
Kelig 32:Silica MRs = (0), (0.03), (0.06), (0.11).

Table 36
Slope and Maximum SiO_2 Solubility Data for Kelig 32 in Water Evaporation Experiments Shown in Figure 43

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (192-952)	**-----**	**-----**	**180** (192)
0.03	**+1.1** (187-409)	**+0.1** (409-717)	**-1.1** (717-969)	**449** (717)
0.06	**+1** (204-563)	**+0.1** (563-936)	**-----**	**578** (936)
0.11	**+0.9** (225-1022)	**-----**	**-----**	**899** (1022)

Effect of Marasperse N-22 on Silica Solubility in Water[1]

Figure 44 shows the effect of the lignosulfonate, Marasperse N-22, on the solubility of silica. Table 37 shows the mass of Marasperse N-22 added for each of the mole ratio additions, along with the mole ratios of the sulfonate reactive groups (RGR) to silica. All three mole ratios show enhanced solubility for silica.

The solubilizing effect on silica was inversely related to the amount of Marasperse N-22 added to the solution. As seen in Table 38, the initial slopes of the MR 0.017, 0.034, and 0.068 runs were +1.05, +0.86, and +0.27 respectively. No silica solubility limit is reached in the Marasperse N-22 runs with MRs of 0.017 and 0.034 within the concentration limits of this work. A sharp resolubilization for silica is indicated in the MR 0.068 run at an expected silica concentration of 552 mg/L. This resolubilization effect of silica occurs in the expected silica range where other anomalously high measured silica values were found to occur, and has been discussed in the writeup of the effect of sodium thiocyanate on silica solubility, as well as in subsequent sections. The magnesium and calcium contents of these solutions do not represent a picture of these ions behavior vis a vis silica. The original lignin material contains appreciable calcium and magnesium.

Table 37
Actual Mole Ratio (MR) and Sulfonate (Reactive Group) Ratio (RGR) Used in Marasperse N-22 Experiments

Marasperse N-22		
Added to Solution (mg/L)	**Actual MR**	**Actual RGR (SO_3^-)**
0	0	0
915	0.02	2.6
1830	0.03	5.2
3660	0.07	10.3

MR = molar ratio of additive to silica
RGR (SO_3^-) = molar ratio of reactive sulfonate groups to silica

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[1] See Appendix N, Tables 137N–140N for data.

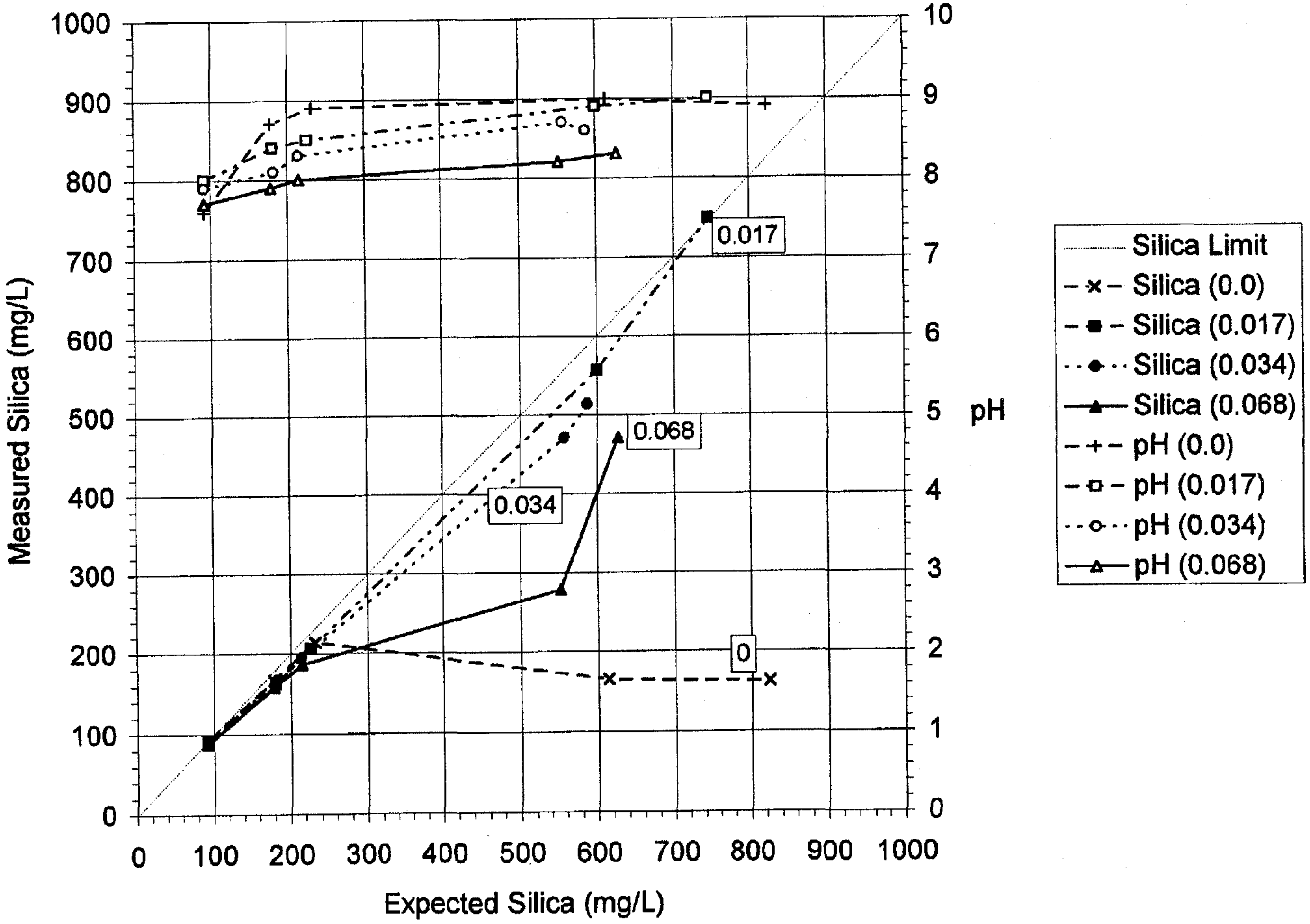

Figure 44. Effect of Marasperse N-22 on the Solubility of Silica in Water.
Marasperse N-22:Silica MRs = (0), (0.017), (0.034), (0.068).

Table 38
Slope and Maximum SiO_2 Solubility Data for Marasperse N-22 in Water Evaporation Experiments Shown in Figure 44

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**-0.1** (232-613)	-----	-----	**214** (232)
0.017	**+1.1** (226-746)	-----	-----	**749** (746)
0.034	**+0.9** (215-587)	-----	-----	**514** (587)
0.068	**+0.3** (216-552)	**+2.6** (552-627)	-----	**471** (627)

Effect of Maracell XE on Silica Solubility in Water[1]

Figure 45 shows the effect of the lignosulfonate Maracell XE on the solubility of silica. Table 39 gives the mass of Maracell XE added for each of the mole ratio additions, along with the mole ratios of the sulfonate reactive groups to silica. All three mole ratios show enhanced solubility of the silica.

The MR 0.11 addition, the lowest amount of Maracell XE, showed the greatest effect on silica solubility. The silica contents fell on a straight line +0.96 slope up to 705 mg/L of expected silica. The other two runs with higher mole ratio additions of Maracell XE also increased the silica solubility but not to the extent of the MR 0.11 addition. No limit of silica solubility was reached in any of the three levels of Maracell XE additions.

Table 39
Actual Mole Ratio (MR) and Sulfonate (Reactive Group) Ratio (RGR)
Used with Maracell XE in Water Experiments

Maracell XE		
Added to Solution (mg/L)	**Actual MR**	**Actual RGR (SO_3^-)**
0	0	0
915	0.11	1.9
1830	0.21	3.9
3660	0.43	7.7

MR = molar ratio of additive to silica
RGR (SO_3^-) = molar ratio of reactive sulfonate groups to silica

The lignosulfonates show definite effects on the solubility of silica and are worth further investigation. Their ready availability also makes them attractive. Both Kelig 32 and Marasperse N-22 show some calcium and magnesium content and a strong tendency to retain them in solution. Maracell XE did not add additional calcium and magnesium to the water and showed good retention of the magnesium.

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[1] See Appendix N, Tables 141N–144N for data.

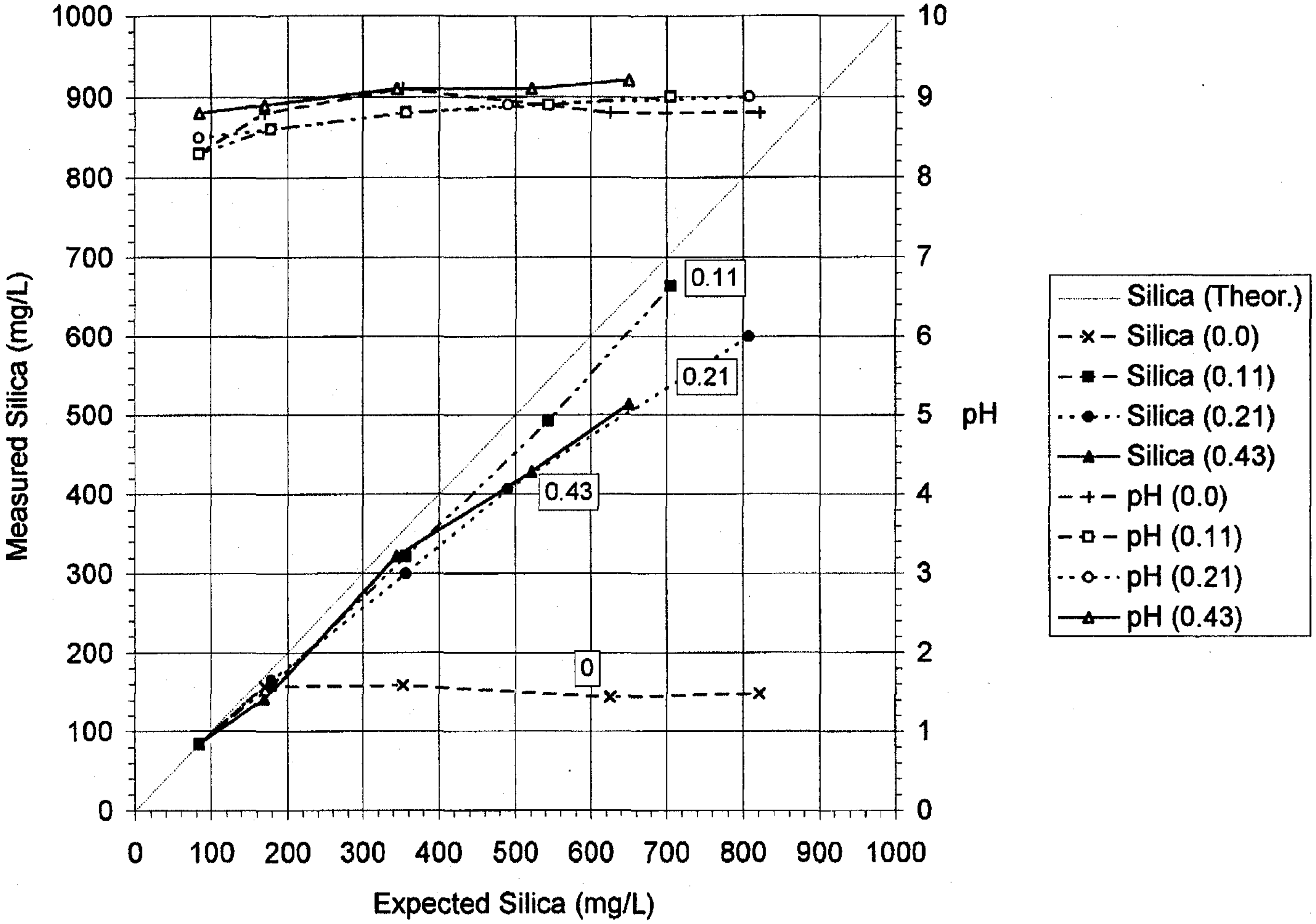

Figure 45. Effect of Maracell XE on the Solubility of Silica in Water.
Maracell XE:Silica MRs = (0), (0.11), (0.21), (0.43).

Table 40
Slope and Maximum SiO_2 Solubility Data for Maracell XE in Water Evaporation Experiments Shown in Figure 45

Additive:SiO_2 Mole Ratio	**Slopes** (expected SiO_2 range)			**Maximum Measured Solubility** (expected SiO_2)
	S_a	S_b	S_c	
0.0	**0** (170-821)	-----	-----	**156** (170)
0.11	**+1** (179-705)	-----	-----	**663** (705)
0.21	**+0.7** (179-808)	-----	-----	**599** (808)
0.43	**+1** (141-345)	**+0.6** (345-650)	-----	**514** (650)

Summary – Organic Anions Additions Work

The effects of the various types of organic compounds on silica solubility have been evaluated by using the evaporative technique. The results have been shown by plotting Measured Silica against the Expected Silica in solution (see Figures 22 - 45).

The solubilizing power for silica of the most effective organic compounds are compared in Table 41 using the slope of the solubility curves as the criterion of solubilizing power. The closer the ratio of Measured Silica to Expected Silica is to 1.0, the more complete the solubilization. The maximum silica concentration reached and the mole ratio of that additive to silica are also shown in Table 41.

Table 41

Comparison of Solubilizing Effect of Various Organic Compounds on the Basis of Slope of Measured Silica:Expected Silica.

Chemical	**Mole Ratio**	**Maximum Measured Silica (mg/L)**	**Slope (Measured SiO_2 /Expected SiO_2)**
p-Phthalate	2.64	963	1.00
Catechol	0.46	749	1.00
Marasperse N-22	0.017	746	1.00
Oxalate	1.7	685	1.00
Maracell XE	0.11	663	0.94
Citrate	0.83	599	0.93
Tiron	0.17	770	0.88
Chelig 32	0.11	890	0.87
Phloroglucinol	0.42	749	0.82
EDTA	0.4	871	0.81
Pyrogallol	0.46	685	0.77
o-Phthalate	1.6	567	0.76

In Figures 46 – 51 we have evaluated the effectiveness of the compounds with various functional groups as solubilizers. These graphs plot, as a function of mole ratio of additive to silica, the Measured Silica in solution, at an Expected Silica value of 600 mg/L (approximately 7.0 to 7.5 concentration factors).

Formate, Acetate (mono-carboxylic acids)

Figure 46 compares the effectiveness of formate and acetate on the solubility of silica on a mole ratio basis. The curve for formate shows marked ability to retain silica in solution, even though showing some anomalous behavior. This contrasts sharply with the behavior of acetate. Acetate shows no effectiveness at all, with increasing mole ratio, as the curve levels off at 160 mg/L.

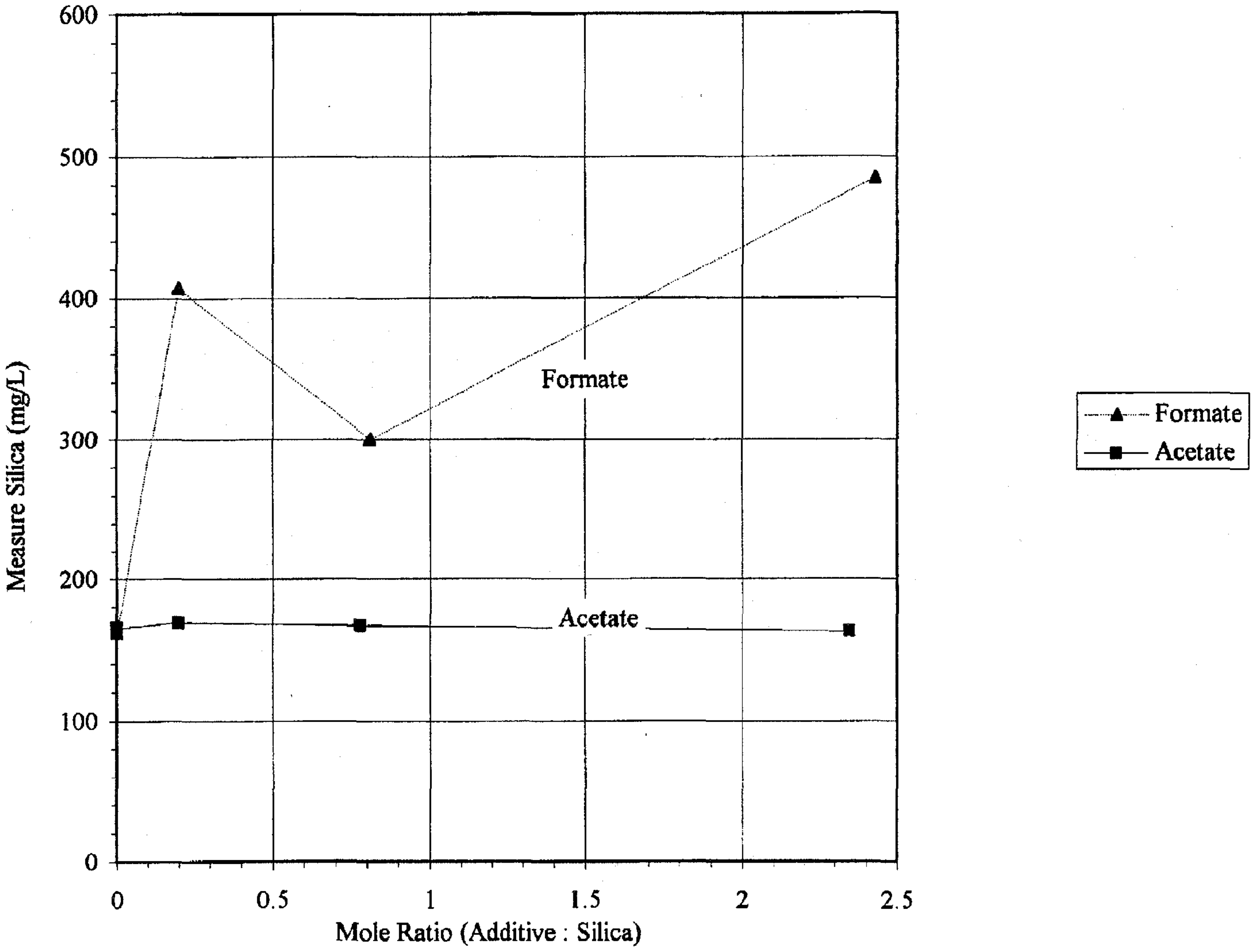

Figure 46. Effect of Additive Mole Ratio on Silica Solubility with Added Formate and Acetate. Expected Silica Concentration Is 600 mg/L SiO_2.

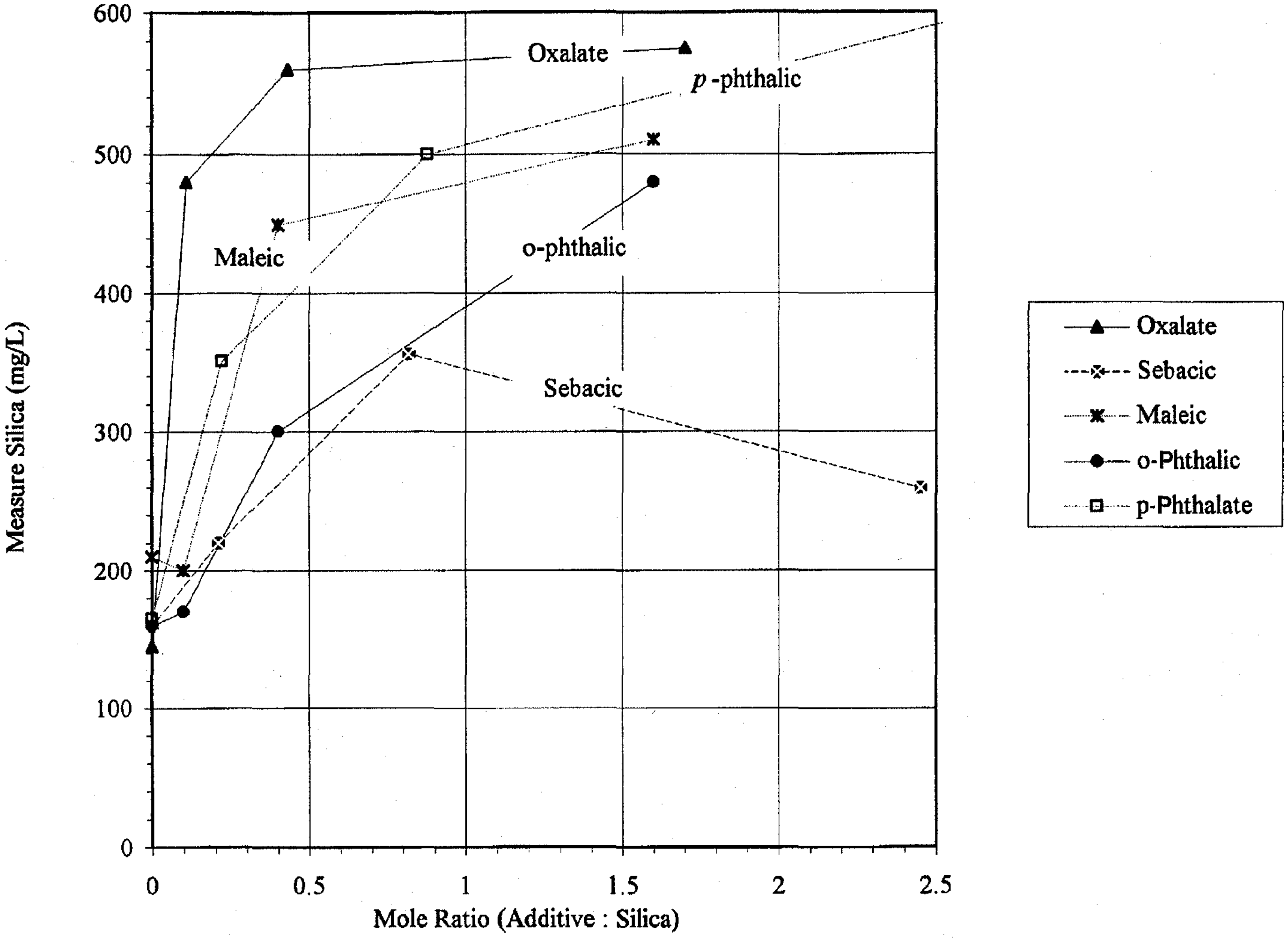

Figure 47. Effect of Additive Mole Ratio on Silica Solubility with Added Oxalate, Phthalate, Maleate, and Sebacate. Expected Silica Concentration Is 600 mg/L SiO_2.

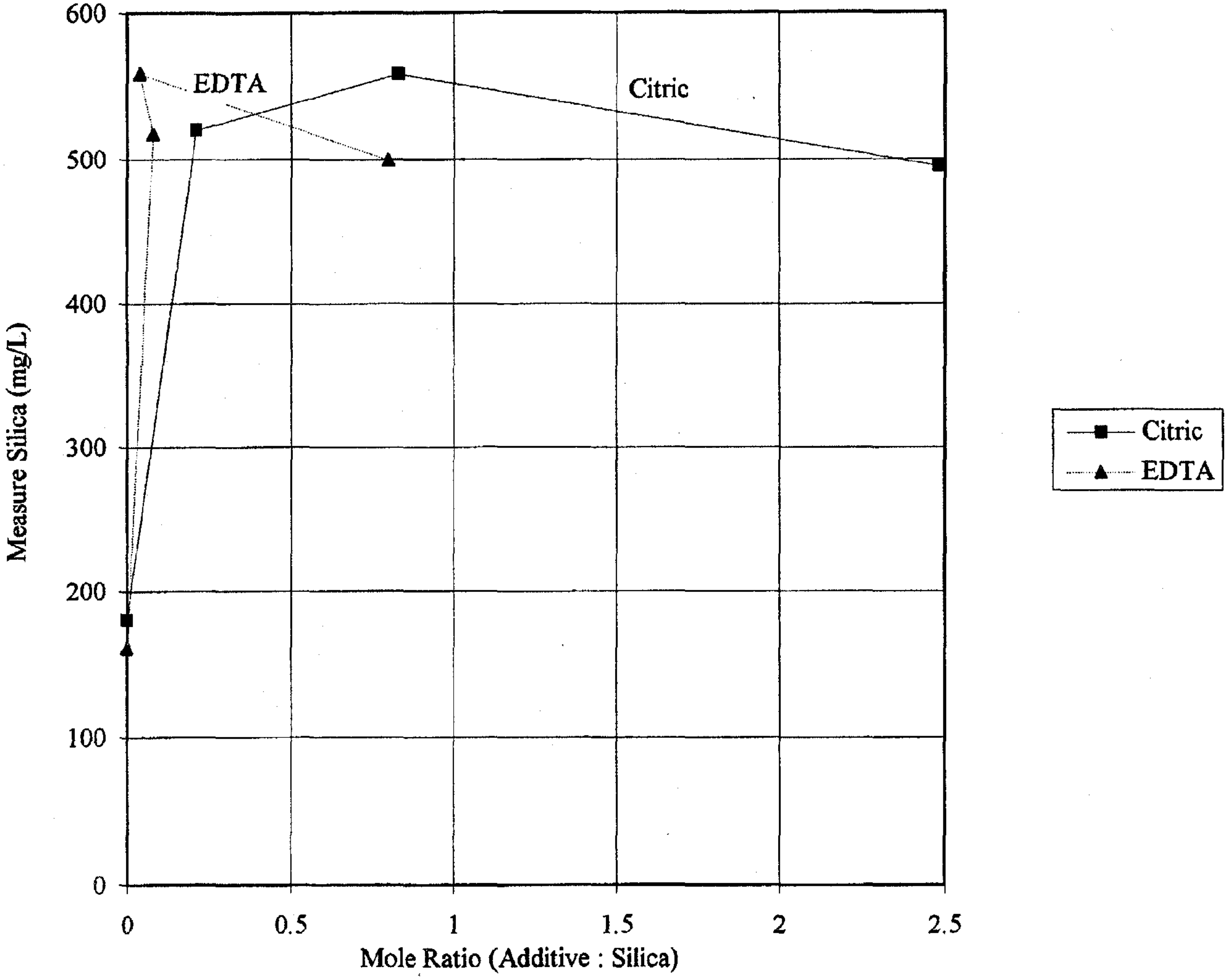

Figure 48. Effect of Additive Mole Ratio on Silica Solubility with Added Citrate and EDTA. Expected Silica Concentration Is 600 mg/L SiO_2.

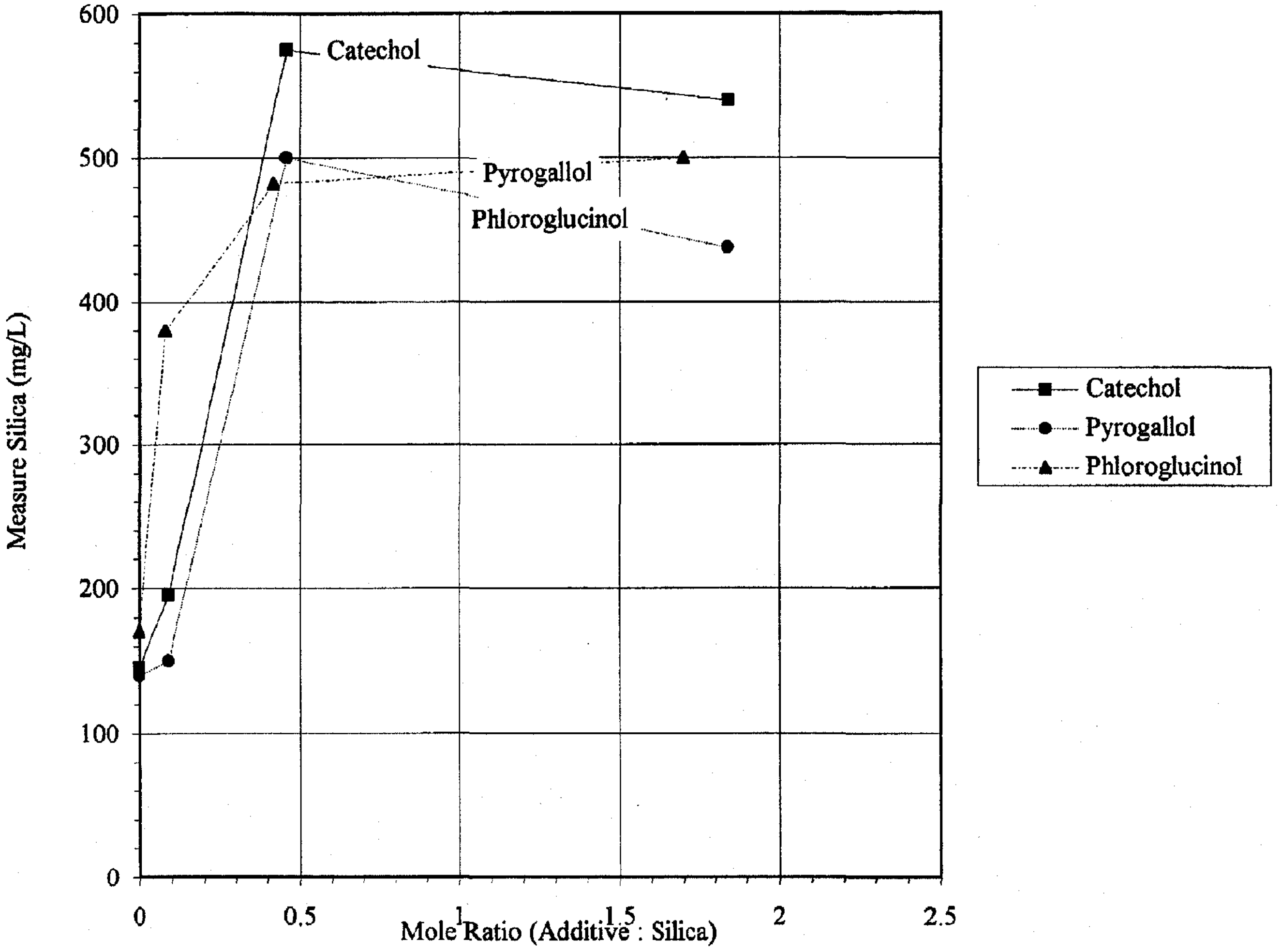

Figure 49. Effect of Additive Mole Ratio on Silica Solubility with Added Catechol, Pyrogallol, and Phloroglucinol. Expected Silica Concentration Is 600 mg/L SiO_2.

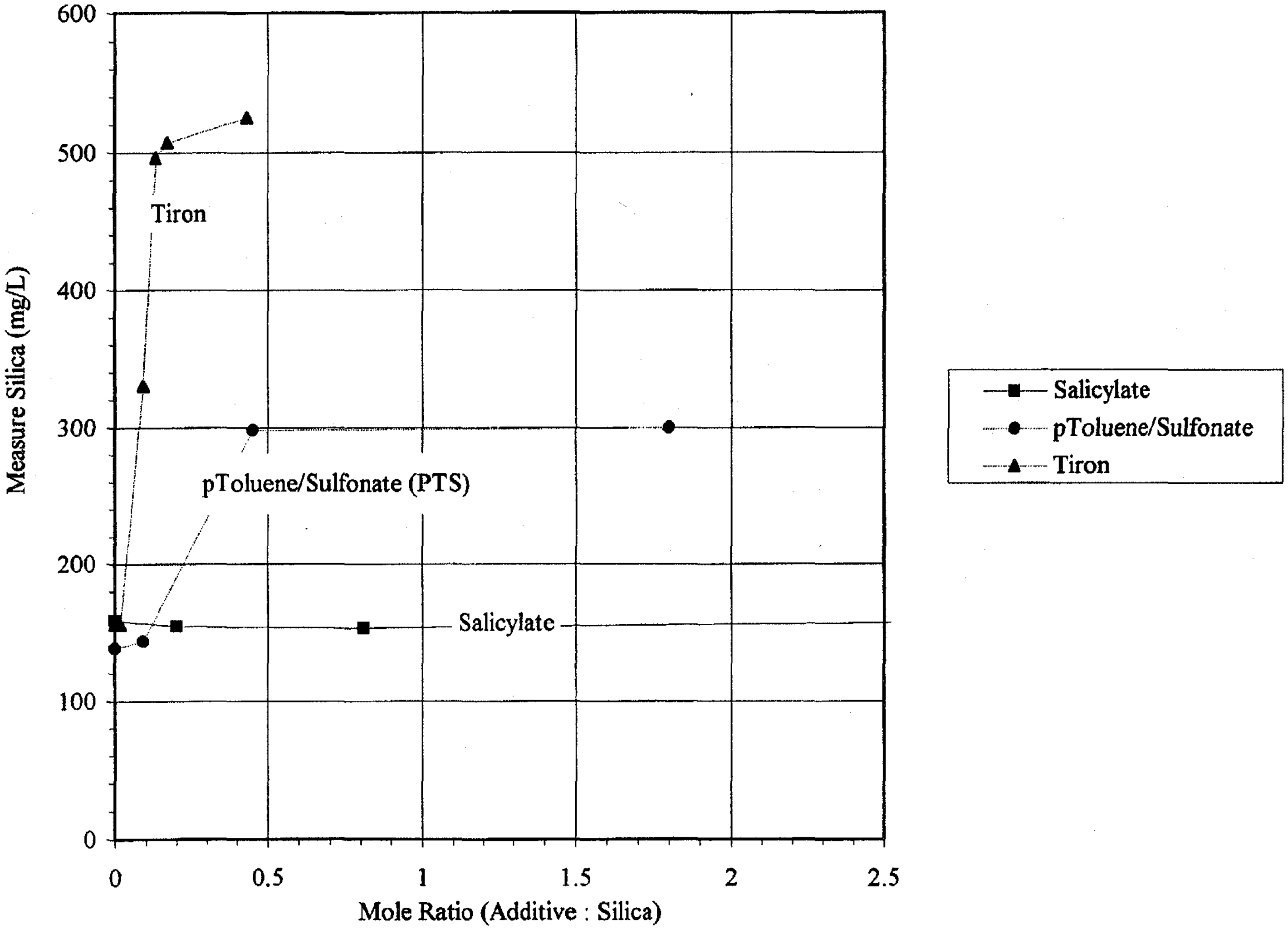

Figure 50. Effect of Additive Mole Ratio on Silica Solubility with Added Salicylate, p-Toluene/Sulfonate, and Tiron. Expected Silica Concentration Is 600 mg/L SiO_2.

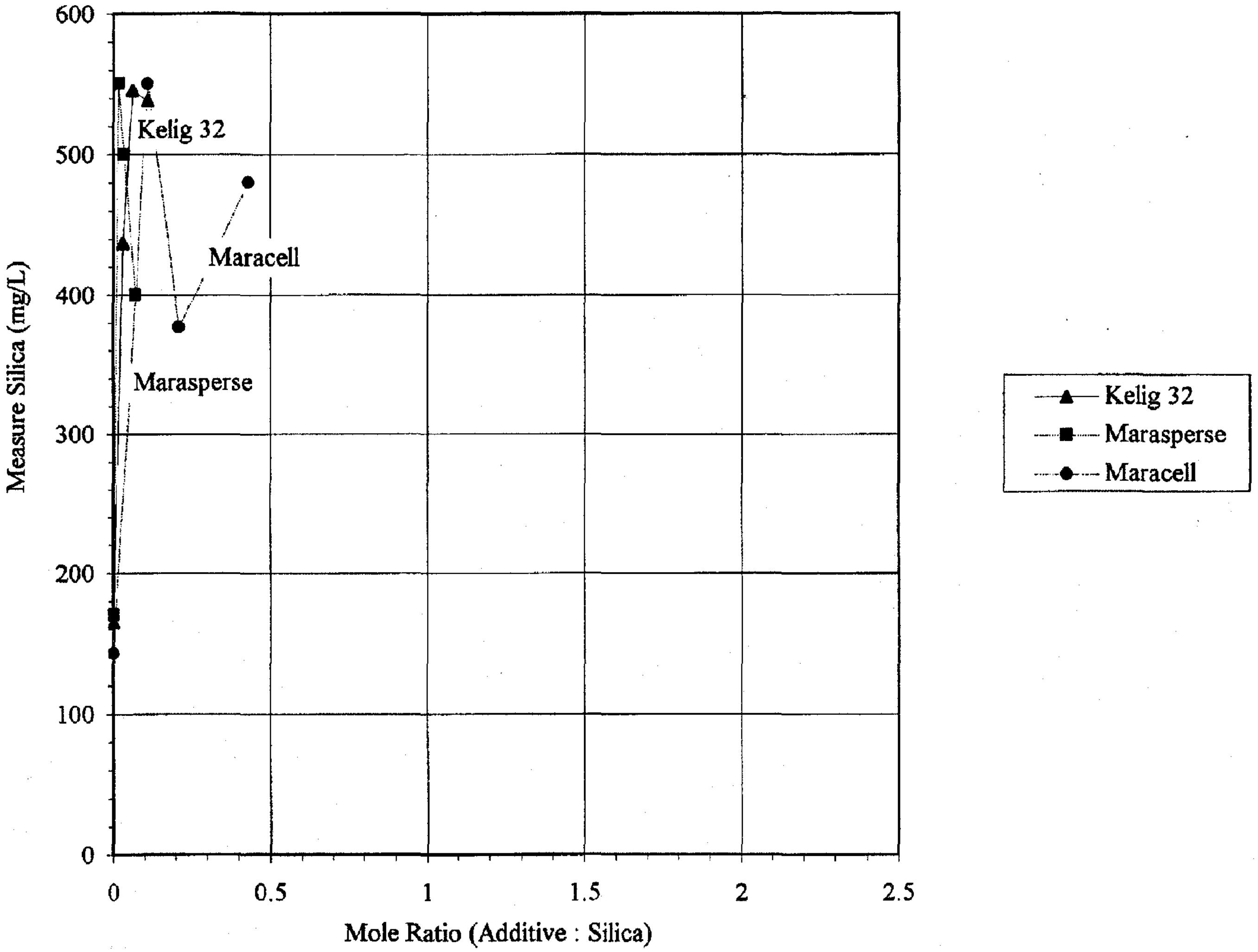

Figure 51. Effect of Additive Mole Ratio on Silica Solubility with Added Kelig 32, Marasperse N-22, and Maracell XE. Expected Silica Concentration Is 600 mg/L SiO_2.

Oxalate, Sebacate, Maleate, o-Phthalate, p-Phthalate (dicarboxylic, dibasic acids)

The solubilizing effectiveness of dibasic acids on a mole ratio basis is compared in Figure 47. Oxalate is the most effective overall at MRs as low as 0.5 at approximately 560 mg/L of silica in solution. The maleate curve shows silica concentrations of approximately 440-500 mg/L at MRs greater than 0.5. Silica solubilities of 500 to 600 mg/L were reached in p-Phthalate solutions at MRs greater than 0.8. Less effectiveness is shown by o-Phthalate, but the curve continues to rise to MR 1.75 and 500 mg/L. Sebacate shows lesser effectiveness.

Citrate and EDTA (monohydroxy tricarboxylic acid and a diamino-tetracarboxylic acid)

Citrate and EDTA are very effective solubilizers for silica as shown in Figure 48. Silica solubilities rise to between 520-560 mg/L at mole ratios as low as 0.1 for EDTA and approximately 0.2 to 0.5 for citrate.

Catechol, Pyrogallol, and Phloroglucinol (polyhydroxy phenols)

Figure 49 shows the effectiveness of the polyhydroxy phenols. Catechol is one of the most effective additives in the work; it makes silica soluble to 580 mg/L at MR 0.4. Its effectiveness slightly declines beyond that mole ratio. The other two polyhydroxy phenols show similar, but lesser, effects on silica solubility with increasing mole ratio. Water solutions containing pyrogallol and phloroglucinol showed silica solubilities of nearly 500 mg/L at MR 0.4.

Salicylate, Sulfonate, and Tiron (phenol carboxylic and phenol sulfonic acids)

Tiron (see Figure 50) is one of the most effective compounds for retaining silica in solution. At MR 0.2 it retained 500 mg/L silica in solution. Paratoluene sulfonate is much less effective overall. Salicylate shows no effectiveness at all.

Kelig 32, Marasperse N-22, and Maracell XE (Lignin Sulfonates)

The lignin sulfonates (see Figure 51) show very strong effectiveness in retaining silica in solution on a mole ratio basis. Silica solubilities as high as 550 mg/L at 600 mg/L Expected Silica were attained at mole ratios less than 0.2.

The organic chemicals that solubilize silica at low mole ratios to at least 500 mg/L have been ranked as solubilizers. These are listed in Table 42 in order of increasing mole ratio of chemical to silica. Those that show solubilizing effect below 500 mg/L silica are listed as rather moderate solubilizers or supersaturants in Table 43. Other organic compounds that did not enhance supersaturation are also included in Table 44. Reference should be made to the original graphs and data and discussions for more detailed information.

Table 42

Organic Chemicals Ranked As Solubilizers of Silica in Decreasing Order

Compounds	**Functional Types**
Kelig 32	lignin sulfonate
Maracell XE	lignin sulfonate
Marasperse N-22	lignin sulfonate
Catechol	1,2-dihydroxybenzene
Oxalate	ethanedioate
Tiron	4,5-dihydroxy-1,3-benzene disulfonate
Pyrogallol	1,2,3-trihydroxybenzene
Phloroglucinol	1,3,5-trihydroxybenzene
Citrate	2-hydroxy-1,2,3-propane tricarboxylate
Ortho-phthalate	1,2-benzene dicarboxylate
Para-phthalate	1,4-benzene dicarboxylate
EDTA	ethylenediaminetetraacetate
Maleate	cis-1,2-ethylenedicarboxylate

Some other types of compounds have considerable effect as supersaturants:

Table 43

Organic Chemicals Ranked As Supersaturants of Silica, in Decreasing Order

Compounds	**Functional Types**
Formate	monocarboxylate
Sebacate	1,8-octanedicarboxylate
Para-toluene sulfonate	4-methylbenzene sulfonate

Other compounds that did not enhance supersaturation include:

Table 44

Organic Chemicals That Did Not Enhance Silica Solubility

Compounds	**Functional Types**
Acetate	methylcarboxylate
Salicylate	2-hydroxybenzoate
Alkyl-napthalene sulfonate	alkyl-napthalene sulfonate

It would seem on the basis of this work that inactivation of magnesium in solution is the effective method of keeping silica in solution. On the basis of the analytical data from the experimental part of the work, it was shown that where magnesium is retained in solution (perhaps by complexation or solubilization as by sulfate or nitrate), the silica remains in solution upon evaporation. This does not rule out the possibility that in some cases silica is also complexed.

Finally, this work may be considered to have defined the problem and to have produced useful and applicable methods of evaluation of solubilizers for silica. It has also identified and evaluated a number of compounds (functional types) that keep silica in solution. The best of these seem to leave the silica in true solution by contrast with some that merely enhance supersaturation.

C. The Effect of Cation Additions on Silica Solubility in LANL Tap Water

1. Introduction

The effect of a number of metal ions on the solubility of silica was studied as a function of pH (see Table 45). The metals added were magnesium, calcium, titanium, ferric iron, copper, zinc, and aluminum. All of these were added as nitrate salts except for titanium, which was added as the sulfate.

A procedure for the flocculation of metal ions was adapted from standard literature sources[17] (see Appendix G). These experiments were performed by adding the metal salts to the LANL tap water and stirring the solution for 10 minutes with a magnetic stir bar as the pH was adjusted using nitric acid or sodium hydroxide. The solutions were then allowed to stand for two days, covered with Parafilm, and then filtered through a 0.2 micron filter before chemical analysis.

It should be repeated that in the pH work and the inorganic and organic anion work, the "solubility" of silica was determined by insolubilizing the silica by evaporation. In this work with metals, the silica was insolubilized (flocced) by metals additions.

2. Metal Ions (Metals 1)

The following table lists the metal salts used as flocculants for the LANL tap water, along with the mole ratio of metal to silica used, and the corresponding mass of the metal ion and metal salt added.

Table 45
Metals Studied for Their Effect on Silica Solubilities
in LANL Tap water
—Metals 1—

Figure	**Metal:SiO_2**	**Actual Mole Ratio**			
Figure 52	**Mg:SiO_2 Mole Ratio**	**0.4**	**0.8**	**1.6**	**3.2**
	Mg (mg/L)	16	32	64	128
	$Mg(NO_3)_2 \cdot 6H_2O$ (mg/L)	169	338	676	1351
Figure 53	**Ca:SiO_2 Mole Ratio**	**0.4**	**0.8**	**1.6**	**3.2**
	Ca (mg/L)	26	53	106	211
	$Ca(NO_3)_2 \cdot 4H_2O$ (mg/L)	156	311	622	1244
Figure 54	**Al:SiO_2 Mole Ratio**	**0.43**	**0.86**	**1.71**	**3.42**
	Al (mg/L)	19	38	77	154
	$Al(NO_3)_3 \cdot 9H_2O$ (mg/L)	267	534	1069	2137
Figure 55	**Ti:SiO_2 Mole Ratio**	**0.57**	**1.13**	**2.27**	
	Ti (mg/L)	45	90	181	
	$TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ (mg/L)	234	468	936	
Figure 56	**Fe:SiO_2 Mole Ratio**	**0.43**	**0.86**	**1.71**	**3.42**
	Fe (mg/L)	40	80	159	318
	$Fe(NO_3)_3 \cdot 9H_2O$ (mg/L)	288	575	1151	2302
Figure 57	**Cu:SiO_2 Mole Ratio**	**0.43**	**0.86**	**1.71**	**3.42**
	Cu (mg/L)	45	91	181	362
	$Cu(NO_3)_2 \cdot 2.5H_2O$ (mg/L)	166	331	663	1325
Figure 58	**Zn:SiO_2 Mole Ratio**	**0.43**	**0.86**	**1.71**	**3.42**
	Zn (mg/L)	47	93	186	373
	$Zn(NO_3)_2 \cdot 6H_2O$ (mg/L)	212	424	847	1695
Figure 59	**Effect of Metal Ions**				
	Final pH of Solution 9.0				

*The order in which the metal ions are shown above is the order in which the experiments were done, not atomic number order.

The Effect of Magnesium Ion on Silica Solubility in LANL Water

The effect of magnesium ion and pH on the silica content in LANL tap water is shown in Figure 52. Five solutions with different mole ratios of magnesium to silica were prepared: 0.0, 0.4, 0.8, 1.6, and 3.2. The contents of four beakers containing each solution were adjusted to the following pH values respectively: 4.0, 6.0, 8.0, and 10.0 using nitric acid or sodium hydroxide.

The amount of silica remaining in solution is clearly a function of both the mole ratio of magnesium added and pH. In the pH range 5.8-8.0, no silica was removed from any of the solutions. The higher the mole ratio, the less the SiO_2 remaining in solution. Figure 52 shows maximum SiO_2 removal was attained at a pH between 9.0-9.1 in these experiments.

The chemical analyses of each solution in this experiment are shown in Table 46, which also shows the ratios of the number of magnesium atoms to silicon atoms removed from solution at pH 9.0-9.1. Thus, at pHs of 9.0 and higher, magnesium and silica removal are coincident. Minimum silica solubilities for each mole ratio metal addition seen in Figure 52 are given in Table 47.

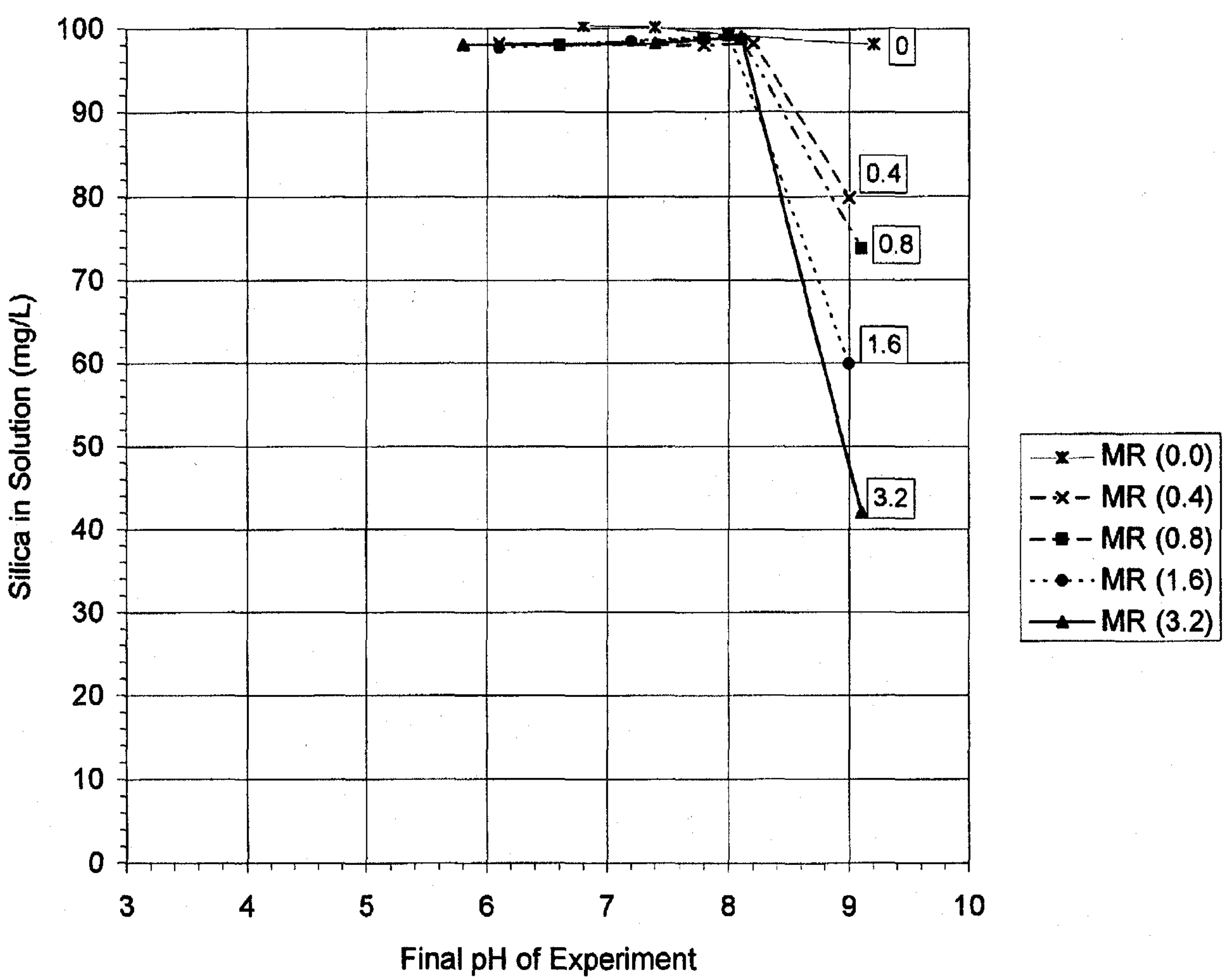

Figure 52. Effect of Magnesium and pH on the Solubility of Silica in Water.
Magnesium:Silica MRs = (0), (0.4), (0.8), (1.6), (3.2).

Table 46
The Effect of Added Magnesium on Silica Solubility.
DATA

Additive:SiO_2 Mole Ratio	**pH Initial (Final)**	**Composition of Hypothetical Solid***	**Final Concentration (mg/L)**		
			SiO_2	**Ca**	**Mg**
0.0	4 **(6.8)**	-----	100	14	4
“	6 **(7.4)**	-----	100	14	4
“	8 **(8.0)**	-----	99	14	4
“	10 **(9.2)**	$Ca_{1.5}Si_{1.0}$	98	12	4
0.4	4 **(6.1)**	-----	98	14	21
“	6 **(7.8)**	-----	98	14	22
“	8 **(8.2)**	-----	98	14	21
“	10 **(9.0)**	$Mg_{0.7}Si_{1.0}$	80	14	14
0.8	4 **(6.6)**	-----	98	14	39
“	6 **(7.8)**	-----	99	14	39
“	8 **(8.1)**	-----	99	14	39
“	10 **(9.1)**	$Mg_{0.6}Si_{1.0}$	74	14	30
1.6	4 **(6.1)**	-----	98	14	73
“	6 **(7.2)**	-----	98	14	73
“	8 **(8.0)**	-----	99	14	73
“	10 **(9.0)**	$Mg_{0.5}Si_{1.0}$	60	14	60
3.2	4 **(5.8)**	-----	98	14	141
“	6 **(7.4)**	-----	98	14	140
“	8 **(8.1)**	-----	99	14	141
“	10 **(9.1)**	$Mg_{0.7}Si_{1.0}$	42	14	116

*Based on SiO_2, Ca, and Mg left in solution.

Table 47
The Effect of Magnesium on Silica Solubility.
Minimum Silica Solubility As a Function of pH and Mole Ratios.

Additive:SiO_2 Mole Ratio	**pH**	**Minimum Solubility**
0.0	**9.2**	**98**
0.4	**9.0**	**80**
0.8	**9.1**	**74**
1.6	**9.0**	**60**
3.2	**9.1**	**42**

The Effect of Calcium Ion on Silica Solubility in LANL Water

The effect of calcium and pH on the silica content in LANL tap water is shown in Figure 53. Five solutions with different mole ratios of calcium to silica were prepared: 0.0, 0.4, 0.8, 1.6, and 3.2. The contents of four beakers containing each solution were adjusted to the following pH values respectively: 4.0, 6.0, 8.0, and 10.0 using nitric acid or sodium hydroxide.

Essentially no removal of silica occurred in these solutions over the pH range 6.2-9.2. Calcium remained in solution until pH 8.0 (see Table 48). From pH 8.0-9.2, calcium concentrations dropped markedly, with no associated silica insolubilization. This observation is significant, as it is often assumed that calcium initiates silica deposition.

The chemical analyses of each solution in this experiment are shown in Table 48. Minimum silica solubilities for each mole ratio metal addition seen in Figure 53 are given in Table 49.

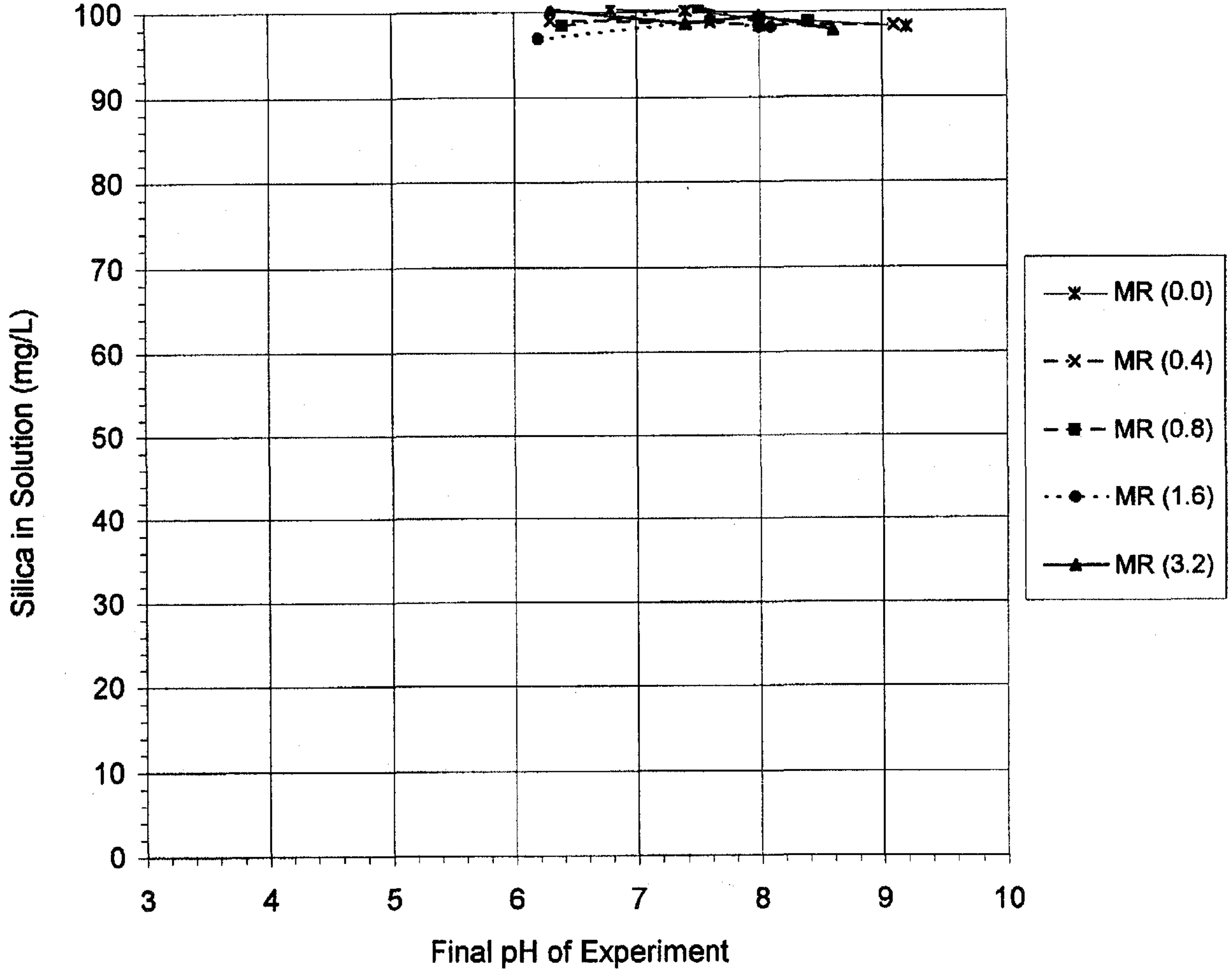

Figure 53. Effect of Calcium and pH on the Solubility of Silica in Water.
Calcium:Silica MRs = (0), (0.4), (0.8), (1.6), and (3.2).

Table 48
The Effect of Added Calcium on Silica Solubility.
DATA

Additive:SiO_2 Mole Ratio	**pH Initial (Final)**	**Composition of Hypothetical Solid***	**Final Concentration (mg/L)**		
			SiO_2	**Ca**	**Mg**
0.0	4 (6.8)	-----	100	14	4
"	6 (7.4)	-----	100	14	4
"	8 (8.0)	-----	99	14	4
"	10 (9.2)	$Ca_{1.5}Si_{1.0}$	98	12	4
0.4	4 (6.3)	-----	99	43	4
"	6 (7.6)	-----	99	43	4
"	8 (8.0)	-----	98	43	4
"	10 (9.1)	$Ca_{23.2}Si_{1.0}$	98	9	4
0.8	4 (6.4)	-----	98	74	4
"	6 (7.5)	-----	101	74	4
"	8 (8.0)	-----	99	72	5
"	10 (8.4)	$Ca_{66.0}Si_{1.0}$	99	23	4
1.6	4 (6.2)	-----	97	131	4
"	6 (7.6)	-----	99	134	4
"	8 (8.0)	$Ca_{58.5}Si_{1.0}$	98	42	4
"	10 (8.1)	$Ca_{39.7}Si_{1.0}$	98	67	4
3.2	4 (6.3)	-----	100	250	4
"	6 (7.4)	-----	99	244	4
"	8 (8.0)	-----	100	249	4
"	10 (8.6)	$Ca_{34.5}Si_{1.0}$	98	179	4

*Based on SiO_2, Ca, and Mg left in solution.

Table 49
The Effect of Calcium on Silica Solubility.
Minimum Silica Solubility As a Function of pH and Mole Ratios.

Additive:SiO_2 Mole Ratio	**pH**	**Minimum Solubility**
0.0	**9.2**	**98**
0.4	**9.1**	**98**
0.8	**6.4**	**98**
1.6	**6.2**	**97**
3.2	**8.6**	**98**

The Effect of Aluminum Ion on Silica Solubility in LANL Water

The effect of aluminum ion and pH on the silica content in LANL tap water is shown in Figure 54. Five solutions with different mole ratios of aluminum to silica were prepared: 0.0, 0.43, 0.86, 1.71, and 3.42. The contents of four beakers containing each solution were adjusted to the following pH values respectively: 4.0, 6.0, 8.0, and 10.0 using nitric acid or sodium hydroxide.

The amount of silica remaining in solution is strongly a function of both the mole ratio of Al^{3+} ion to silica and pH. Apparently, the floccing reaction of aluminum occurs at pH <6.

In the MR 0.43 and 0.86 solutions the silica solubility continued to decrease as pH rose above 7.5. Low values of silica solubility at pH 7.7 were 10 and 5 mg/L for mole ratios 1.71 and 3.42 respectively. These latter solutions show a slight resolubilization of silica as the pH increases above 7.6.

The chemical analyses of each solution in this experiment are shown in Table 50. Minimum silica solubilities for each mole ratio metal addition seen in Figure 54 are given in Table 51. Table 45 shows that, at pHs of 9.2 and above, aluminum also begins to resolubilize in the solutions.

It is evident that the pH range of 7.5 to about 9.0 is optimum for silica removal. In summary, it may be said that the mole ratio of aluminum has an increasing effect on silica removal from solution, but increasing the pH of the MR 1.71 and 3.42 solutions beyond pH 7.8 has little or no further effect.

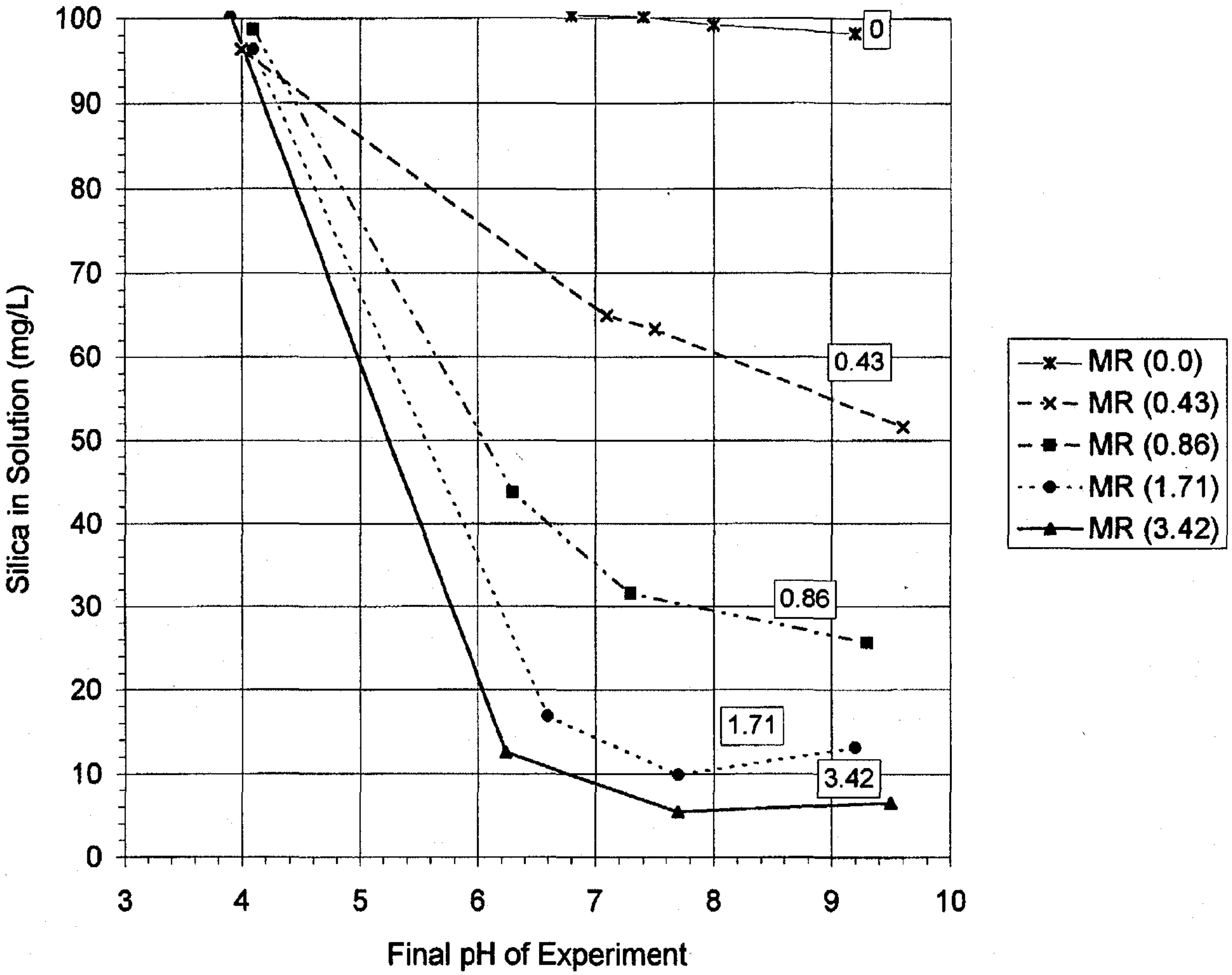

Figure 54. Effect of Aluminum and pH on the Solubility of Silica in Water. Aluminum:Silica MRs = (0), (0.43), (0.86), (1.71), (3.42).

Table 50
The Effect of Added Aluminum on Silica Solubility.
DATA

Additive:SiO_2 Mole Ratio	**pH Initial (Final)**	**Composition of Hypothetical Solid***	**Final Concentration (mg/L)**			
			SiO_2	**Ca**	**Mg**	**Al**
0.0	4 (6.8)	-----	100	14	4	0
"	6 (7.4)	-----	100	14	4	0
"	8 (8.0)	-----	99	14	4	0
"	10 (9.2)	$Ca_{1.5}Si_{1.0}$	98	12	4	0
0.43	4 (4.0)	-----	96	14	5	20
"	6 (7.1)	$Ca_{0.1}Al_{1.1}Si_{1.0}$	65	12	4	2
"	8 (7.5)	$Mg_{0.1}Ca_{0.2}Al_{1.0}Si_{1.0}$	63	9	3	2
"	10 (9.6)	$Mg_{0.1}Ca_{0.3}Al_{0.8}Si_{1.0}$	52	6	2	2
0.86	4 (4.1)	-----	99	14	4	39
"	6 (6.3)	$Al_{1.4}Si_{1.0}$	44	13	4	4
"	8 (7.3)	$Ca_{0.1}Al_{1.2}Si_{1.0}$	32	9	3	2
"	10 (9.3)	$Mg_{0.1}Ca_{0.2}Al_{1.0}Si_{1.0}$	26	2	1	5
1.71	4 (4.1)	$Al_{1.1}Si_{1.0}$	96	14	4	75
"	6 (6.6)	$Al_{2.0}Si_{1.0}$	17	12	4	3
"	8 (7.7)	$Mg_{0.1}Ca_{0.1}Al_{1.8}Si_{1.0}$	10	7	2	3
"	10 (9.2)	$Mg_{0.1}Ca_{0.2}Al_{1.8}Si_{1.0}$	13	1	0	6
3.42	4 (3.9)	-----	101	14	4	146
"	6 (6.2)	$Al_{3.8}Si_{1.0}$	13	13	4	6
"	8 (7.7)	$Ca_{0.1}Al_{3.5}Si_{1.0}$	5	10	3	3
"	10 (9.5)	$Mg_{0.1}Ca_{0.2}Al_{2.2}Si_{1.0}$	7	2	0	64

*Based on SiO_2, Ca, and Mg left in solution.

Table 51
The Effect of Aluminum on Silica Solubility.
Minimum Silica Solubility As a Function of pH and Mole Ratios.

Additive:SiO_2 Mole Ratio	**pH**	**Minimum Solubility**
0.0	**9.2**	**98**
0.43	**9.6**	**52**
0.86	**9.3**	**26**
1.71	**7.7**	**10**
3.42	**7.7**	**5**

The Effect of Titanium Ion on Silica Solubility in LANL Water

The effect of titanium and pH on the silica content of LANL tap water is shown graphically in Figure 55. Detailed data are shown in Table 52. Four solutions with different mole ratios of titanium to silica were prepared: 0.0, 0.57, 1.13, and 2.27. The contents of three beakers containing each solution were adjusted to the following pH values respectively: 5.0, 8.0, and 10.0 using nitric acid or sodium hydroxide.

The amount of silica remaining in solution is clearly a function of both the mole ratio of titanium to silica and pH. pHs in the 7.5-8.5 range appear to be optimum for silica removal. The curves of the silica content vs. pH, for the higher pHs, show different characteristic slopes from those for magnesium, which would indicate different reaction chemistries.

The chemical analyses of each solution in this experiment are shown in Table 52, which gives composition of hypothetical solid phases in equilibrium with the solution. Minimum silica solubilities for each mole ratio metal addition seen in Figure 55 are shown in Table 53.

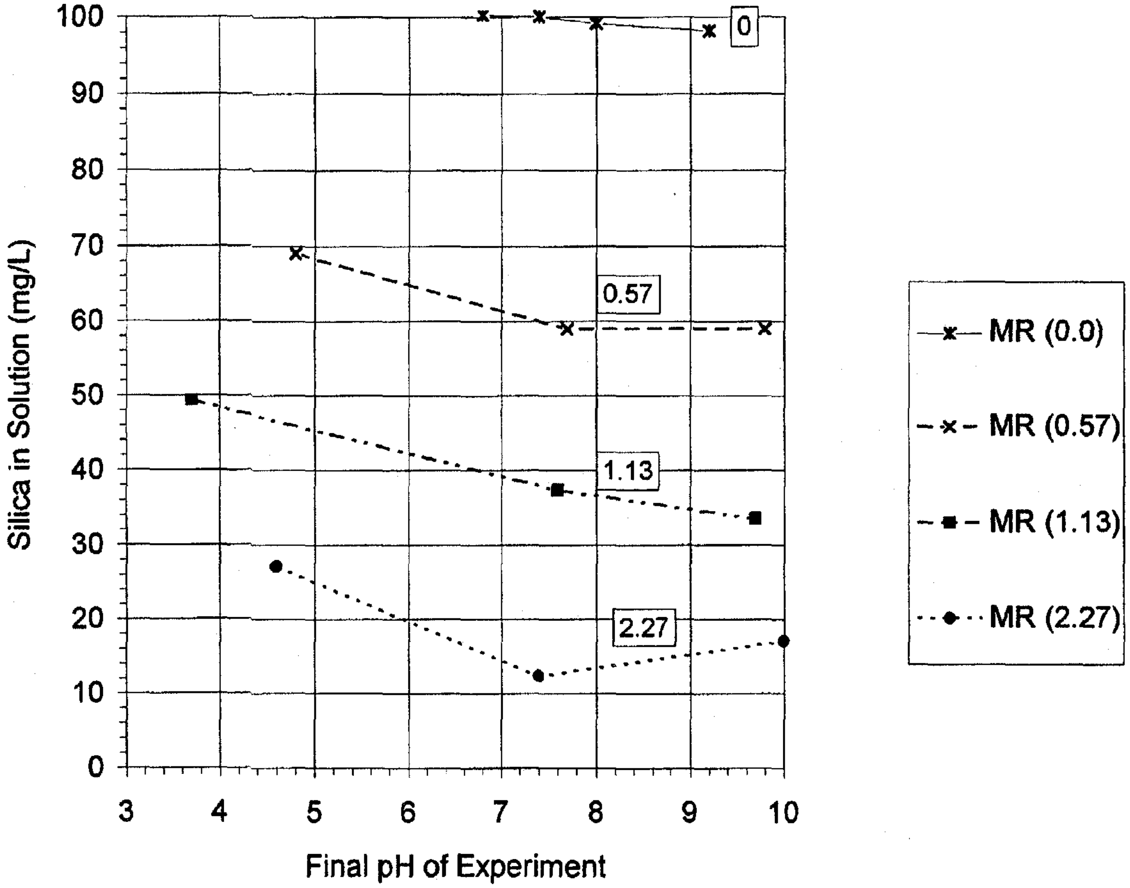

Figure 55. Effect of Titanium and pH on the Solubility of Silica in Water. Titanium:Silica MRs = (0), (0.57), (1.13), (2.27).

Table 52
The Effect of Added Titanium on Silica Solubility.
DATA

Additive:SiO_2 Mole Ratio	**pH Initial (Final)**	**Composition of Hypothetical Solid***	**Final Concentration (mg/L)**			
			SiO_2	**Ca**	**Mg**	**Ti**
0.0	4 **(6.8)**	-----	100	14	4	0
“	6 **(7.4)**	-----	100	14	4	0
“	8 **(8.0)**	-----	99	14	4	0
“	10 **(9.2)**	$Ca_{1.5}Si_{1.0}$	98	12	4	0
0.57	5 **(4.8)**	$Ti_{1.8}Si_{1.0}$	69	14	5	0.4
“	8 **(7.7)**	$Ca_{0.2}Ti_{1.4}Si_{1.0}$	59	10	5	0.4
“	10 **(9.8)**	$Mg_{0.1}Ca_{0.4}Ti_{1.4}Si_{1.0}$	59	4	3	0.6
1.13	5 **(3.7)**	$Ti_{2.2}Si_{1.0}$	49	15	5	0.1
“	8 **(7.6)**	$Ca_{0.2}Ti_{1.8}Si_{1.0}$	37	7	4	0.8
“	10 **(9.7)**	$Mg_{0.1}Ca_{0.3}Ti_{1.7}Si_{1.0}$	34	1	2	0.8
2.27	5 **(4.6)**	$Ti_{3.1}Si_{1.0}$	27	14	5	0.4
“	8 **(7.4)**	$Ca_{0.1}Ti_{2.6}Si_{1.0}$	12	6	4	1
“	10 **(10.0)**	$Mg_{0.1}Ca_{0.2}Ti_{2.6}Si_{1.0}$	17	1	1	12

*Based on SiO_2, Ca, and Mg left in solution.

Table 53
The Effect of Titanium on Silica Solubility.
Minimum Silica Solubility As a Function of pH and Mole Ratios.

Additive:SiO_2 Mole Ratio	**pH**	**Minimum Solubility**
0.0	**9.2**	**98**
0.57	**7.7-9.8**	**59**
1.13	**9.7**	**34**
2.27	**7.4**	**12**

The Effect of Ferric Ion on Silica Solubility in LANL Water

The effect of ferric ion and pH on the solubility of silica content of LANL tap water is shown in Figure 56. Five solutions with different mole ratios of ferric ion to silica were prepared: 0.0, 0.43, 0.86, 1.71, and 3.42. The contents of four beakers containing each solution were adjusted to the following pH values respectively: 4.0, 6.0, 8.0, and 10.0 using nitric acid or sodium hydroxide.

The amount of silica remaining in solution is clearly a function of both the mole ratio of ferric ion added and solution pH. Between pH 7.0 and 7.5, the slopes of the silica in solution lines decrease dramatically. Above pH 7.5, the silica solubility remains essentially constant in each of the ferric ion solutions. A minimum silica solubility of 10 mg/L was reached in the MR 3.42 solution in the pH range of 7.6-8.9.

The chemical analyses of each solution in this experiment are shown in Table 54. Minimum silica solubilities for each mole ratio metal addition seen in Figure 56 are given in Table 55.

Some hypothetical solid phases in equilibrium with solutions were also calculated.

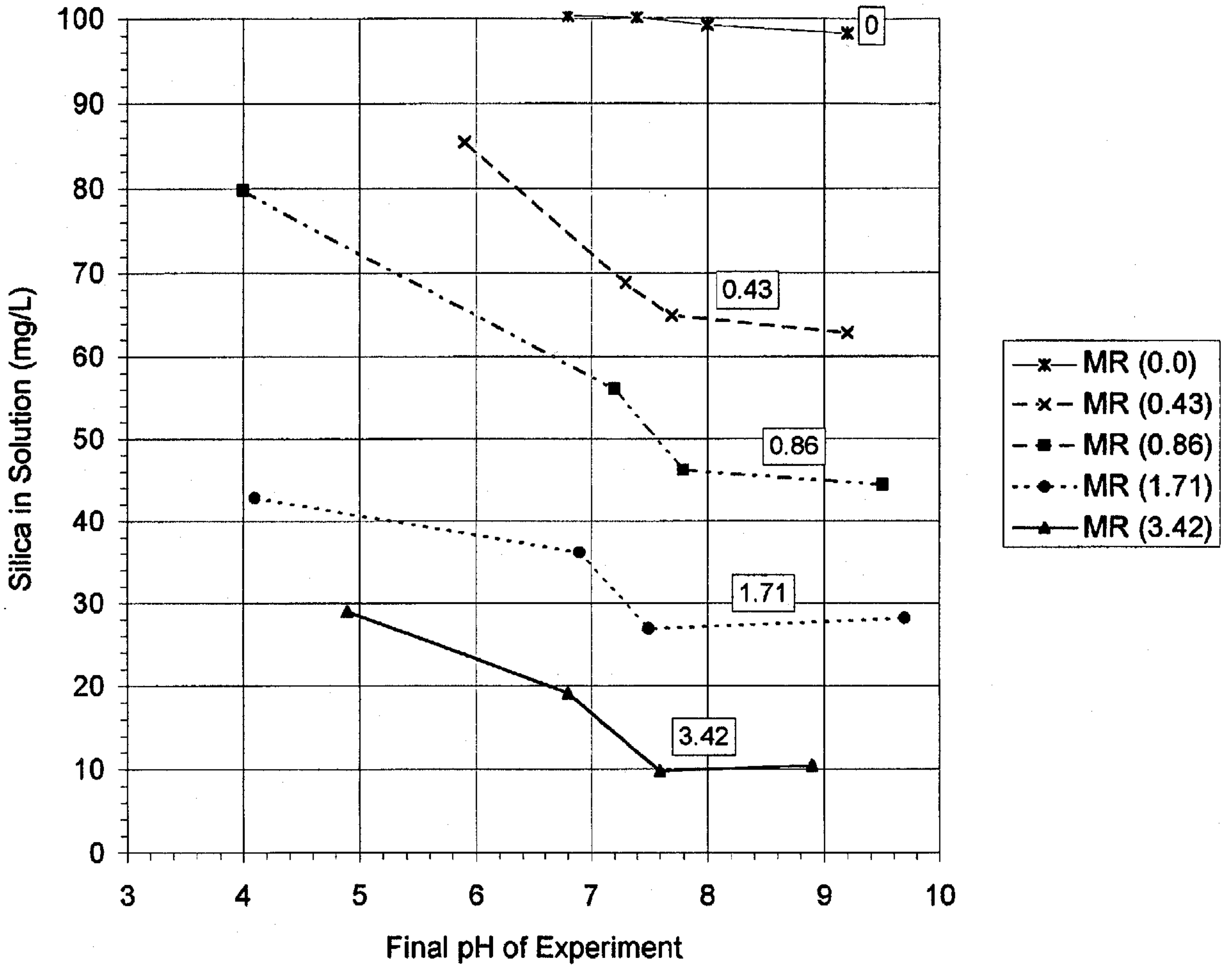

Figure 56. Effect of Ferric Ion and pH on the Solubility of Silica in Water.
Ferric Ion:Silica MRs = (0), (0.43), (0.86), (1.71), (3.42).

Table 54
The Effect of Added Ferric Ion on Silica Solubility.
DATA

Additive:SiO_2 Mole Ratio	**pH Initial (Final)**	**Composition of Hypothetical Solid***	**Final Concentration (mg/L)**			
			SiO_2	**Ca**	**Mg**	**Fe**
0.0	4 **(6.8)**	-----	100	14	4	0
"	6 **(7.4)**	-----	100	14	4	0
"	8 **(8.0)**	-----	99	14	4	0
"	10 **(9.2)**	$Ca_{1.5}Si_{1.0}$	98	12	4	0
0.43	4 **(5.9)**	$Fe_{1.0}Si_{1.0}$	85	15	4	26
"	6 **(7.3)**	$Fe_{1.4}Si_{1.0}$	69	14	4	0.3
"	8 **(7.7)**	$Ca_{0.1}Fe_{1.2}Si_{1.0}$	65	12	4	0.4
"	10 **(9.2)**	$Mg_{0.1}Ca_{0.2}Fe_{1.5}Si_{1.0}$	63	10	3	0.3
0.86	4 **(4.0)**	$Fe_{1.8}Si_{1.0}$	80	14	4	47
"	6 **(7.2)**	$Fe_{1.9}Si_{1.0}$	56	13	4	0.5
"	8 **(7.8)**	$Ca_{0.1}Fe_{1.6}Si_{1.0}$	46	10	4	1.1
"	10 **(9.5)**	$Mg_{0.1}Ca_{0.2}Fe_{1.5}Si_{1.0}$	44	5	2	0.6
1.71	4 **(4.1)**	$Fe_{3.0}Si_{1.0}$	43	14	4	2
"	6 **(6.9)**	$Ca_{0.1}Fe_{2.7}Si_{1.0}$	36	12	4	0.9
"	8 **(7.5)**	$Ca_{0.1}Fe_{2.3}Si_{1.0}$	27	8	3	0.3
"	10 **(9.7)**	$Mg_{0.1}Ca_{0.3}Fe_{2.3}Si_{1.0}$	28	2	1	4.1
3.42	4 **(4.9)**	$Fe_{4.8}Si_{1.0}$	29	14	4	0.8
"	6 **(6.8)**	$Fe_{4.2}Si_{1.0}$	19	13	4	0.2
"	8 **(7.6)**	$Ca_{0.1}Fe_{3.8}Si_{1.0}$	10	6	3	0.1
"	10 **(8.9)**	$Mg_{0.1}Ca_{0.2}Fe_{3.8}Si_{1.0}$	10	2	1	0.2

*Based on SiO_2, Ca, and Mg left in solution.

Table 55
The Effect of Ferric Ion on Silica Solubility.
Minimum Silica Solubility As a Function of pH and Mole Ratios.

Additive:SiO_2 Mole Ratio	**pH**	**Minimum Solubility**
0.0	**9.2**	**98**
0.43	**9.2**	**63**
0.86	**9.5**	**44**
1.71	**7.5**	**27**
3.42	**7.6**	**10**

The Effect of Copper Ion on Silica Solubility in LANL Water

Copper at mole ratios of 0.0, 0.43, 0.86, 1.71, and 3.42 was added to LANL tap water. The contents of four beakers containing each solution were adjusted to initial pH values of 4.0, 6.0, 8.0, and 10.0, respectively. Copper's effect on silica solubility is shown in Figure 57.

The amount of silica remaining in solution is clearly a function of both the mole ratio of copper added and pH. Silica in solution was essentially unchanged up to a pH of 5.8. Between pH 5.8 and 7.5 a marked removal of silica is observed in all the copper solutions. At pHs greater than 7.5 a resolubilization of silica occurred in the MR 0.43 solution. Silica solubilities in the MR 0.86, 1.71, and 3.42 solutions continued to decrease as the pH increased above 7.5, to a low value of 18 mg/L.

The chemical analyses of each solution in this experiment are shown in Table 56. Minimum silica solubilities for each mole ratio metal addition seen in Figure 57 are given in Table 57.

Solutions with pHs greater than 7.4 show very low copper concentrations remaining in solution. Copper, as well as zinc, was investigated to study typical silica reactions in order to get an idea of SiO_2 behavior with "regular" metallic ions.

Silica seems to show anionic behavior with copper. Some hypothetical solid phase compositions based on loss of ions from solution are shown in Table 56.

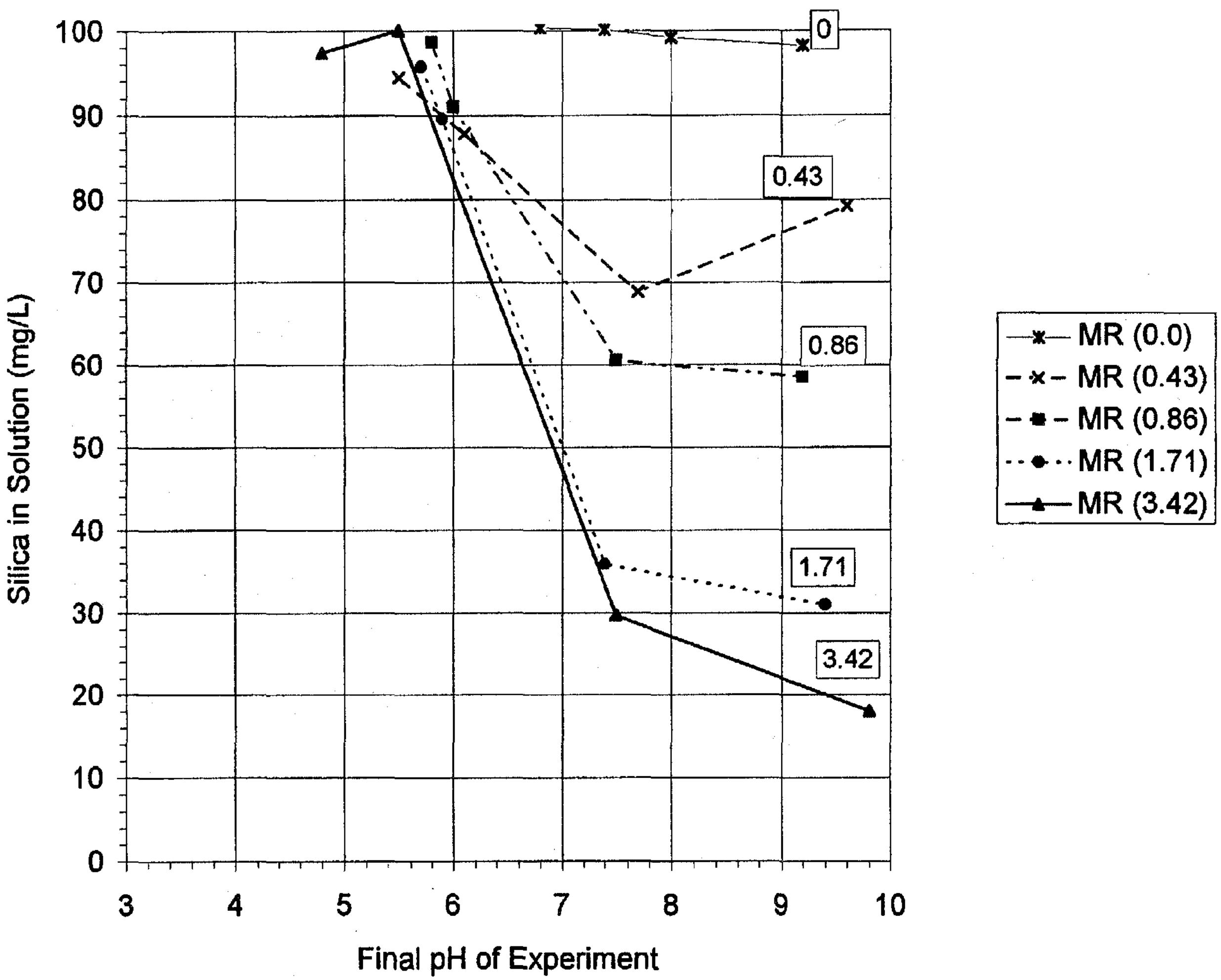

Figure 57. Effect of Copper and pH on the Solubility of Silica in Water. Copper:Silica MRs = (0), (0.43), (0.86), (1.71), (3.42).

Table 56
The Effect of Added Copper on Silica Solubility.
DATA

Additive:SiO_2 Mole Ratio	**pH Initial (Final)**	**Composition of Hypothetical Solid***	**Final Concentration (mg/L)**			
			SiO_2	**Ca**	**Mg**	**Cu**
0.0	4 **(6.8)**	-----	100	14	4	0
"	6 **(7.4)**	-----	100	14	4	0
"	8 **(8.0)**	-----	99	14	4	0
"	10 **(9.2)**	$Ca_{1.5}Si_{1.0}$	98	12	4	0
0.43	4 **(5.5)**	$Cu_{4.5}Si_{1.0}$	95	14	4	21
"	6 **(6.1)**	$Cu_{2.8}Si_{1.0}$	88	14	4	10
"	8 **(7.7)**	$Cu_{1.4}Si_{1.0}$	69	14	4	0.3
"	10 **(9.6)**	$Mg_{0.1}Ca_{0.1}Cu_{2.0}Si_{1.0}$	79	13	3	0.3
0.86	4 **(5.8)**	$Cu_{40.7}Si_{1.0}$	99	15	4	48
"	6 **(6.0)**	$Cu_{5.9}Si_{1.0}$	91	14	4	35
"	8 **(7.5)**	$Cu_{2.2}Si_{1.0}$	61	14	4	2
"	10 **(9.2)**	$Mg_{0.1}Ca_{0.1}Cu_{2.1}Si_{1.0}$	59	12	3	0.6
1.71	4 **(5.7)**	$Cu_{22.0}Si_{1.0}$	96	15	4	88
"	6 **(5.9)**	$Cu_{9.6}Si_{1.0}$	90	14	4	79
"	8 **(7.4)**	$Cu_{2.6}Si_{1.0}$	36	14	4	3
"	10 **(9.4)**	$Mg_{0.1}Ca_{0.1}Cu_{2.5}Si_{1.0}$	31	11	2	1
3.42	4 **(4.8)**	$Cu_{52.3}Si_{1.0}$	97	15	4	196
"	6 **(5.5)**	-----	109	14	4	179
"	8 **(7.5)**	$Cu_{4.7}Si_{1.0}$	30	13	4	12
"	10 **(9.8)**	$Mg_{0.1}Ca_{0.1}Cu_{4.1}Si_{1.0}$	18	8	2	3

*Based on SiO_2, Ca, and Mg left in solution.

Table 57
The Effect of Copper on Silica Solubility.
Minimum Silica Solubility As a Function of pH and Mole Ratios.

Additive:SiO_2 Mole Ratio	**pH**	**Minimum Solubility**
0.0	**9.2**	**98**
0.43	**7.7**	**69**
0.86	**9.2**	**59**
1.71	**9.4**	**31**
3.42	**9.8**	**18**

The Effect of Zinc Ion on Silica Solubility in LANL Water

The effect of zinc ions and pH on the silica content in LANL tap water is shown in Figure 58. Five solutions with different mole ratios of zinc to silica were prepared: 0.0, 0.43, 0.86, 1.71, and 3.42. The contents of four beakers containing each solution were adjusted to the following pH values respectively: 4.0, 6.0, 8.0, and 10.0 using nitric acid or sodium hydroxide.

The amount of silica remaining in solution is clearly a function of both the mole ratio of zinc added and pH. Silica content in solution was essentially unchanged up to a pH of 6.0. Between pH 6.0 and 7.0, a definite removal of silica was observed in all the zinc solutions. Silica solubilities in the zinc solutions continued to decrease as the pH increased above 7.0.

The chemical analyses of each solution in this experiment are shown in Table 58. Minimum silica solubilities for each mole ratio metal addition seen in Figure 58 are given in Table 59.

Solutions with pHs of 6.9 or greater show very low zinc concentrations remaining in solution. Again, some hypothetical solid phase compositions are shown. Zinc has, in the case of the MR 3.42, removed SiO_2 below the 10 ppm level at a pH as low as 7.0. Zinc is probably reacted with, and is an insolubilizer for, SiO_2 under these conditions.

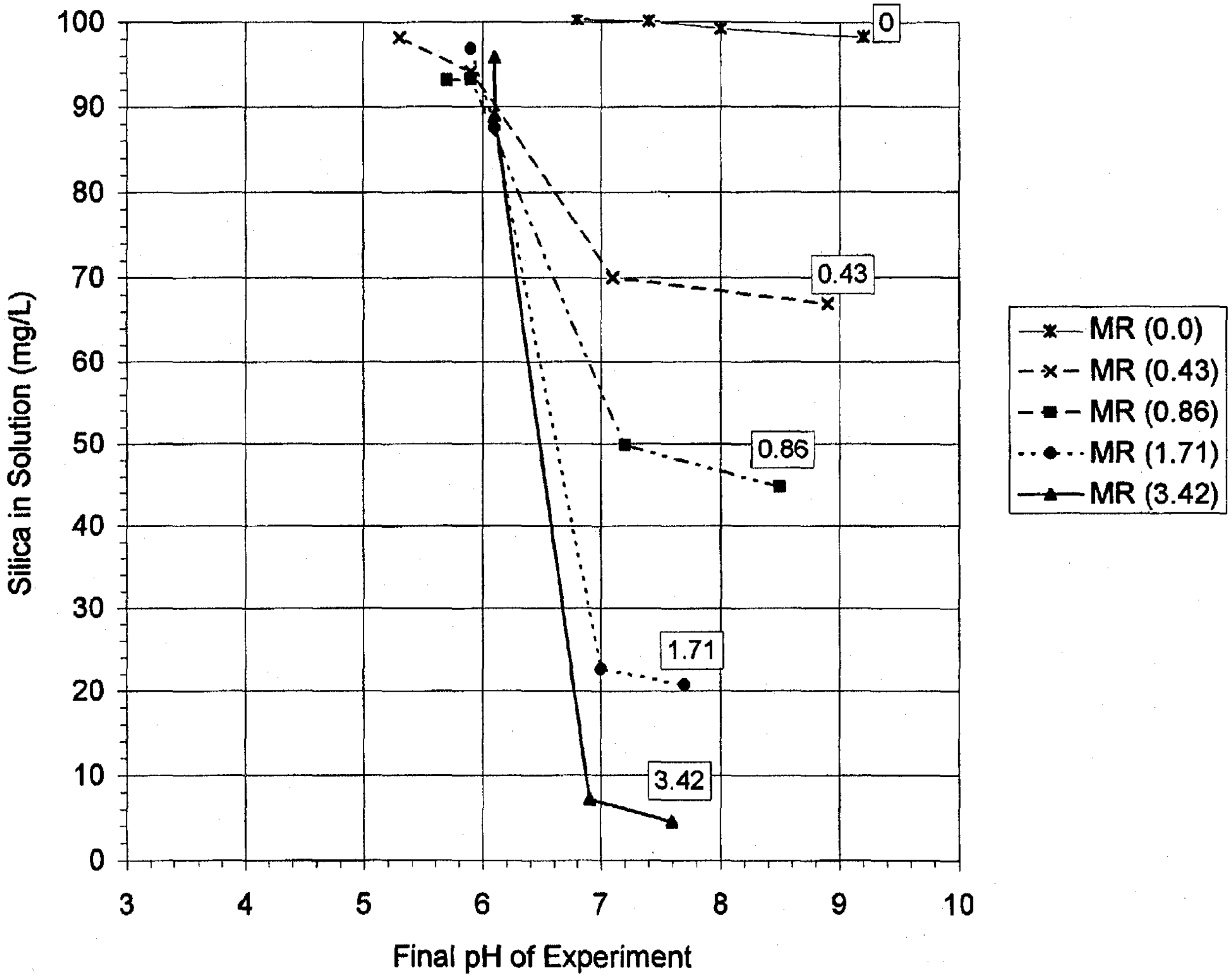

Figure 58. Effect of Zinc and pH on the Solubility of Silica in Water.
Zinc:Silica MRs = (0), (0.43), (0.86), (1.71), (3.42).

Table 58
The Effect of Added Zinc on Silica Solubility.
DATA

Additive:SiO_2 Mole Ratio	**pH Initial (Final)**	**Composition of Hypothetical Solid***	**Final Concentration (mg/L)**			
			SiO_2	**Ca**	**Mg**	**Zn**
0.0	4 **(6.8)**	-----	100	14	4	0
“	6 **(7.4)**	-----	100	14	4	0
“	8 **(8.0)**	-----	99	14	4	0
“	10 **(9.2)**	$Ca_{1.5}Si_{1.0}$	98	12	4	0
0.43	4 **(5.3)**	$Ca_{0.8}Zn_{0.9}Si_{1.0}$	98	13	4	50
“	6 **(5.9)**	$Ca_{0.3}Zn_{1.1}Si_{1.0}$	94	13	4	40
“	8 **(7.1)**	$Ca_{0.1}Zn_{1.4}Si_{1.0}$	70	12	4	2
“	10 **(8.9)**	$Mg_{0.1}Ca_{0.1}Zn_{1.3}Si_{1.0}$	67	11	3	0.5
0.86	4 **(5.7)**	$Ca_{0.2}Zn_{2.4}Si_{1.0}$	93	13	4	75
“	6 **(5.9)**	$Zn_{3.9}Si_{1.0}$	93	14	4	63
“	8 **(7.2)**	$Ca_{0.1}Zn_{1.7}Si_{1.0}$	50	12	4	1
“	10 **(8.5)**	$Mg_{0.1}Ca_{0.1}Zn_{1.6}Si_{1.0}$	45	10	2	0.3
1.71	4 **(5.9)**	$Zn_{22.7}Si_{1.0}$	97	14	4	112
“	6 **(6.1)**	$Ca_{0.1}Zn_{7.1}Si_{1.0}$	88	13	4	93
“	8 **(7.0)**	$Zn_{2.2}Si_{1.0}$	23	13	4	1
“	10 **(7.7)**	$Ca_{0.1}Zn_{2.2}Si_{1.0}$	21	10	3	1
3.42	4 **(6.1)**	$Zn_{44.3}Si_{1.0}$	96	14	4	180
“	6 **(6.1)**	$Ca_{0.1}Zn_{16.2}Si_{1.0}$	89	13	4	179
“	8 **(6.9)**	$Zn_{3.7}Si_{1.0}$	7	13	4	3
“	10 **(7.6)**	$Zn_{3.6}Si_{1.0}$	5	12	3	1

*Based on SiO_2, Ca, and Mg left in solution.

Table 59
The Effect of Zinc on Silica Solubility.
Minimum Silica Solubility As a Function of pH and Mole Ratios.

Additive:SiO_2 Mole Ratio	**pH**	**Minimum Solubility**
0.0	9.2	98
0.43	8.9	67
0.86	8.5	45
1.71	7.7	21
3.42	7.6	5

Summary - Metals Part 1

The Metals Part 1 work showed that the silica removal capability of each of the metals used is sharply pH dependent. Each metal ion showed a characteristic pH value of the hydrolysis reaction at which silica removal began. The following listing, developed by inspection of Figures 52 through 58, shows an order of pH at which a substantial loss of silica was first noted in the solutions with various metal ion additions.

Metal	pH
Ti^{+4}	3.7
Fe^{+3}	4.0
Al^{+3}	6.2
Zn^{+2}	6.9
Cu^{+2}	7.4
Mg^{+2}	9.0
Ca^{+2}	---

It may be noted in the preceding list that hydrolysis and silica removal takes place at a lower pH with the quadrivalent and trivalent metal cations than for the divalent cations.

Figure 59 summarizes, at a pH of 9.0, the relative effectiveness of the various cations in removing silica from the LANL tap water in the Metals Part 1 flocculation work.

Inspection of Figure 59 shows that each of the metals, except calcium, reduces silica content, as the mole ratio of metal to silica increased. By extrapolation of the curves in Figure 59, solutions with 0 mg/l silica would be reached with all the metal solutions (except calcium) between mole ratios of 3.4 to 6.0.

The qualitative order of effectiveness as seen in Figure 59 for silica removal at pH 9.0 and a mole ratio of 2.0 would be:

Al > Zn > Ti > Fe (III) > Cu > Mg > Ca

Extrapolation of the titanium silica content curve in Figure 59 indicates that at titanium additions greater than MR 2.4, it might be one of the more effective metals for silica removal. Titanium does not show a marked pH dependence on its effectiveness in silica insolubilization (Figure 55). However, its effectiveness is sharply dependent on mole ratio of titanium to silica. At mole ratio 2.27 the silica is removed to 12 mg/L at pH 7.4.

It is important to note that the curves shown in Figure 59 are similar and give a fair description of the behavior of the cations used, except for magnesium. The reason is that magnesium is most effective as a silica remover at pH values greater than 9.0. The Metals Part 1 work showed the influence of pH and of additions of metals on silica solubility. These results were used as a guide to the Metals Part 2 work.

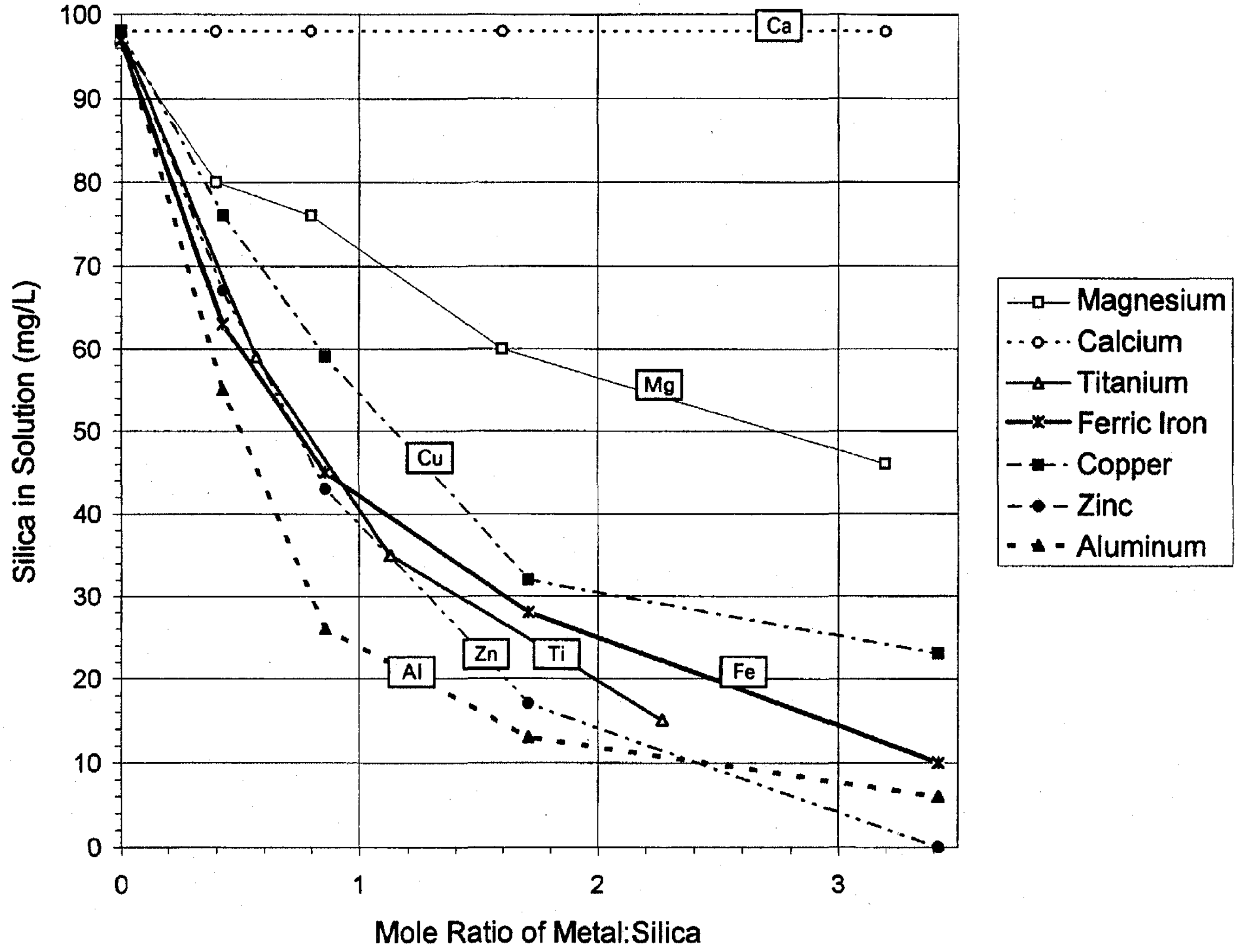

Figure 59. Effect of Metal Ions on the Solubility of Silica in Water.
Final pH of Solution: 9.0.

3. Valence II and III Cations (Metals 2)

In the first part of the cation work the solubility of silica in the presence of added individual metal ions was determined.

In part 2 of the work the solubility of silica was determined in the presence of spinel-type metals of Valence II and III hydrous oxide flocs. Simultaneously, the effect of the individual metals on solubility was also determined.

The spinel type hydrous oxides combinations were $MgO \cdot Al_2O_3$, $MgO \cdot Fe_2O_3$, $CaO \cdot Al_2O_3$, $CaO \cdot Fe_2O_3$, $FeO \cdot Al_2O_3$, $FeO \cdot Fe_2O_3$, $ZnO \cdot Al_2O_3$, and $ZnO \cdot Fe_2O_3$. The experiments were performed in standard jar-test equipment, as described in Appendix H. Table 60 presents the mole ratios and the pH of the solutins used in the Part 2 metals work.

The variables used were

- The mole ratios of the two metals to each other
- Total metals to silica
- pH

Table 60
Metals Studied for Their Effect on Silica Solubilities in LANL Tapwater
—Metals 2—
Valence II Metal:Valence III Metal:Silicon Ratios

II + III Valence Metal Mixtures			
Figure	**Me(II):Me(III):SiO_2**	Theoretical Mole Ratio **Actual Mole Ratio**	**Initial pH of Solution**
60	Mg:Fe(III):Si	(2:0:1) (1:1:1) (0:2:1) **(1.92:0:1) (0.96:0.83:1) (0:1.65:1)**	6, 8, 10
61	Mg:Fe(III):Si	(4:0:1) (2:2:1) (0:4:1) **(3.84:0:1) (1.92:1.65:1) (0:3.31:1)**	6, 8, 10
62	Mg:Al:Si	(2:0:1) (1:1:1) (0:2:1) **(1.92:0:1) (0.96:0.87:1) (0:1.75:1)**	6, 8, 10
63	Mg:Al:Si	(4:0:1) (2:2:1) (0:4:1) **(3.84:0:1) (1.92:1.75:1) (0:3.50:1)**	6, 8, 10
64	Ca:Fe(III):Si	(2:0:1) (1:1:1) (0:2:1) **(1.89:0:1) (0.95:0.83:1) (0:1.65:1)**	6, 8, 10
65	Ca:Fe(III):Si	(4:0:1) (2:2:1) (0:4:1) **(3.78:0:1) (1.89:1.65:1) (0:3.31:1)**	6, 8, 10
66	Ca:Al:Si	(2:0:1) (1:1:1) (0:2:1) **(1.89:0:1) (0.95:0.87:1) (0:1.75:1)**	6, 8, 10
67	Ca:Al:Si	(4:0:1) (2:2:1) (0:4:1) **(3.78:0:1) (1.89:1.75:1) (0:3.50:1)**	6, 8, 10
68	Fe(II):Fe(III):Si	(2:0:1) (1:1:1) (0:2:1) **(2:0:1) (1:0.83:1) (0:1.65:1)**	6, 8, 10
69	Fe(II):Fe(III):Si N_2 Sparged Water	(2:0:1) (1:1:1) (0:2:1) **(2:0:1) (1:0.83:1) (0:1.65:1)**	6, 8, 10
70	Fe(II):Fe(III):Si	(4:0:1) (2:2:1) (0:4:1) **(4:0:1) (2:1.65:1) (0:3.31:1)**	6, 8, 10
71	Fe(II):Fe(III):Si N_2 Sparged Water	(4:0:1) (2:2:1) (0:4:1) **(4:0:1) (2:1.65:1) (0:3.31:1)**	6, 8, 10
72	Fe(II):Al:Si	(2:0:1) (1:1:1) (0:2:1) **(2:0:1) (1:0.87:1) (0:1.75:1)**	6, 8, 10
73	Fe(II):Al:Si N_2 Sparged Water	(2:0:1) (1:1:1) (0:2:1) **(2:0:1) (1:0.87:1) (0:1.75:1)**	6, 8, 10
74	Fe(II):Al:Si	(4:0:1) (2:2:1) (0:4:1) **(4:0:1) (2:1.75:1) (0:3.50:1)**	6, 8, 10
75	Fe(II):Al:Si N_2 Sparged Water	(4:0:1) (2:2:1) (0:4:1) **(4:0:1) (2:1.75:1) (0:3.50:1)**	6, 8, 10
76	Zn:Fe(III):Si	(2:0:1) (1:1:1) (0:2:1) **(1.88:0:1) (0.94:0.83:1) (0:1.65:1)**	6, 8, 10
77	Zn:Fe(III):Si	(4:0:1) (2:2:1) (0:4:1) **(3.76:0:1) (1.88:1.65:1) (0:3.31:1)**	6, 8, 10
78	Zn:Al:Si	(2:0:1) (1:1:1) (0:2:1) **(1.88:0:1) (0.94:0.87:1) (0:1.75:1)**	6, 8, 10
79	Zn:Al:Si	(4:0:1) (2:2:1) (0:4:1) **(3.76:0:1) (1.88:1.75:1) (0:3.50:1)**	6, 8, 10

Effect of Magnesium and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio $\cong$ (2:1)

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (1.92:0 :1) (0.96:0.83:1) (0:1.65:1)

The effect of magnesium and ferric ions (metals:silica MR $\cong$ 2) on the silica solubility in LANL tap water is graphically shown in Figure 60. Data for each solution is given in Table 61.

All three mole ratios exhibited greater silica removal as the pH increased. The negative slope of the magnesium alone (2:0:1) solution suggests 0 would be reached at pH 10.4. The slope of the silica content line of the ferric alone (0:2:1) solution seems to be anomalous and does not extrapolate to 0 in the pHs shown.

The magnesium alone (2:0:1) solution showed no removal of silica at pH 7.6 and below. A large loss of silica from solution occurred at pH 8.9. The slope of this line indicates that it would intercept the 0 mg/L SiO_2 in solution at pH 9.7. Silica was insolubilized with a corresponding insolubilization of magnesium in this solution.

The magnesium/ferric mix (1:1:1) solution demonstrated silica removal at pH 7.5 down to 58 mg/L. Increasing the pH to 9.5 showed enhanced silica removal effectiveness. Extrapolation of this curve would intersect 0 mg/L SiO_2 at pH 10.4 if no resolution of silica occurred. The removal of silica from the pH 7.4 and 7.5 solutions is probably due to the ferric ion. No magnesium was missing from these solutions. The pH 9.5 solution, which showed the lowest silica solubility, had lost all the iron and most of the added magnesium from solution.

At pH 7.6 the concentration of silica remaining in the ferric alone (0:2:1) solution was 36 mg/L. The (0:2:1) solution was the most effective at removing silica up to pH 9.0. Above pH 9.0 the data suggest that both the (2:0:1) and the (1:1:1) solutions would have equal or greater effect in removing silica than the ferric alone.

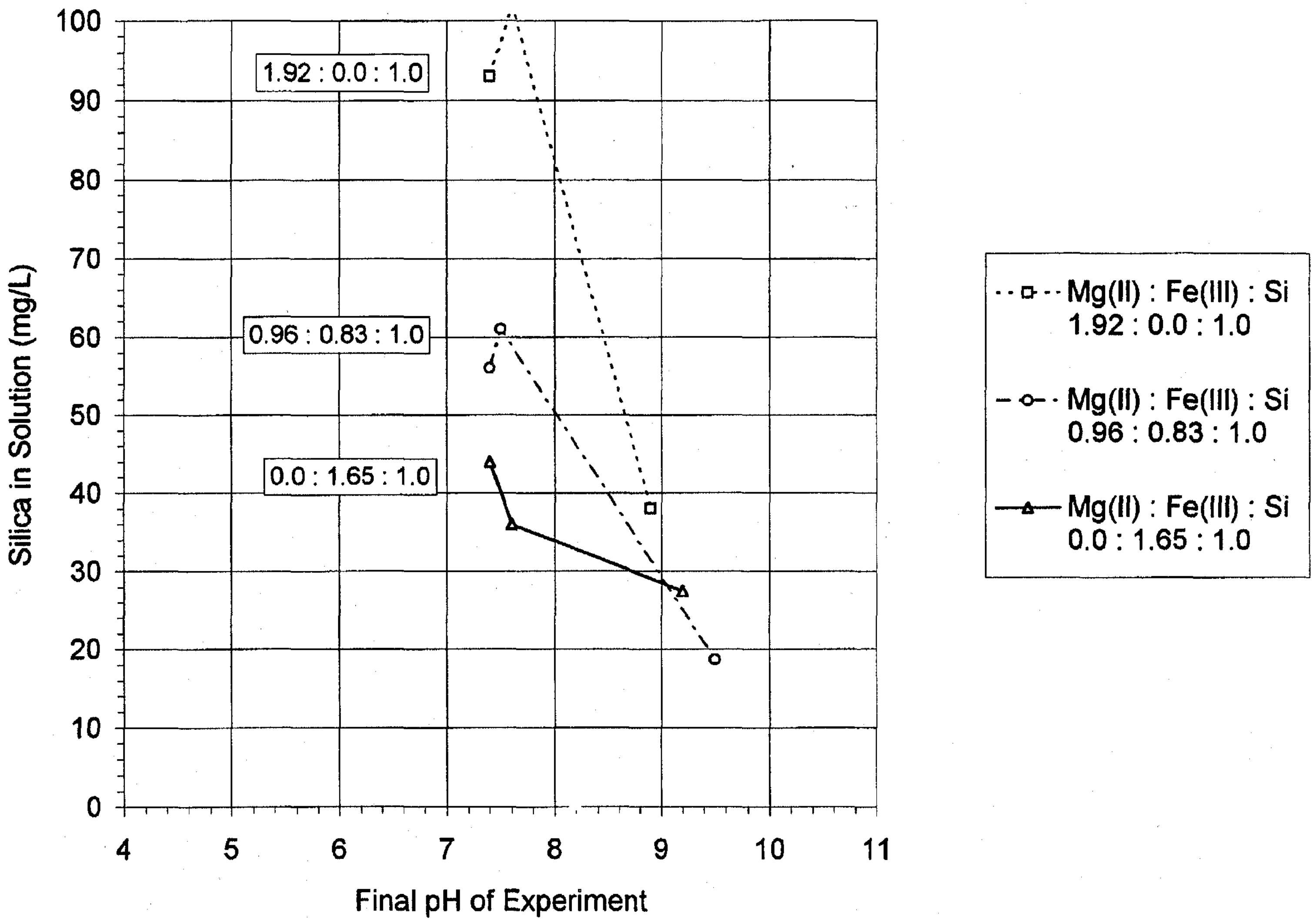

Figure 60. Effect of Magnesium, Ferric, and pH on the Solubility of Silica in Water.

Mg(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 2

Table 61
Data from the Magnesium and Ferric Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1.
Concentration Units = mg/L.

Mg(II):Fe(III):SiO_2 Mole Ratios Hypothetical **(Actual)**			
	2:0:1 **(1.92:0:1)**	1:1:1 **(0.96:0.83:1)**	0:2:1 **(0:1.65:1)**
Initial pH: 6.0			
SiO_2	93	56	44
Ca	14	13	14
Mg	75	38	5
Fe	0	0.1	0.1
Final pH	7.4	7.4	7.4
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Mg_{0.13}Ca_{0.04}Fe(III)_{2.09}$	$Ca_{0.03}Fe(III)_{3.16}$
Initial pH: 8.0			
SiO_2	102	61	36
Ca	15	13	10
Mg	79	41	4
Fe	0	0.12	0
Final pH	7.6	7.5	7.6
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Ca_{0.05}Fe(III)_{2.42}$	$Ca_{0.03}Fe(III)_{2.72}$
Initial pH: 10.0			
SiO_2	38	18.7	27.5
Ca	13	8	4
Mg	52	8	2
Fe	0	0	0.1
Final pH	8.9	9.5	9.2
Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{1.08}Ca_{0.03}$	$Mg_{1.07}Ca_{0.12}Fe(III)_{1.05}$	$Mg_{0.08}Ca_{0.14}Fe(III)_{2.38}$

Effect of Magnesium and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)

Theoretical MR = (4:0:1) (2:2:1) (0:4:1)
Actual MR = (3.84:0 :1) (1.92:1.65:1) (0:3.31:1)

The effect of magnesium and ferric ions (metals:silicon MR ≅ 4) on the silica solubility in LANL tap water is graphically shown in Figure 61. Data for each solution is given in Table 62.

The shapes of the curves in this set of experiments (MR ≅ 4) are very similar to the curves shown in Figure 60 (MR ≅ 2). The concentrations of silica remaining in solution are lower due to twice the metal ratio being added to the solutions. Silica removal is enhanced as the pH increases in the magnesium alone (4:0:1) solution and in the magnesium/ferric mix (2:2:1) solution. The ferric alone (0:4:1) solution appears to reach a maximum silica removal efficiency at pH 7.7.

The magnesium alone (4:0:1) solution shows no removal of silica below pH 7.5. A large removal of silica from solution occurred at pH 8.8. The slope suggests that this line, if continued to pH 9.0, would intersect with 0 mg/L SiO_2 in solution. Silica in this solution insolubilized with a corresponding insolubilization of magnesium.

The magnesium/ferric mix (2:2:1) solution demonstrated silica removal at pH 7.3 down to 39 mg/L. Increasing the pH to 9.2 showed enhanced silica removal effectiveness. Extension of this curve would intersect 0 mg/L SiO_2 at pH 9.5. The removal of silica from the pH 7.3 and 7.4 solutions is entirely due to the ferric ion. No magnesium was missing from these solutions. The pH 9.2 solution, which showed the lowest silica solubility, had lost all the iron and most of the added magnesium from solution.

At pH 7.3 the concentration of silica remaining in the ferric alone (0:4:1) solution was 20 mg/L. The (0:4:1) solution was the most effective at removing silica up to pH 8.8. Above pH 8.8 the data suggest that both the (4:0:1) and the (2:2:1) solutions had equal or greater effect in removing silica than the ferric alone.

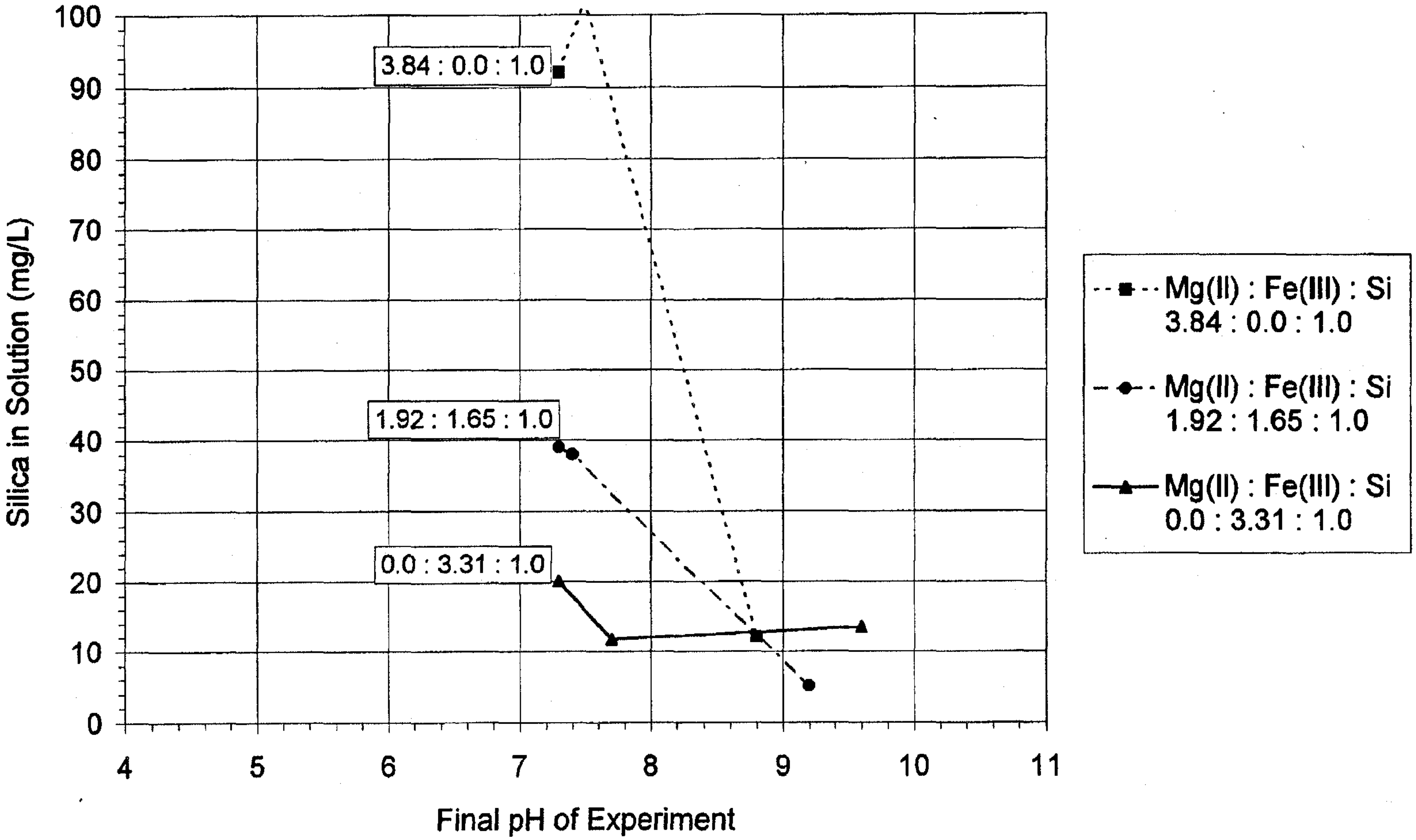

Figure 61. Effect of Magnesium, Ferric, and pH on the Solubility of Silica in Water.

Mg(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 4

Table 62
Data from the Magnesium and Ferric Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.
Concentration Units = mg/L.

Mg(II):Fe(III):SiO_2 Mole Ratios Hypothetical **(Actual)**			
	4:0:1 **(3.84:0:1)**	2:2:1 **(1.92:1.65:1)**	0:4:1 **(0:3.31:1)**
Initial pH: 6.0			
SiO_2	92	39	20
Ca	14	13	13
Mg	142	73	5
Fe	0	0.1	0.1
Final pH	7.3	7.3	7.3
Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{12.36}$	$Mg_{0.14}Ca_{0.03}Fe(III)_{2.87}$	$Ca_{0.02}Fe(III)_{4.23}$
Initial pH: 8.0			
SiO_2	102	38	12
Ca	15	13	4
Mg	157	74	2
Fe	0	0.1	0
Final pH	7.5	7.4	7.7
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Mg_{0.09}Ca_{0.03}Fe(III)_{2.82}$	$Mg_{0.06}Ca_{0.19}Fe(III)_{3.81}$
Initial pH: 10.0			
SiO_2	12	5	14
Ca	14	6	2
Mg	103	9	2
Fe	0	0	0.5
Final pH	8.8	9.2	9.6
Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{1.34}$	$Mg_{1.88}Ca_{0.14}Fe(III)_{1.75}$	$Mg_{0.06}Ca_{0.23}Fe(III)_{3.90}$

Effect of Magnesium and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (2:1)

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (1.92:0 :1) (0.96:0.87:1) (0:1.75:1)

The effect of magnesium and aluminum ions (metals:silicon MR ≅ 2) on the silica solubility in LANL tap water is shown in Figure 62. Data for each solution is given in Table 63.

Higher pHs favor the removal of silica from the magnesium only (2:0:1) solution and the magnesium/aluminum (1:1:1) solution.

The magnesium/aluminum (1:1:1) solution produced a straight line relating the silica remaining in solution to final pH. At pH 7.2 the silica concentration was 42 mg/L. The removal of silica from the pH 7.2 and 7.4 solutions is entirely due to the aluminum; aluminum was missing from these solutions. In the pH 9.8 solution only 8 mg/L silica, no aluminum, and a small amount of magnesium remained. The continuation of this slope implies that perhaps no silica would be found in solution at a pH of 10.4. In this (1:1:1) solution no resolubilization of silica or aluminum occurred. It seems probable, judging from these results, that a ternary compound (Mg-Al-Si) may have precipitated.

The aluminum alone (0:2:1) solution shows a minimum silica solubility at pH 8.0. The silica concentration was reduced to 21 mg/L at pH 7.2 in the aluminum alone (0:2:1) solution. Silica concentration was at a minimum of 10 mg/L in this solution at pH 8.0. A resolubilization of both silica and aluminum were noted in this solution at pH 9.8.

This data suggests that, at pHs greater than 9.4, the magnesium alone would be a greater influence on insolubilizing silica than the mixed magnesium/aluminum solutions or the aluminum alone solution.

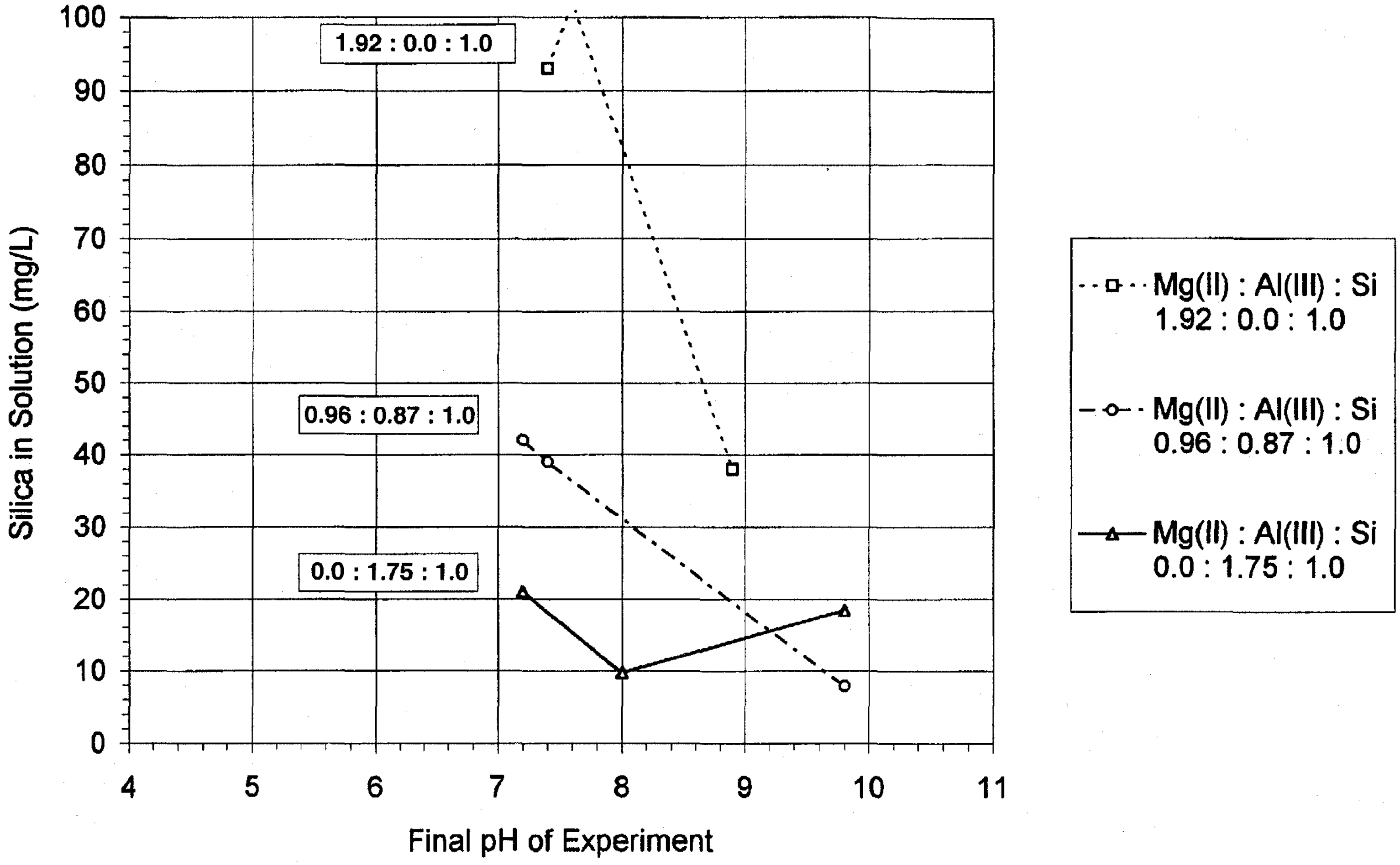

Figure 62. Effect of Magnesium, Aluminum, and pH on the Solubility of Silica in Water. Mg(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. **Metals:SiO_2 appx. = 2**

Table 63

Data from the Magnesium and Aluminum Ions Mixed Valence Metals Work.

Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1.

Concentration Units = mg/L.

Mg(II):Al(III):SiO$_2$ Mole Ratios Hypothetical **(Actual)**					
2:0:1 **(1.92:0:1)**		1:1:1 **(0.96:0.87:1)**		0:2:1 **(0:1.75:1)**	
Initial pH: 6.0					
SiO$_2$	93	SiO$_2$	42	SiO$_2$	21
Ca	14	Ca	14	Ca	14
Mg	75	Mg	38	Mg	5
Al	0	Al	0.7	Al	0.7
Final pH	7.4	Final pH	7.2	Final pH	7.2
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.10}Al_{1.59}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Al_{2.30}$
Initial pH: 8.0					
SiO$_2$	102	SiO$_2$	39	SiO$_2$	10
Ca	15	Ca	13	Ca	6
Mg	79	Mg	37	Mg	2
Al	0	Al	0.7	Al	1.5
Final pH	7.6	Final pH	7.4	Final pH	8.0
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.14}Ca_{0.03}Al_{1.50}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.06}Ca_{0.14}Al_{1.97}$
Initial pH: 10.0					
SiO$_2$	38	SiO$_2$	8	SiO$_2$	18
Ca	13	Ca	8	Ca	1
Mg	52	Mg	13	Mg	0.4
Al	0	Al	0	Al	26
Final pH	8.9	Final pH	9.8	Final pH	9.8
Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{1.08}Ca_{0.03}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.79}Ca_{0.11}Al_{0.97}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.10}Ca_{0.26}Al_{1.45}$

Effect of Magnesium and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)

Theoretical MR ≅	(4:0:1)	(2:2:1)	(0:4:1)
Actual MR =	(3.84:0 :1)	(1.92:1.75:1)	(0:3.50:1)

The effect of magnesium and aluminum ions (metals:silicon MR ≅ 4) on the silica solubility in LANL tap water is shown in Figure 63. Data for each solution is given in Table 64.

The effect of pH on the removal of silica from the magnesium alone (4:0:1) solution is again very noticeable. No removal of silica occurred at pH 7.5 and below. At pH 8.8 the silica had dropped to 12 mg/L from an initial concentration of 93 mg/L. The removal of silica from this solution coincided with the removal of some of the magnesium in solution.

The mixed magnesium/aluminum (2:2:1) and the aluminum alone (0:4:1) solutions exhibited powerful silica removal properties over the pH range 7.6-9.5. The aluminum (0:4:1) solution showed lower silica content than the magnesium/aluminum (2:2:1) solution at pHs up to 8.4. At pHs greater than 8.4 the magnesium/aluminum solution was more effective in silica removal. If extended to 0 silica, the pH would be approximately 8.9.

The magnesium/aluminum (2:2:1) solution reduced the silica to 17 mg/L at pH 7.2. This same solution at pH 9.1 contained essentially zero mg/L SiO_2. Though no resolubilization of silica is seen in this solution at pH 9.1, there is some resolubilization of aluminum, as seen in Table 64.

The silica concentration in the aluminum alone (0:4:1) solution was 10 mg/L at pH 7.1. The silica reached a minimum of 4 mg/L SiO_2 in this solution at pH 7.7. Above pH 7.7 resolubilization of both silica and aluminum occurred.

This data indicates that at pHs greater than 8.4 the magnesium/aluminum (2:2:1) solution would remove more silica than the aluminum alone (0:4:1) solution. Also at pHs greater than 8.9, it is suggested that both the magnesium alone (4:0:1) solution and the mixed magnesium/aluminum (2:2:1) solution would reduce the silica in solution to lowest concentrations at pH 9.0.

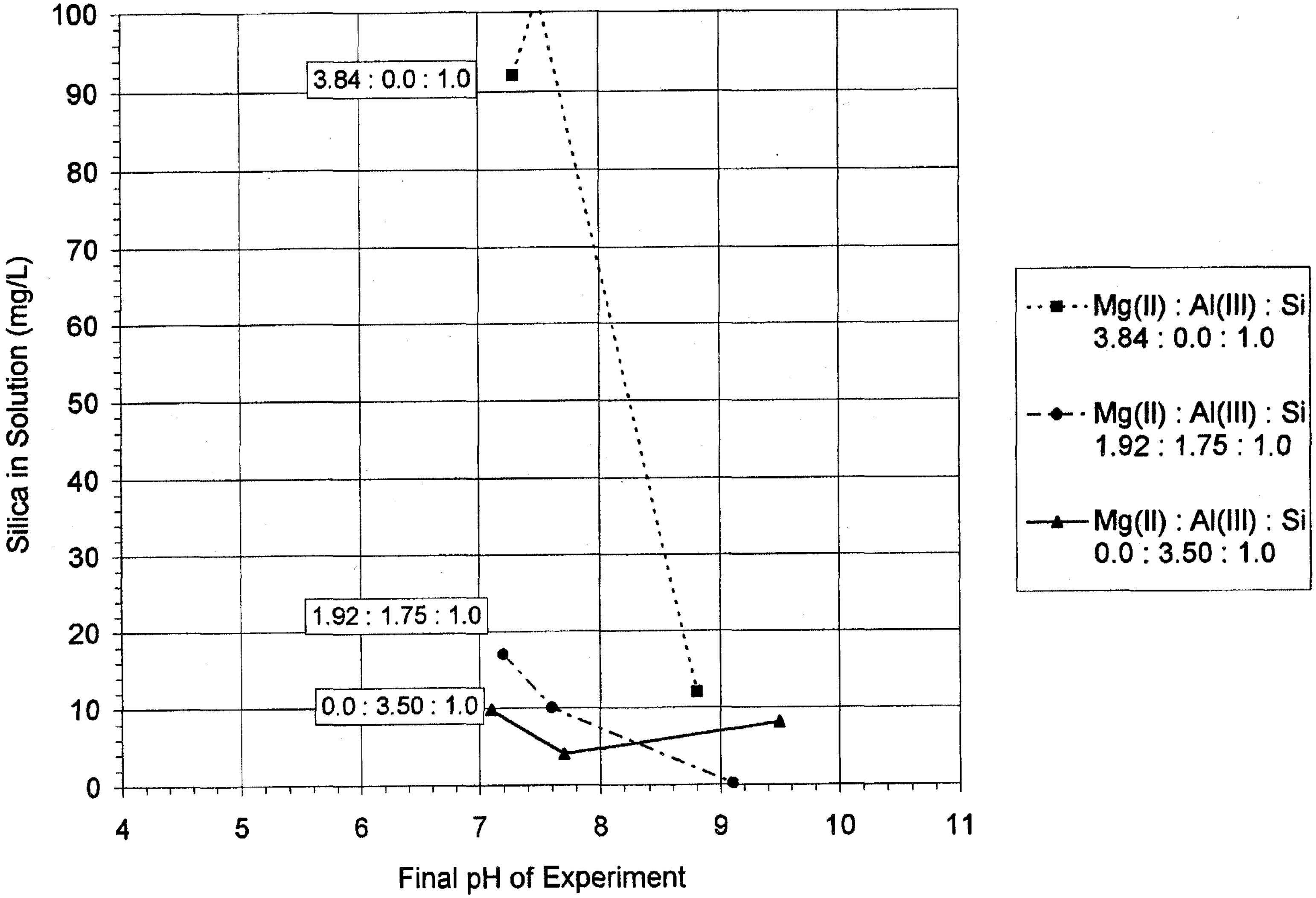

Figure 63. Effect of Magnesium, Aluminum, and pH on the Solubility of Silica in Water. Mg(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 4

Table 64

Data from the Magnesium and Aluminum Ions Mixed Valence Metals Work.

Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.

Concentration Units = mg/L.

Mg(II):Al(III):SiO_2 Mole Ratios Hypothetical **(Actual)**					
4:0:1 **(3.84:0:1)**		2:2:1 **(1.92:1.75:1)**		0:4:1 **(0:3.50:1)**	
Initial pH: 6.0					
SiO_2	92	SiO_2	17	SiO_2	10
Ca	14	Ca	13	Ca	14
Mg	142	Mg	64	Mg	5
Al	0	Al	0.8	Al	1.2
Final pH	7.3	Final pH	7.2	Final pH	7.1
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Mg_{12.36}$		$Mg_{0.39}Ca_{0.02}Al_{2.17}$		$Al_{3.99}$	
Initial pH: 8.0					
SiO_2	102	SiO_2	10	SiO_2	4
Ca	15	Ca	11	Ca	11
Mg	157	Mg	53	Mg	4
Al	0	Al	1	Al	0.5
Final pH	7.5	Final pH	7.6	Final pH	7.7
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
No Solid		$Mg_{0.69}Ca_{0.05}Al_{1.98}$		$Ca_{0.05}Al_{3.74}$	
Initial pH: 10.0					
SiO_2	12	SiO_2	0.2	SiO_2	8
Ca	14	Ca	8	Ca	2
Mg	103	Mg	3	Mg	2
Al	0	Al	7.1	Al	47
Final pH	8.8	Final pH	9.1	Final pH	9.5
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Mg_{1.34}$		$Mg_{1.94}Ca_{0.10}Al_{1.63}$		$Mg_{0.06}Ca_{0.21}Al_{2.70}$	

Effect of Calcium and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (2:1)

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (1.89:0 :1) (0.95:0.83:1) (0:1.65:1)

The effect of calcium and ferric ion (metals:silicon MR ≅ 2) on the silica solubility in LANL tap water is graphically shown in Figure 64. Data for each solution is given in Table 65.

This experiment clearly demonstrates that calcium has a very minimal effect on silica solubility in the pH range 7.0-9.6. The calcium alone (2:0:1) solution in the pH 9.6 solution only lost 2 mg/L SiO_2.

The calcium/ferric ion (1:1:1) mix reduced the silica to 56 mg/L at a pH of 7.3 and to 47 mg/L at pH 8.1. These silica concentrations are intermediate between the values noted in the calcium alone and ferric alone solutions.

The ferric ion alone (0:2:1) solution was the only effective remover of silica in this experiment, as it was in Metals 1. A minimum concentration of 28 mg/L SiO_2 was reached in the pH 9.2 solution.

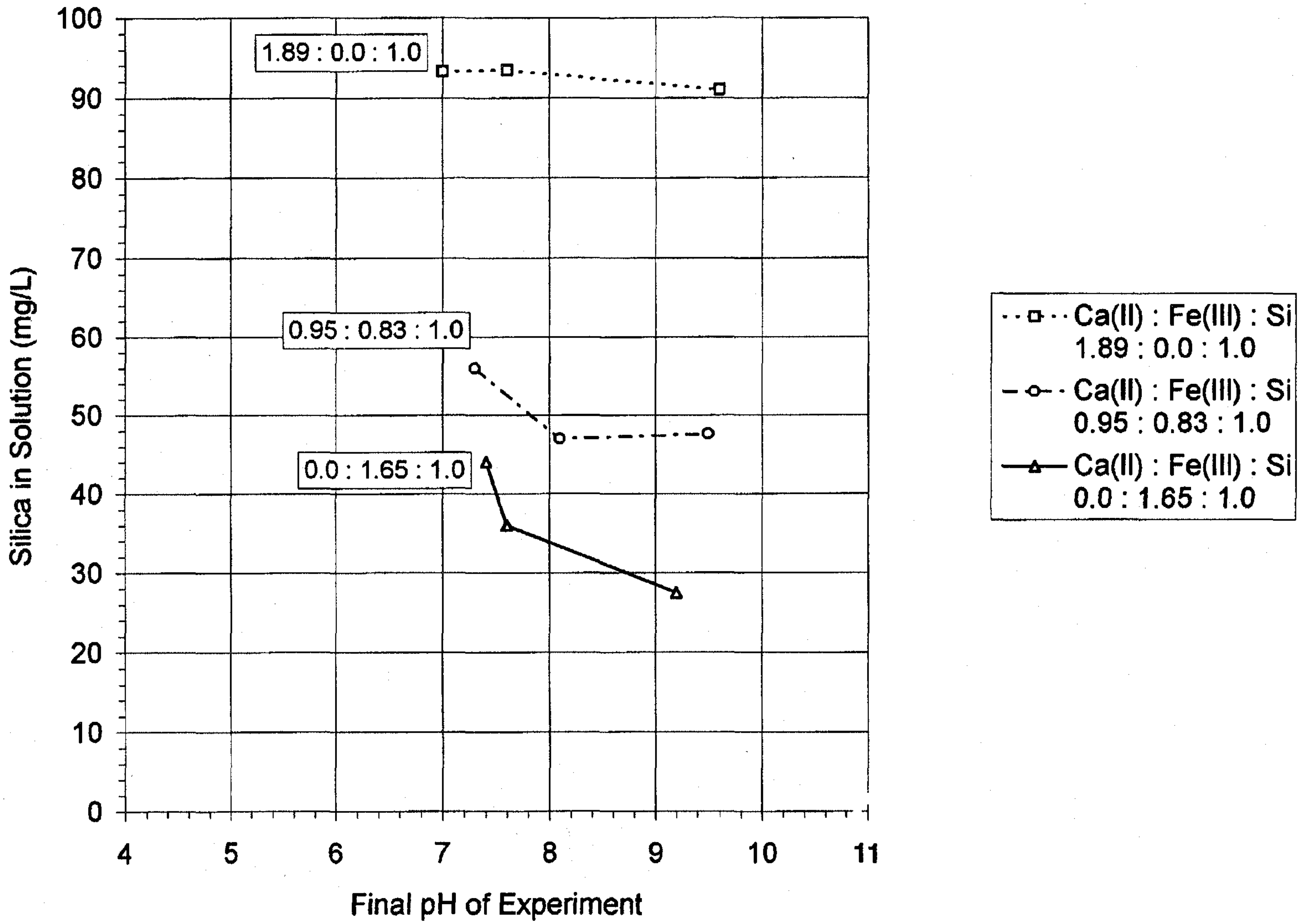

Figure 64. Effect of Calcium, Ferric, and pH on the Solubility of Silica in Water. Ca(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 2

Table 65
Data from the Calcium and Ferric Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1.
Concentration Units = mg/L.

	$Ca(II):Fe(III):SiO_2$ Mole Ratios Hypothetical **(Actual)**		
	2:0:1 **(1.89:0:1)**	1:1:1 **(0.95:0.83:1)**	0:2:1 **(0:1.65:1)**
Initial pH: 6.0			
SiO_2	93	56	44
Ca	125	69	14
Mg	5	5	5
Fe	0	0.1	0.1
Final pH	7.0	7.3	7.4
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Ca_{0.16}Fe(III)_{2.09}$	$Fe(III)_{3.16}$
Initial pH: 8.0			
SiO_2	93	47	36
Ca	122	62	10
Mg	4	3	4
Fe	0	0	0
Final pH	7.6	8.1	7.6
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Ca_{0.36}Fe(III)_{1.68}$	$Ca_{0.10}Fe(III)_{2.72}$
Initial pH: 10.0			
SiO_2	91	48	28
Ca	70	15	4
Mg	5	3	2
Fe	0	0.1	0.1
Final pH	9.6	9.5	9.2
Hypothetical Solid Composition Per $Si_{1.0}$	$Ca_{45.73}$	$Ca_{1.93}Fe(III)_{1.72}$	$Mg_{0.08}Ca_{0.23}Fe(III)_{2.38}$

Effect of Calcium and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)

Theoretical MR = (4:0:1) (2:2:1) (0:4:1)
Actual MR = (3.78:0 :1) (1.89:1.65:1) (0:3.31:1)

The effect of calcium and ferric ion (metals:silica MR ≅ 4) on the silica solubility in LANL tap water is graphically shown in Figure 65. Data for each solution is given in Table 66.

As before, the calcium alone (4:0:1) solution did not remove silica over the pH range 7.1-9.7. In the pH 9.7 solution, there was a very slight reduction in silica from 93 to 90 mg/L SiO_2.

The calcium/ferric ion (2:2:1) and the ferric ion alone (0:4:1) solutions both removed silica over the pH range 7.1-9.6. The ferric iron is the effective ion involved in silica removal from solution as before.

The calcium/ferric ion (2:2:1) solution reduced the silica in solution to 35 and 37 mg/L at pHs 7.1 and 7.5, respectively. As the pH increased to 8.6, the silica was removed to 23 mg/L SiO_2. No suggestion of silica resolubilization was seen in the data as the pH increased. This phenomenon was also seen in the (1:1:1) calcium/aluminum mix and the mixes of magnesium with both ferric ion and aluminum.

The ferric ion alone (0:4:1) solution was the most effective in removing silica from solution. At pH 7.3 the silica concentration was 20 mg/L. At pH 7.7 this was reduced to 12 mg/L. A slight resolubilization occurred in the pH 9.6 solution.

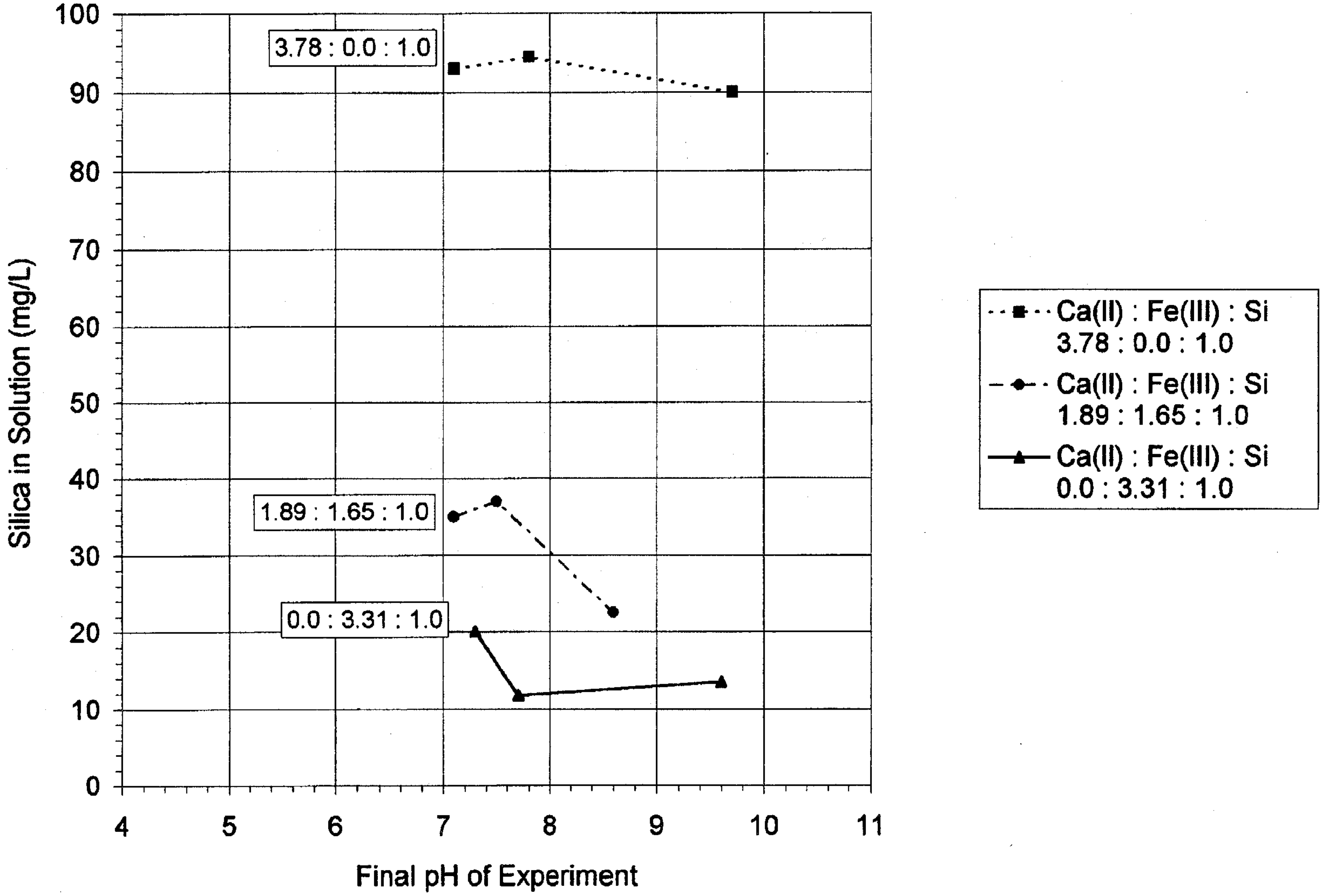

Figure 65. Effect of Calcium, Ferric, and pH on the Solubility of Silica in Water. Ca(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 4

Table 66
Data from the Calcium and Ferric Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.
Concentration Units = mg/L.

	$Ca(II):Fe(III):SiO_2$ Mole Ratios Hypothetical **(Actual)**		
	4:0:1 **(3.78:0:1)**	2:2:1 **(1.89:1.65:1)**	0:4:1 **(0:3.31:1)**
Initial pH: 6.0			
SiO_2	93	35	20
Ca	237	125	13
Mg	5	5	5
Fe	0	0.1	0.1
Final pH	7.1	7.1	7.3
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Ca_{0.15}Fe(III)_{2.67}$	$Ca_{0.02}Fe(III)_{4.22}$
Initial pH: 8.0			
SiO_2	94	37	12
Ca	241	121	4
Mg	4	4	2
Fe	0	0	0
Final pH	7.8	7.5	7.7
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Ca_{0.27}Fe(III)_{2.77}$	$Mg_{0.06}Ca_{0.19}Fe(III)_{3.81}$
Initial pH: 10.0			
SiO_2	90	23	14
Ca	179	57	2
Mg	5	4	2
Fe	0	0.1	0.5
Final pH	9.7	8.6	9.6
Hypothetical Solid Composition Per $Si_{1.0}$	$Ca_{34.98}$	$Ca_{1.58}Fe(III)_{2.21}$	$Mg_{0.06}Ca_{0.23}Fe(III)_{3.90}$

Effect of Calcium and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (2:1)

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (1.89:0 :1) (0.95:0.87:1) (0:1.75:1)

The effect of calcium and aluminum (metals:silicon MR ≅ 2) on the silica solubility in LANL tap water is graphically shown in Figure 66. Data for each solution is in Table 67.

The calcium alone (2:0:1) solution clearly demonstrates that calcium, as seen before, has a very minimal effect on silica solubility in the pH range 7.0-9.6. The calcium alone solution (2:0:1) in the pH 9.6 solution lost ≈ 55 mg/L calcium for a corresponding loss of 2 mg/L SiO_2. Silica and calcium are not forming an insoluble compound.

Both of the solutions with aluminum additions, (1:1:1) and (0:2:1), demonstrated silica removal capacity. As in the experiments with calcium/ferric ion mixes, it appears that aluminum, rather than calcium, is the effective silica removal agent.

The calcium/aluminum (1:1:1) solution reduced silica to 42 and 36 mg/L at pHs 7.5 and 7.6, respectively. As the pH increased to 9.4 the silica in solution was lowered to 26 mg/L SiO_2. This mixed calcium/aluminum solution showed no resolubilization of silica in the pH 9.4 solution.

The silica concentration was reduced to 21 mg/L at pH 7.2 in the aluminum alone (0:2:1) solution. Silica concentration was at a minimum of 10 mg/L in this solution at pH 8.0. Some resolubilization of both silica and aluminum were noted in this solution at pH 9.8.

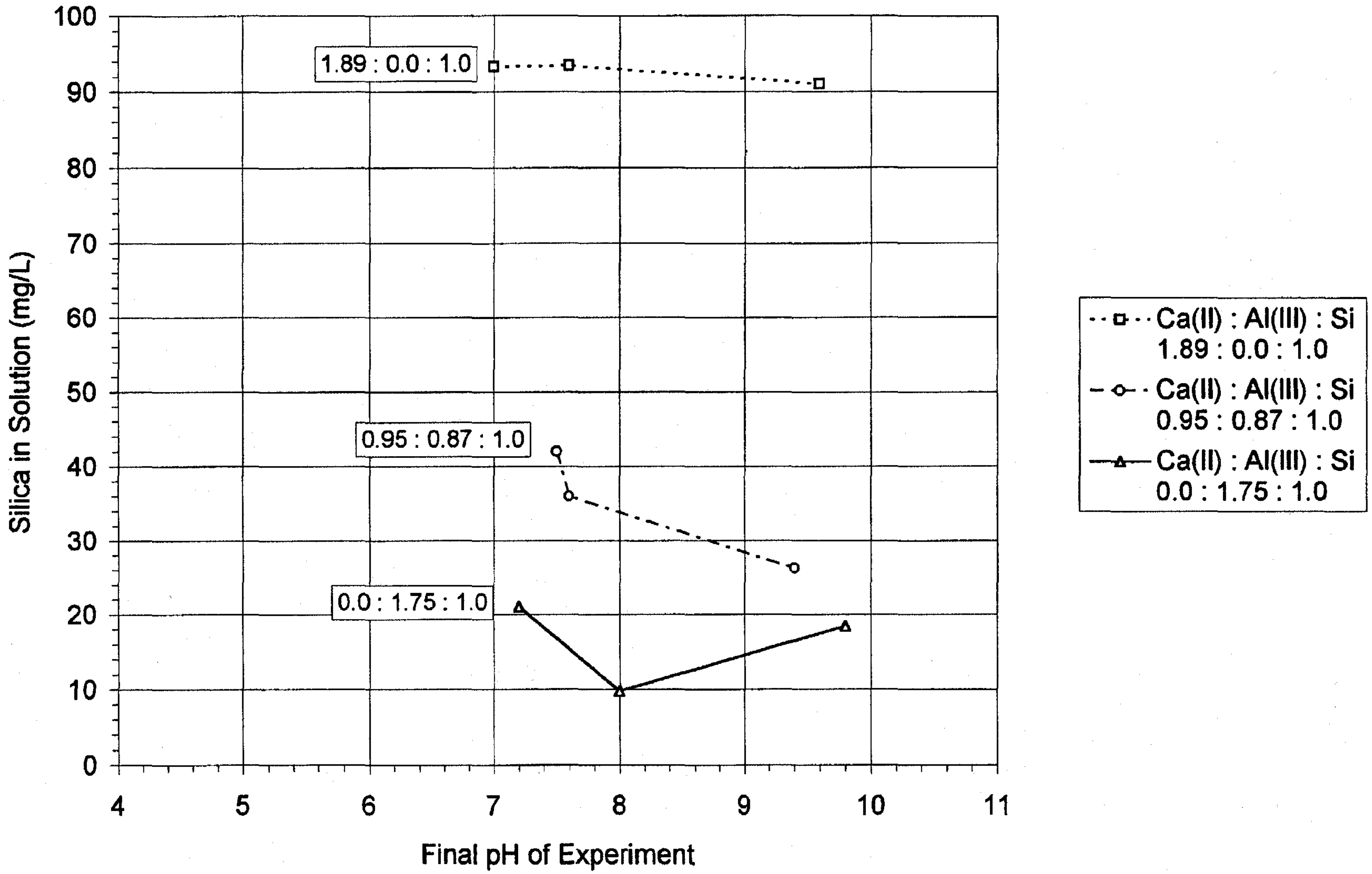

Figure 66. Effect of Calcium and Aluminum and pH on the Solubility of Silica in Water. Ca(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 2

Table 67
Data from the Calcium and Aluminum Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1.
Concentration Units = mg/L.

Ca(II):Al(III):SiO_2 Mole Ratios Hypothetical **(Actual)**					
2:0:1 **(1.89:0:1)**		1:1:1 **(0.95:0.87:1)**		0:2:1 **(0:1.75:1)**	
Initial pH: 6.0					
SiO_2	93	SiO_2	42	SiO_2	21
Ca	125	Ca	70	Ca	14
Mg	5	Mg	5	Mg	5
Al	0	Al	1	Al	1
Final pH	7.0	Final pH	7.5	Final pH	7.2
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
No Solid		$Ca_{0.09}Al_{1.59}$		$Al_{2.30}$	
Initial pH: 8.0					
SiO_2	93	SiO_2	36	SiO_2	10
Ca	122	Ca	64	Ca	6
Mg	4	Mg	4	Mg	2
Al	0	Al	0.1	Al	2
Final pH	7.6	Final pH	7.6	Final pH	8.0
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
No Solid		$Ca_{0.24}Al_{1.44}$		$Mg_{0.06}Ca_{0.14}Al_{1.97}$	
Initial pH: 10.0					
SiO_2	91	SiO_2	26	SiO_2	18
Ca	70	Ca	17	Ca	1
Mg	5	Mg	2	Mg	0
Al	0	Al	1	Al	26
Final pH	9.6	Final pH	9.4	Final pH	9.8
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Ca_{45.73}$		$Mg_{0.07}Ca_{1.25}Al_{1.20}$		$Mg_{0.10}Ca_{0.26}Al_{1.46}$	

Effect of Calcium and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)

Theoretical MR = (4:0:1) (2:2:1) (0:4:1)
Actual MR = (3.78:0 :1) (1.89:1.75:1) (0:3.50:1)

The effect of calcium and aluminum (metals:silicon MR ≅ 4) on the silica solubility in LANL tap water is shown in Figure 67. Data for each solution is given in Table 68.

The calcium alone (4:0:1) solution showed almost negligible removal of silica. The calcium alone (4:0:1) solution did not remove silica over the pH range 7.1-9.7. In the pH 7.1 and 7.8 solutions no calcium was missing from solution. About 60 mg/L of calcium was insolubilized in the pH 9.7 solution, accompanied by a very slight reduction in silica from 93 to 90 mg/L SiO_2.

However, there were extremely low silica concentrations remaining in the calcium/aluminum (2:2:1) and the aluminum alone (0:4:1) solutions. The calcium/aluminum (2:2:1) solution removed silica to 22 mg/L at pH 7.3 and even further to 11 mg/L at pH 7.6. These large amounts of silica removed from these two solutions were accompanied by very minor calcium removals. This suggests that once again the calcium is a very minor player in silica removal. These silica concentrations are nearly identical to the silica removals found when an aluminum alone (0:2:1) solution is analyzed. The pH 8.4 solution reduced silica content to 8 mg/L. Aluminum was starting to resolubilize at this pH. It is probable that, if the pH were increased, a resolubilization of both silica and aluminum would occur.

The silica concentration in the aluminum alone (0:4:1) solution was 10 mg/L at pH 7.1. The silica reached a minimum of 4 mg/L SiO_2 in this solution at pH 7.7. Above pH 7.7 resolubilization of aluminum occurred, with only a slight effect on silica content.

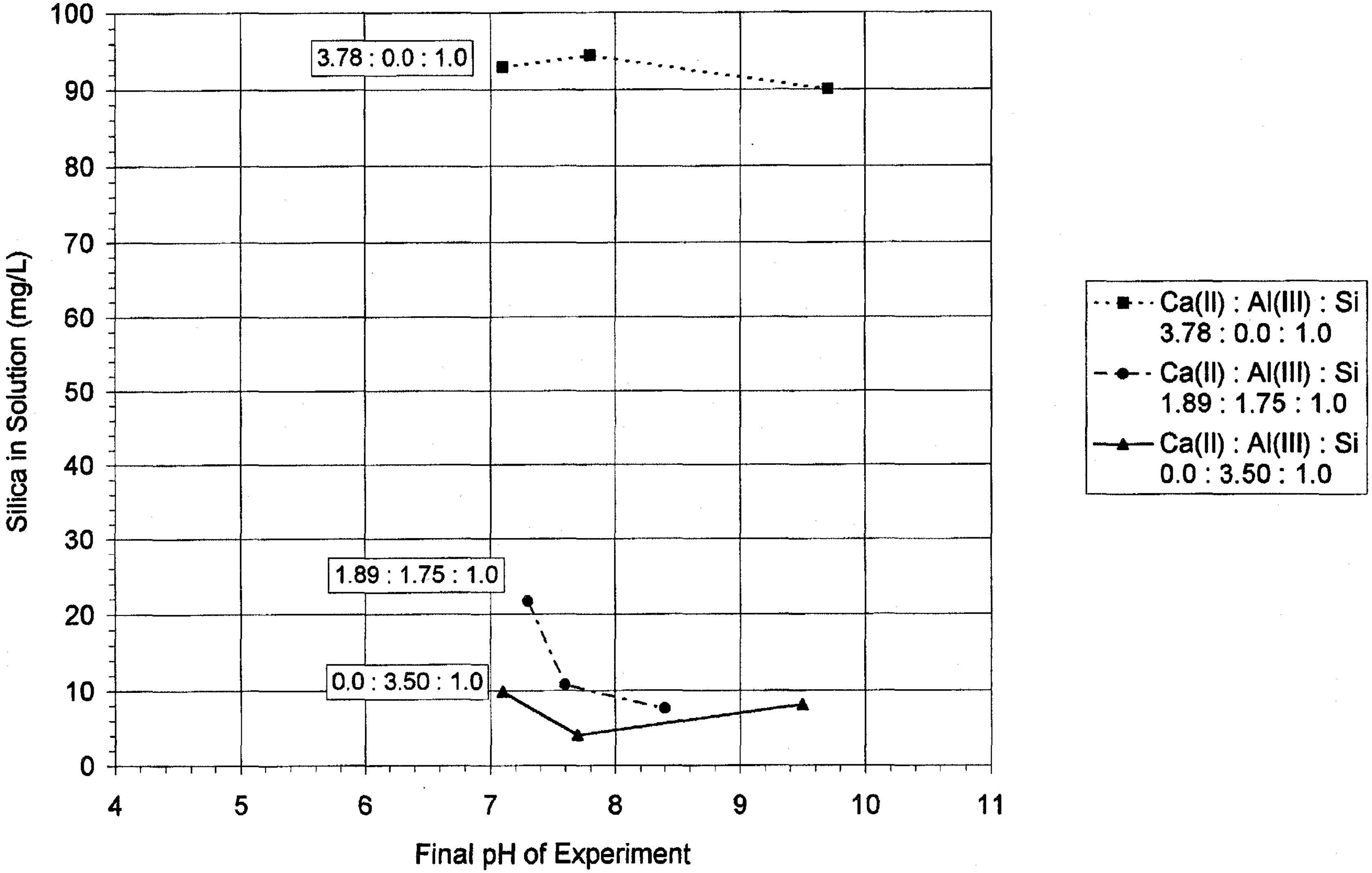

Figure 67. Effect of Calcium, Aluminum, and pH on the Solubility of Silica in Water. Ca(II) : Al(III) : Silica Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 4

Table 68
Data from the Calcium and Aluminum Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.
Concentration Units = mg/L.

Ca(II):Al(III):SiO_2 Mole Ratios Hypothetical **(Actual)**			
	4:0:1 **(3.78:0:1)**	2:2:1 **(1.89:1.75:1)**	0:4:1 **(0:3.50:1)**
Initial pH: 6.0			
SiO_2	93	22	10
Ca	237	124	14
Mg	5	5	5
Al	0	1	1
Final pH	7.1	7.3	7.1
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Ca_{0.15}Al_{2.33}$	$Al_{3.99}$
Initial pH: 8.0			
SiO_2	94	11	4
Ca	241	116	11
Mg	4	4	4
Al	0	0	1
Final pH	7.8	7.6	7.7
Hypothetical Solid Composition Per $Si_{1.0}$	No Solid	$Ca_{0.27}Al_{2.03}$	$Ca_{0.05}Al_{3.74}$
Initial pH: 10.0			
SiO_2	90	8	8
Ca	179	72	2
Mg	5	3	2
Al	0	8	47
Final pH	9.7	8.4	9.5
Hypothetical Solid Composition Per $Si_{1.0}$	$Ca_{34.98}$	$Mg_{0.03}Ca_{1.04}Al_{1.76}$	$Mg_{0.06}Ca_{0.21}Al_{2.70}$

Effect of Ferrous and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (2:1)

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (2:0:1) (1:0.83:1) (0:1.65:1)

Ferrous hydroxide is the product of hydrolysis of ferrous salts and alkali. It is described as a whitish precipitate that turns green and eventually black on standing.[18] It is rated as a strong alkali with some solubility. In our work it appeared as a relatively dense precipitate, greenish black in color. Our source of Fe(II) was derived from ferrous sulfate (Reagent Grade). In all likelihood the crystalline material also contained Fe(III) and the water contained dissolved oxygen.

The effect of ferrous and ferric ion (metals:silicon MR ≅ 2) on the silica solubility in LANL tap water is graphically shown in Figure 68. Data for each solution is given in Table 69.

Silica removal in the ferrous alone (2:0:1) solution showed a strong dependence on pH. Silica concentrations in the pH 5.8, 6.8, and 9.0 solutions were 88, 37, and 19 mg/L, respectively. In the pH 6.8 and 9.0 solutions essentially complete insolubilization of ferrous ion is noted. Ferrous ion appears to be a more effective remover of silica than ferric ion or the ferrous/ferric ion mixture in this set of experiments. A word of caution is needed about this hypothesis. Consideration of the actual mole ratios reveals that 2.00 moles of ferrous ion to silica were added in the (2:0:1) solution. The (0:2:1) solution had 1.65 moles of ferric ion to silica. The total ion to silica added in the (1:1:1) solution was 1.83.

The shape of the ferrous/ferric (1:1:1) mixture curve was nearly a straight line. This same trend is also seen in the ferrous/aluminum mixture (1:1:1) in Figure 72. The silica remaining in solution at pH 4.9 was 56 mg/L. The silica in solution decreased linearly to 25 mg/L at pH 10.0. Twenty-one mg/L of iron remained in solution in the pH 4.9 solution, whereas iron was totally absent in the pH 7.3 and pH 10.0 solutions.

The ferrous ion alone (2:0:1) and the mixture of ferric and ferrous ion solutions were the effective removers of silica in this experiment. The greater basicity of the ferrous ion and the greater solubility of $Fe(OH)_2$ may be reasons. When ferric ion was added by itself to a solution, a haze developed immediately. Qualitatively, this would mean that many nuclei formed immediately. Quite possibly, the ferric hydroxide never has the time or opportunity to react with silica before becoming an inactive polymeric hydroxide.

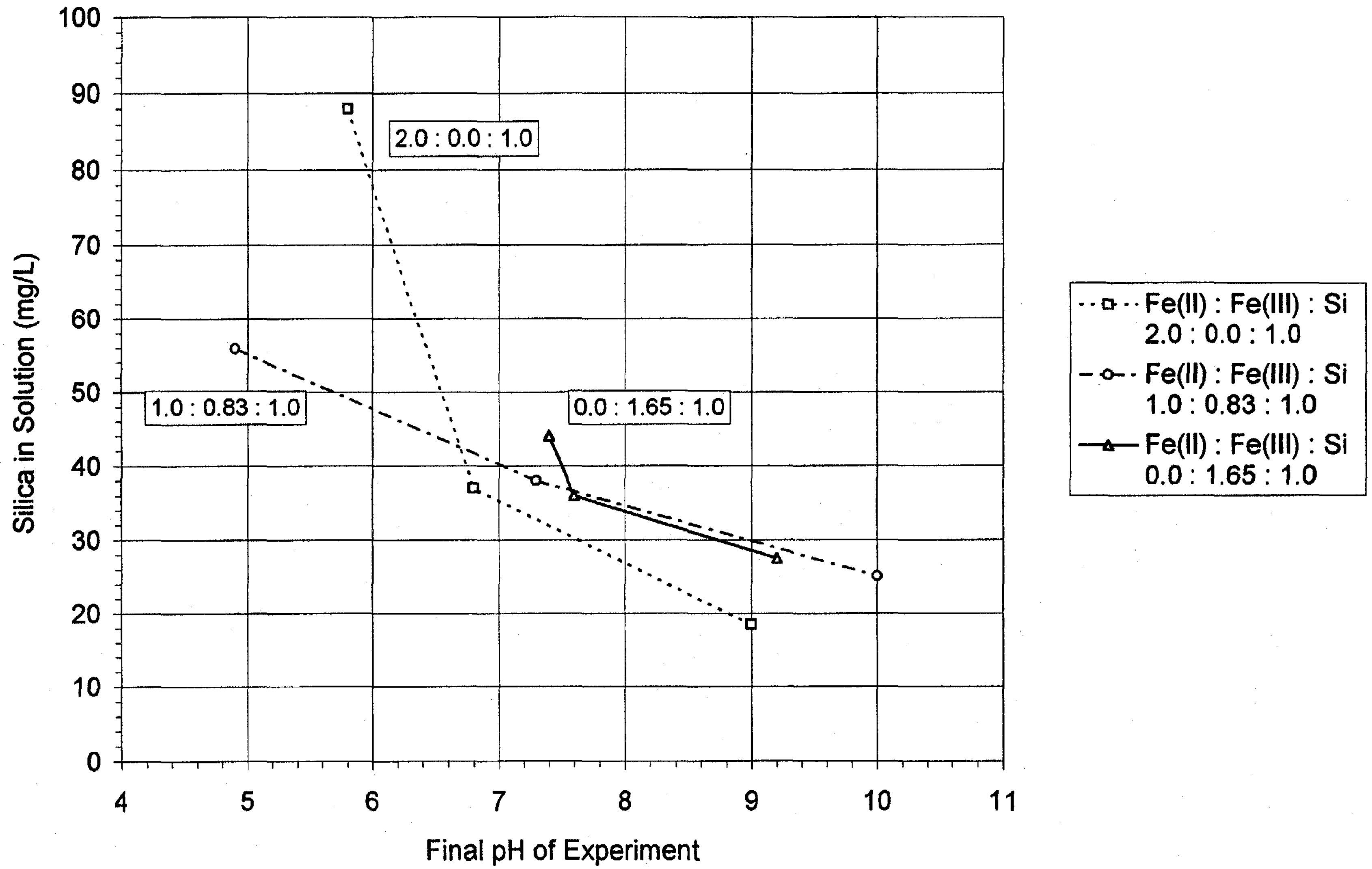

Figure 68. Effect of Ferrous, Ferric, and pH on the Solubility of Silica in Water.
Fe(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 2

Table 69

Data from the Ferrous and Ferric Ions Mixed Valence Metals Work.

Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1.

Concentration Units = mg/L.

Fe(II):Fe(III):SiO_2 Mole Ratios Hypothetical **(Actual)**					
2:0:1 **(2:0:1)**		1:1:1 **(1:0.83:1)**		0:2:1 **(0:1.65:1)**	
Initial pH: 6.0					
SiO_2	88	SiO_2	56	SiO_2	44
Ca	15	Ca	14	Ca	14
Mg	5	Mg	4	Mg	5
Fe	124	Fe	21	Fe	0.1
Final pH	5.8	Final pH	4.9	Final pH	7.4
Hypothetical Solid Composition Per $Si_{1.0}$	$Fe(II)_{10.54}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Fe_{4.01}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Fe(III)_{3.16}$
Initial pH: 8.0					
SiO_2	37	SiO_2	38	SiO_2	36
Ca	13	Ca	11	Ca	10
Mg	5	Mg	4	Mg	4
Fe	0.1	Fe	0.2	Fe	0
Final pH	6.8	Final pH	7.3	Final pH	7.6
Hypothetical Solid Composition Per $Si_{1.0}$	$Fe(II)_{3.32}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Ca_{0.08}Fe_{3.11}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Ca_{0.11}Fe(III)_{2.72}$
Initial pH: 10.0					
SiO_2	19	SiO_2	25	SiO_2	28
Ca	8	Ca	2	Ca	4
Mg	2	Mg	0	Mg	2
Fe	0.1	Fe	0	Fe	0.1
Final pH	9.0	Final pH	10.0	Final pH	9.2
Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.07}Ca_{0.12}Fe(II)_{2.51}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.15}Ca_{0.26}Fe_{2.52}$	Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.08}Ca_{0.23}Fe(III)_{2.38}$

Effect of Ferrous and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (2:1)
Nitrogen Sparged Tap water

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (2:0:1) (1:0.83:1) (0:1.65:1)

The effect of ferrous and ferric ions (metals:silicon MR ≅ 2), in a nitrogen sparged solution on the solubility of silica in LANL tap water is graphically shown in Figure 69. Data for each solution is given in Table 70.

This experiment differed from the previous one in that an attempt was made to deoxygenate the water. The purpose of this was to keep the ferrous ion in the +2 oxidation state. Dissolved oxygen is a strong enough oxidizing agent to convert ferrous to ferric ion. The tap water was sparged with nitrogen gas for two hours prior to the addition of the ferrous and ferric ions and the solutions were also sparged during their pH adjustment period. Analyses for dissolved oxygen and ferrous ion were not performed on the solutions. The assumption was made that the initial solutions were oxygen free and "ferrous" ion was in its original state.

The shapes of the curves and silica values of the ferrous alone (2:0:1) solution and the ferrous/ferric mix (1:1:1) solution differ from those shown in Figure 68. The deoxygenation of the water improved the removal of silica in both of these solutions.

The ferrous alone solution (2:0:1) was more effective in silica removal than the ferrous/ferric mix (1:1:1) solution. Both of these solutions also removed more silica than the ferric alone (0:2:1) solution. A word of caution is needed about the above statements. Consideration of the actual mole ratios reveals that 2.00 moles of ferrous ion to silica were added in the (2:0:1) solution. The total iron to silica added in the (1:1:1) solution was 1.83. The (0:2:1) solution had 1.65 moles of ferric ion to 1 mole silica.

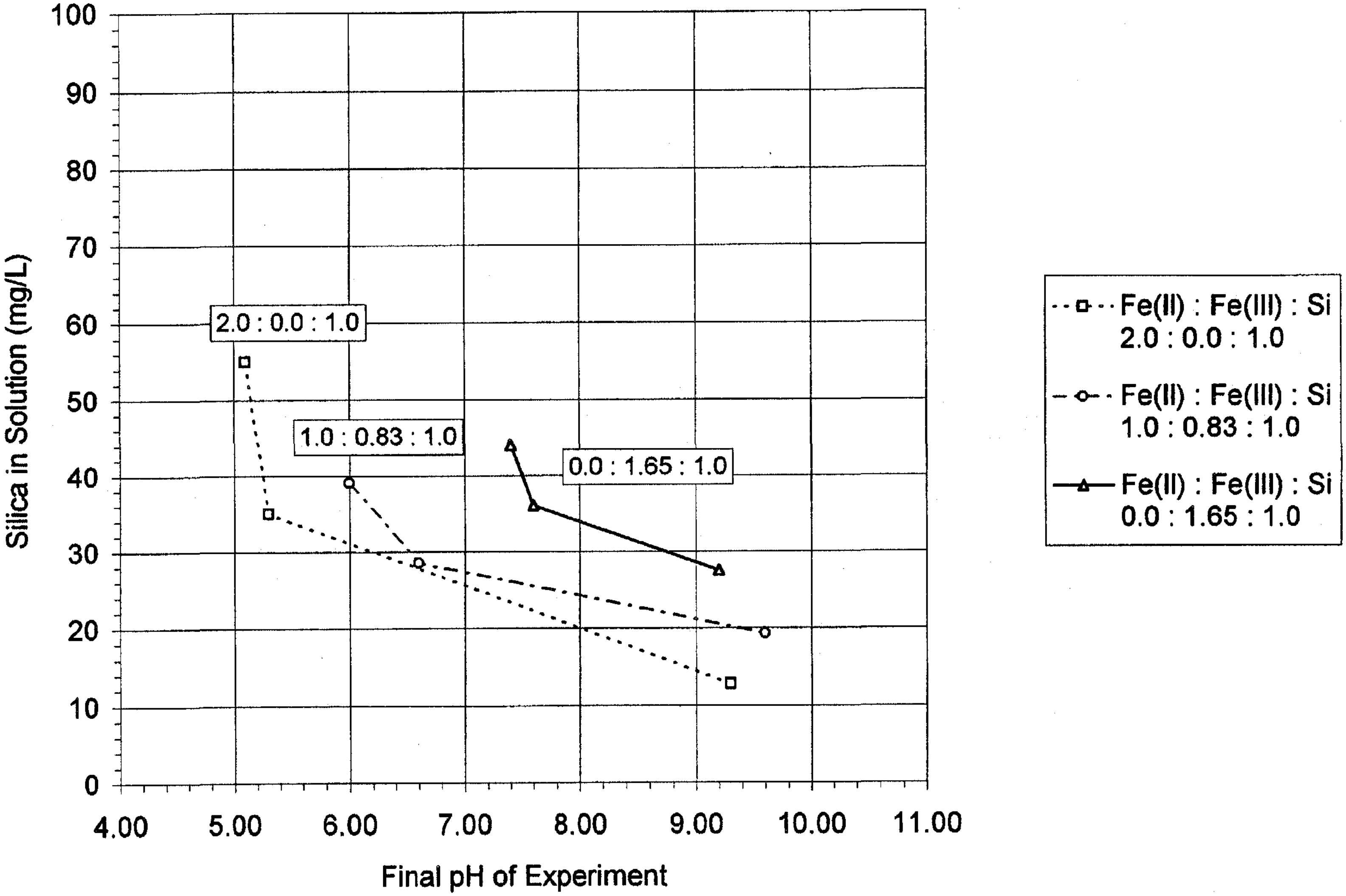

Figure 69. Effect of Ferrous, Ferric, and pH on the Solubility of Silica in Water.
Fe(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Nitrogen Sparged Water. Metals:SiO_2 appx. = 2

Table 70
Data from the Ferrous and Ferric Ions Mixed Valence Metals Work. Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1. Concentration Units = mg/L.
(Nitrogen Sparged Water)

Fe(II) : Fe(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**					
2 : 0 : 1 **(2 : 0 : 1)**		1 : 1 : 1 **(1 : 0.83 : 1)**		0 : 2 : 1 **(0 : 1.65 : 1)**	
Initial pH: 6.0					
SiO_2	55	SiO_2	39	SiO_2	44
Ca	14	Ca	13	Ca	14
Mg	4.5	Mg	4	Mg	5
Fe	44	Fe	0.5	Fe	0.1
Final pH	5.1	Final pH	6.0	Final pH	7.4
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Fe(II)_{3.65}$		$Ca_{0.03}Fe_{3.16}$		$Fe(III)_{3.16}$	
Initial pH: 8.0					
SiO_2	35	SiO_2	29	SiO_2	36
Ca	14	Ca	11	Ca	10
Mg	4	Mg	4	Mg	4
Fe	7	Fe	0.1	Fe	0
Final pH	5.3	Final pH	6.6	Final pH	7.6
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Fe(II)_{3.08}$		$Ca_{0.07}Fe_{2.67}$		$Ca_{0.11}Fe(III)_{2.72}$	
Initial pH: 10.0					
SiO_2	13	SiO_2	19	SiO_2	28
Ca	4	Ca	2	Ca	4
Mg	0	Mg	0	Mg	2
Fe	0	Fe	0	Fe	0.1
Final pH	9.3	Final pH	9.6	Final pH	9.2
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Mg_{0.12}Ca_{0.19}Fe(II)_{2.33}$		$Mg_{0.13}Ca_{0.24}Fe_{2.31}$		$Mg_{0.08}Ca_{0.23}Fe(III)_{2.38}$	

Effect of Ferrous and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)

Theoretical MR = (4:0:1) (2:2:1) (0:4:1)
Actual MR = (4:0:1) (2:1.65:1) (0:3.31:1)
No Nitrogen Sparging

The effect of ferrous and ferric ion (metals:silicon MR ≅ 4) on the silica solubility in LANL tap water is graphically shown in Figure 70. Data for each solution is given in Table 71.

The silica content of the (4:0:1) solution went down from 84 mg/L at pH 5.2 to ~12 mg/L at pH 6.8. It was only slightly lower, ~6.5 mg/L at pH 8.7. For the (2:2:1) mixture ratio, the SiO_2 content was ~6 mg/L at pH ~9.5.

The shapes of the curves in this experiment were very similar to those found in Figure 68, in which the same ratios of metals were used but they had a total metals:silicon MR = 2. The silica removal effectiveness for each solution showed a dependence on pH.

All three solutions brought the silica concentrations in solution down to about 10 mg/L in the pH range 8.0-9.4. The ferric alone (0:4:1) curve shows a slight but definite resolubilization of silica at pH 9.6. This resolubilization implies that the chemical bond between ferric ion and silica is not very strong.

The ferrous-containing solutions do not show resolubilization of silica. Ferrous ion formed what appeared to be a faster settling floc than the ferric ion. It is possible that the ferrous hydroxide, because of its higher solubility and greater basicity than ferric hydroxides, reacts faster and more completely with silica than the ferric ion.

The ferrous/ferric (2:2:1) solution produced a curve that is very nearly a straight line. The silica remaining in solution at pH 4.6 was 49 mg/L. The silica in solution decreased as a nearly linear function of pH to 5 mg/L at pH 9.5. Calcium and magnesium were also removed from the solutions above pH 7.5 (Table 71).

It seems from the results of this work with the mixed ferrous and ferric ions that they are outstanding in their ability to reduce silica content to the desired 10 mg/L level at relatively low pH.

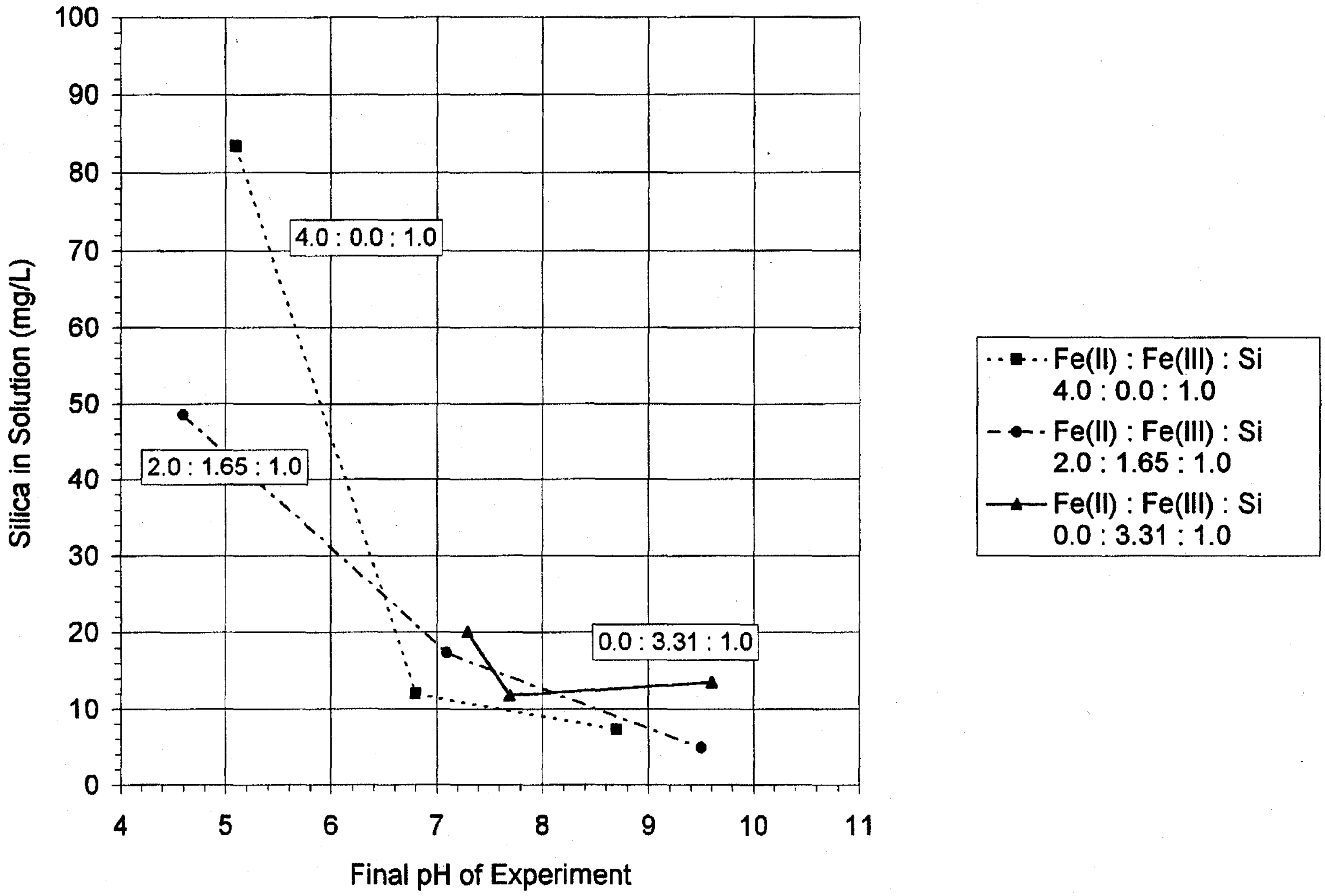

Figure 70. Effect of Ferrous, Ferric, and pH on the Solubility of Silica in Water.
Fe(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. No Nitrogen Sparging. Metals:SiO_2 appx. = 4

Table 71
Data from the Ferrous and Ferric Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.
Concentration Units = mg/L.

Fe(II) : Fe(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**					
4 : 0 : 1 **(4 : 0 : 1)**		2 : 2 : 1 **(2 : 1.65 : 1)**		0 : 4 : 1 **(0 : 3.31 : 1)**	
Initial pH: 6.0					
SiO_2	83	SiO_2	49	SiO_2	20
Ca	15	Ca	14	Ca	13
Mg	6	Mg	4	Mg	5
Fe	252	Fe	70	Fe	0.1
Final pH	5.1	Final pH	4.6	Final pH	7.3
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Fe(II)_{10.11}$		$Fe_{6.04}$		$Ca_{0.02}Fe(III)_{4.23}$	
Initial pH: 8.0					
SiO_2	12	SiO_2	17	SiO_2	12
Ca	14	Ca	13	Ca	4
Mg	5	Mg	5	Mg	2
Fe	0.1	Fe	0.1	Fe	0
Final pH	6.8	Final pH	7.1	Final pH	7.7
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Fe(II)_{4.59}$		$Ca_{0.02}Fe_{4.49}$		$Mg_{0.06}Ca_{0.19}Fe(III)_{3.81}$	
Initial pH: 10.0					
SiO_2	7	SiO_2	5	SiO_2	14
Ca	10	Ca	2	Ca	2
Mg	2	Mg	0	Mg	2
Fe	0.2	Fe	0	Fe	0.5
Final pH	8.7	Final pH	9.5	Final pH	9.6
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Mg_{0.06}Ca_{0.07}Fe(II)_{4.33}$		$Mg_{0.11}Ca_{0.20}Fe_{3.88}$		$Mg_{0.06}Ca_{0.23}Fe(III)_{3.90}$	

Effect of Ferrous and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)
Nitrogen Sparged Tap water

Theoretical MR = (4:0:1) (2:2:1) (0:4:1)
Actual MR = (4:0:1) (2:1.65:1) (0:3.31:1)

The effect of ferrous and ferric ion (metals:silicon MR ≅ 4) in a deoxygenated solution (sparged) on the solubility of silica in LANL tap water is graphically shown in Figure 71. Data for each solution is given in Table 72.

This graph shows that deoxygenating the tap water did enhance the silica removal in the ferrous alone (4:0:1) solution and the ferrous/ferric (2:2:1) mixture as compared to the non-sparged solutions in Figure 70.

An outstanding result of this experiment is that only 0.4 mg/L of silica remains in solution at pH 8.6 in the ferrous alone (4:0:1) solution. The ferrous ion also was totally missing from solution.

The ferrous ion seems to be the best remover of silica of all the ions used at a pH as low as 5.3.

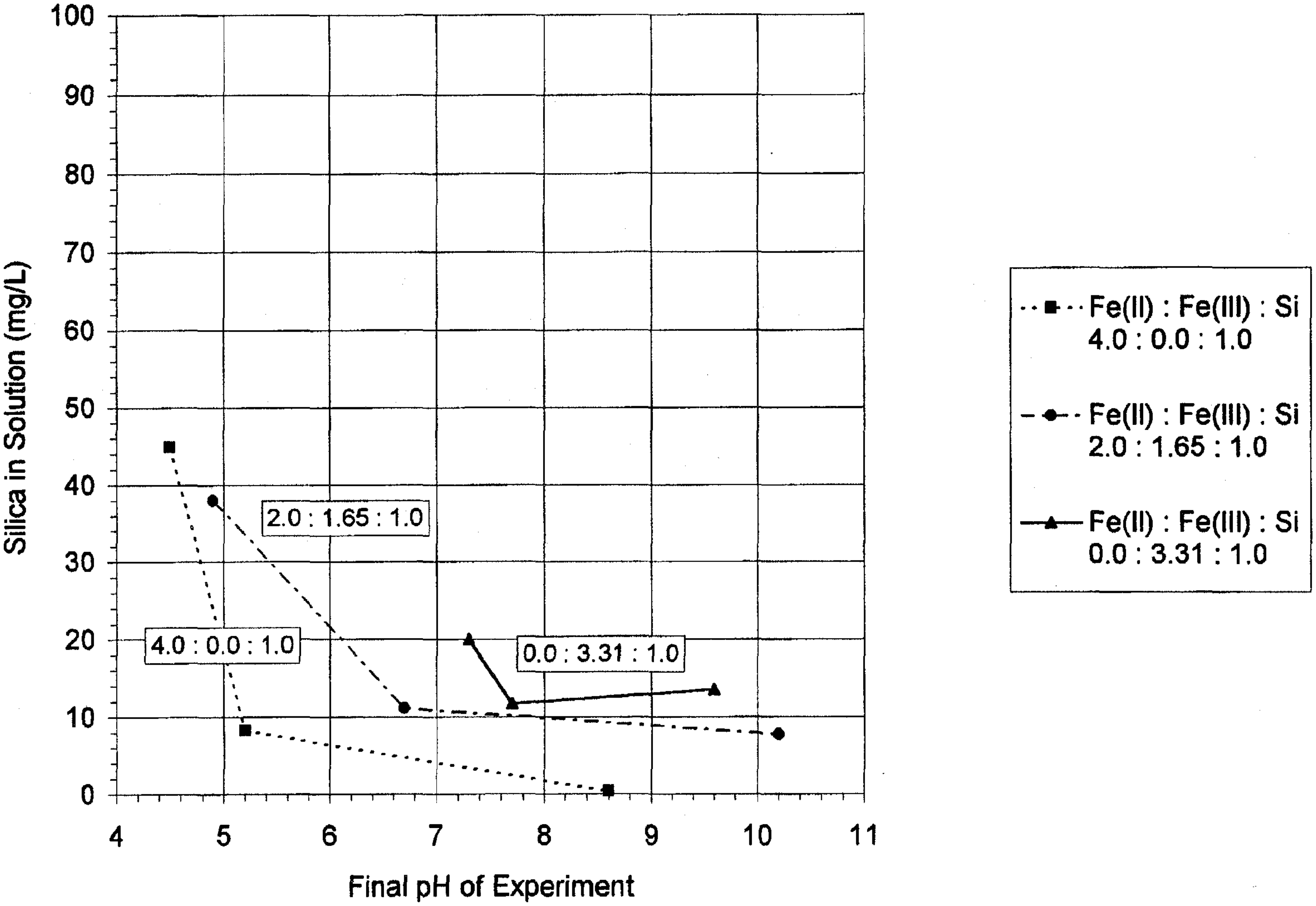

Figure 71. Effect of Ferrous, Ferric, and pH on the Solubility of Silica in Water. Fe(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Nitrogen Sparged Water. Metals:SiO_2 appx. = 4

Table 72
Data from the Ferrous and Ferric Ions Mixed Valence Metals Work. Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1. Concentration Units = mg/L.
(Nitrogen Sparged Water)

Fe(II) : Fe(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**					
4 : 0 : 1 **(4 : 0 : 1)**		2 : 2 : 1 **(2 : 1.65 : 1)**		0 : 4 : 1 **(0 : 3.31 : 1)**	
Initial pH: 6.0					
SiO_2	45	SiO_2	38	SiO_2	20
Ca	13	Ca	14	Ca	13
Mg	4	Mg	4	Mg	5
Fe	163	Fe	53	Fe	0.1
Final pH	4.5	Final pH	4.9	Final pH	7.3
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Ca_{0.03}Fe(II)_{4.10}$		$Fe_{5.16}$		$Ca_{0.02}Fe(III)_{4.23}$	
Initial pH: 8.0					
SiO_2	8	SiO_2	11	SiO_2	12
Ca	13	Ca	13	Ca	4
Mg	4	Mg	4	Mg	2
Fe	5	Fe	0	Fe	0
Final pH	5.2	Final pH	6.7	Final pH	7.7
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Ca_{0.02}Fe(II)_{4.32}$		$Ca_{0.02}Fe_{4.16}$		$Mg_{0.06}Ca_{0.19}Fe(III)_{3.81}$	
Initial pH: 10.0					
SiO_2	0.4	SiO_2	8	SiO_2	14
Ca	8	Ca	1	Ca	2
Mg	1	Mg	0	Mg	2
Fe	0	Fe	0	Fe	0.5
Final pH	8.6	Final pH	10.2	Final pH	9.6
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Mg_{0.08}Ca_{0.10}Fe(II)_{4.00}$		$Mg_{0.11}Ca_{0.22}Fe_{4.01}$		$Mg_{0.06}Ca_{0.22}Fe(III)_{3.90}$	

Effect of Ferrous and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (2:1)

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (2:0:1) (1:0.87:1) (0:1.75:1)

The effect of ferrous and aluminum ions (metals:silicon MR ≅ 2) on the solubility of silica in LANL tap water is graphically shown in Figure 72. Data for each solution is given in Table 73.

The effects on silica solubility of ferrous/aluminum mixtures are similar to the ferrous/ferric mixtures shown in Figure 68. A notable difference is that the silica solubilities in the aluminum alone (0:2:1) solution and the ferrous/aluminum (1:1:1) solution are 15 to 20 mg/L lower than in the corresponding ferric ion solutions as shown in Figure 68.

The aluminum alone (0:2:1) solution lost silica most effectively at pH 8.0. At pH 9.8 appreciable amounts of silica and aluminum both resolubilized.

The ferrous/aluminum solution (1:1:1) demonstrated the straight line silica solubility vs. pH slope that is characteristic of the mixed valence metals solutions. No resolubilization of silica was evident at the highest pH value of 9.5. Some resolubilization of aluminum, though, was noted in the solution (Table 73). The solubility of silica in the mixed solutions was intermediate between the ferrous only and aluminum only solutions.

The ferrous ion alone (2:0:1) solution showed appreciable silica solubility in the pH 5.8 solution. The silica solubility decreased markedly in the pH 6.8 and pH 9.0 solutions.

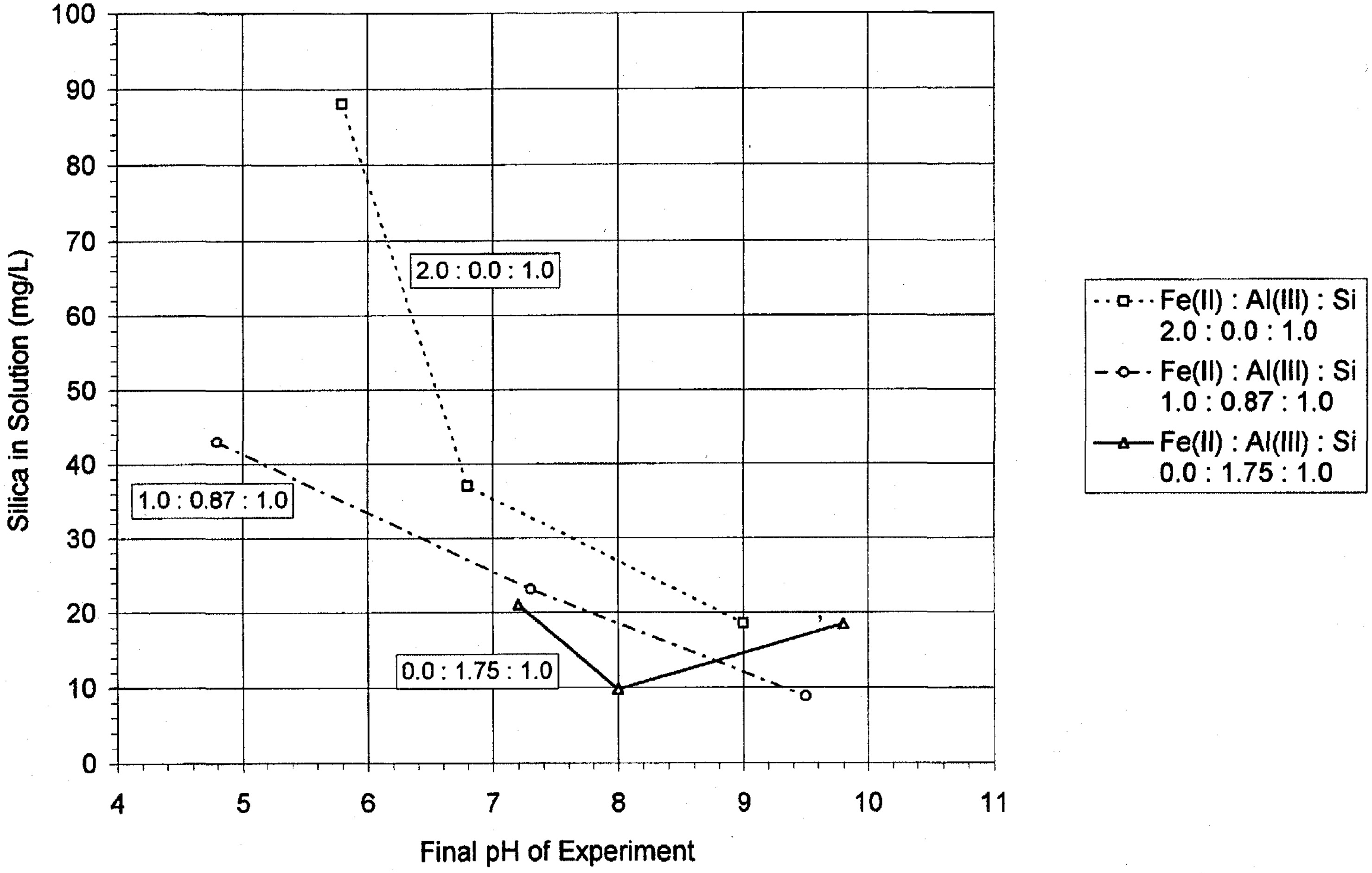

Figure 72. Effect of Ferrous, Aluminum, and pH on the Solubility of Silica in Water.
Fe(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 2:1.

Table 73
Data from the Ferrous and Aluminum Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1.
Concentration Units = mg/L.

Fe(II) : Al(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**			
	2 : 0 : 1 **(2 : 0 : 1)**	1 : 1 : 1 **(1 : 0.87 : 1)**	0 : 2 : 1 **(0 : 1.75 : 1)**
Initial pH: 6.0			
SiO_2	88	43	21
Ca	15	14	14
Mg	5	5	5
Fe	124	35	0
Al	0	0.2	0.7
Final pH	5.8	4.8	7.2
Hypothetical Solid Composition Per $Si_{1.0}$	$Fe(II)_{10.54}$	$Fe(II)_{1.11}Al_{1.63}$	$Al_{2.29}$
Initial pH: 8.0			
SiO_2	37	23	10
Ca	13	11	6
Mg	5	4	2
Fe	0.1	0.1	0
Al	0	1	2
Final pH	6.8	7.3	8.0
Hypothetical Solid Composition Per $Si_{1.0}$	$Ca_{0.02}Fe(II)_{3.32}$	$Ca_{0.06}Fe(II)_{1.33}Al_{1.15}$	$Mg_{0.05}Ca_{0.14}Al_{1.97}$
Initial pH: 10.0			
SiO_2	19	9	18
Ca	8	1	1
Mg	2	0	0
Fe	0.1	0.1	0
Al	0	7	26
Final pH	9.0	9.5	9.8
Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.07}Ca_{0.12}Fe(II)_{2.51}$	$Mg_{0.11}Ca_{0.23}Fe(II)_{1.11}Al_{0.80}$	$Mg_{0.10}Ca_{0.26}Al_{1.45}$

Effect of Ferrous and Aluminum Ions and pH on Silica Solubility

Total Metals:Silica Mole Ratio ≅ (2:1)
Nitrogen Sparged Tap Water

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (2:0:1) (1:0.87:1) (0:1.75:1)

The effect of ferrous and aluminum ions (metals:silicon MR ≅ 2), in a deoxygenated (sparged) solution on the solubility of silica in LANL tap water is graphically shown in Figure 73. Data for each solution is given in Table 74.

An appreciable reduction in silica solubility was noticed in this experiment, as compared to the same experiment in nonnitrogen sparged tap water shown in Figure 72. Both of the ferrous solutions (2:0:1) and (1:1:1) in the deoxygenated tap water removed about 10 mg/L more of the silica than the nonnitrogen sparged water. The ferrous alone (2:0:1) solution exhibited a great enhancement in silica removal at a pH as low as 5.1, as before.

An unusual feature of the data in this experiment is that the silica content in the mixed solution (1:1:1) is lower than the ferrous alone (2:0:1) solution. This mexed metal solution (1:1:1) reduced the silica to 7 mg/L at pH 8.9.

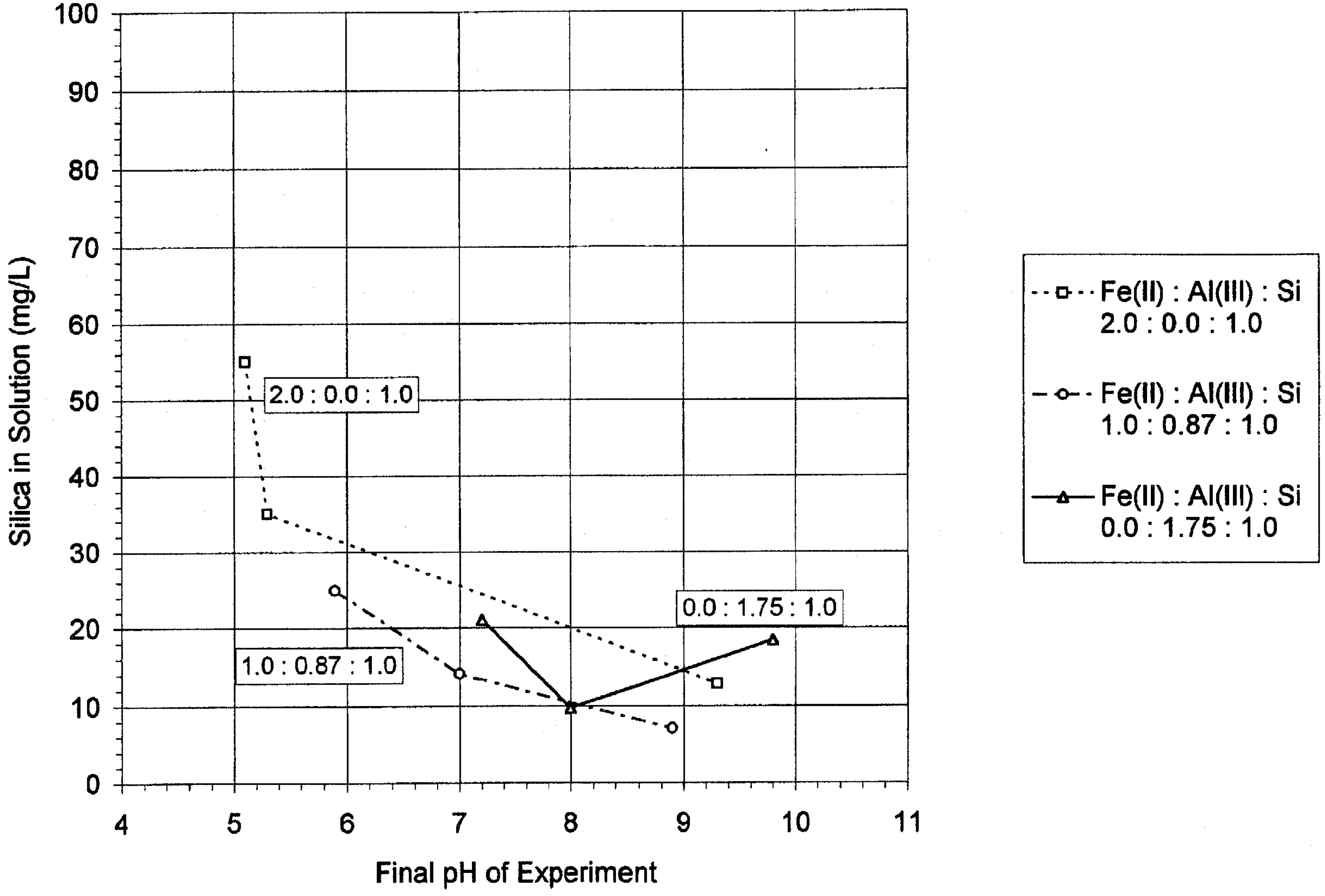

Figure 73. Effect of Ferrous, Aluminum, and pH on the Solubility of Silica in Water.
Fe(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. Nitrogen Sparged Water. Metals:SiO_2 appx. = 2:1

Table 74
Data from the Ferrous and Aluminum Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1.
Concentration Units = mg/L.
(Nitrogen Sparged Water)

Fe(II) : Al(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**					
2 : 0 : 1 **(2 : 0 : 1)**		1 : 1 : 1 **(1 : 0.87 : 1)**		0 : 2 : 1 **(0 : 1.75 : 1)**	
Initial pH: 6.0					
SiO_2	55	SiO_2	25	SiO_2	21
Ca	14	Ca	13	Ca	14
Mg	5	Mg	4	Mg	5
Fe	44	Fe	1	Fe	0
Al	0	Al	0	Al	1
Final pH	5.1	Final pH	5.9	Final pH	7.2
Hypothetical Solid Composition Per $Si_{1.0}$ $Fe(II)_{3.65}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Ca_{0.02}Fe(II)_{1.36}Al_{1.21}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Al_{2.30}$	
Initial pH: 8.0					
SiO_2	35	SiO_2	14	SiO_2	10
Ca	14	Ca	11	Ca	6
Mg	4	Mg	4	Mg	2
Fe	7	Fe	0	Fe	0
Al	0	Al	0.1	Al	2
Final pH	5.3	Final pH	7.0	Final pH	8.0
Hypothetical Solid Composition Per $Si_{1.0}$ $Fe(II)_{3.10}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Ca_{0.06}Fe(II)_{1.18}Al_{1.04}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.06}Ca_{0.14}Al_{1.97}$	
Initial pH: 10.0					
SiO_2	13	SiO_2	7	SiO_2	18
Ca	4	Ca	2	Ca	1
Mg	0	Mg	0	Mg	0
Fe	0	Fe	0.1	Fe	0
Al	0	Al	6	Al	26
Final pH	9.3	Final pH	8.9	Final pH	9.8
Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.12}Ca_{0.18}Fe(II)_{2.33}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.11}Ca_{0.21}Fe(II)_{1.09}Al_{0.80}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.13}Ca_{0.26}Al_{1.46}$	

Effect of Ferrous and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)

Theoretical MR = (4:0:1) (2:2:1) (0:4:1)
Actual MR = (4:0:1) (2:1.75:1) (0:3.50:1)

The effect of ferrous and aluminum ions (metals:silicon MR ≅ 4) on the silica solubility in LANL tap water is graphically shown in Figure 74. Data for each solution is given in Table 75.

The solution of ferrous ion mixed with aluminum (2:2:1) produced a straight line; 1 mg/L of silica remained in solution at pH 9.2. Aluminum resolubilized to 23 mg/L in this solution at pH 9.2. Thus, where the ferrous ion is present, it seems to control the reaction.

The aluminum alone solution (0:4:1) gave the familiar bent lines and the slight resolubilization of silica and aluminum at the highest pH. The effect of the ferrous is truly remarkable. However, it is a matter of conjecture whether a true compound formation or a "coprecipitation" is occurring.

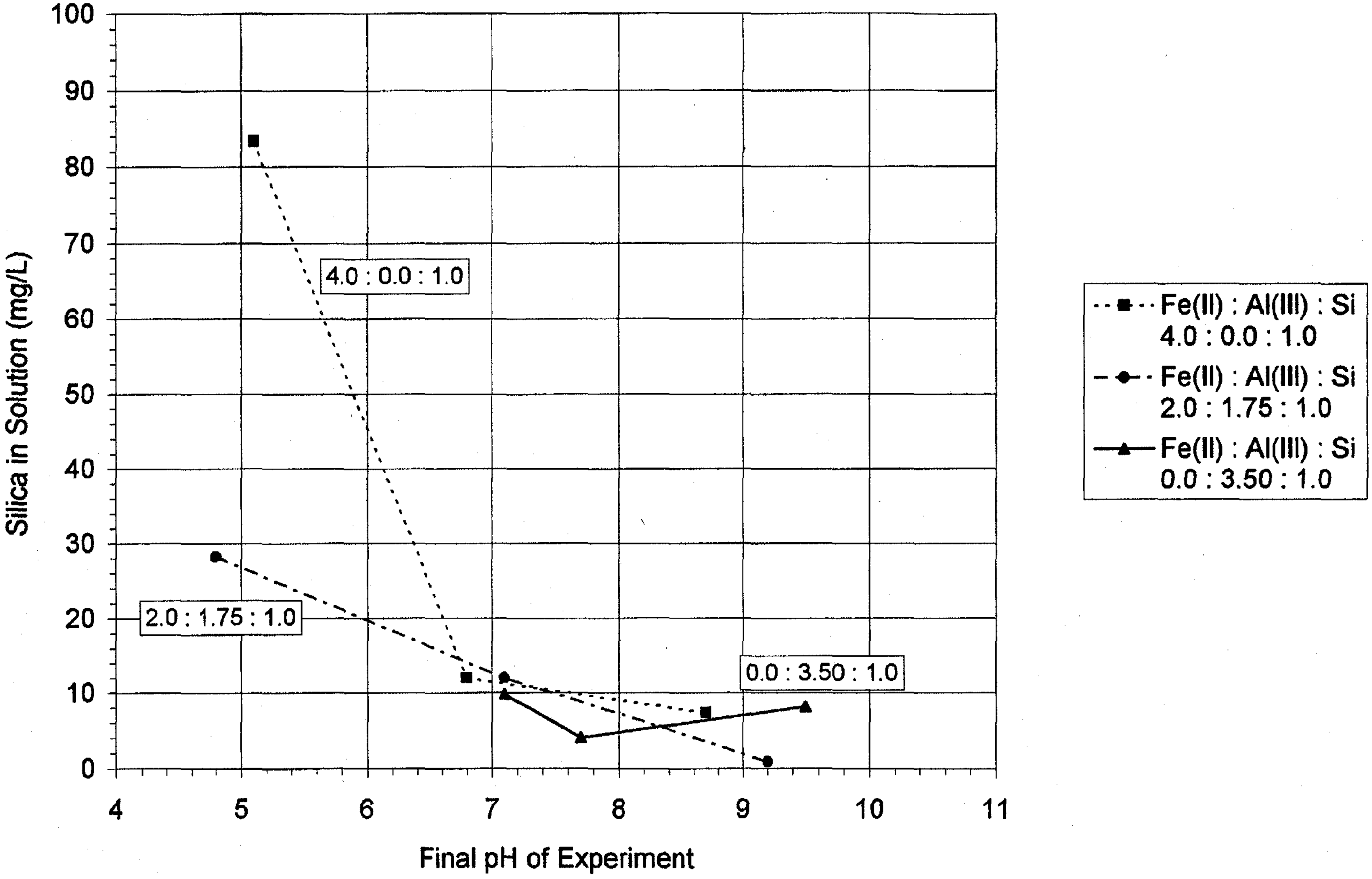

Figure 74. Effect of Ferrous, Aluminum, and pH on the Solubilitv of Silica in Water.
Fe(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. No Nitrogen Sparged Water. Metals:SiO_2 appx. = 4

Table 75
Data from the Ferrous and Aluminum Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.
Concentration Units = mg/L.

Fe(II) : Al(III) : SiO$_2$ Mole Ratios Hypothetical **(Actual)**					
4 : 0 : 1 **(4 : 0 : 1)**		2 : 2 : 1 **(2 : 1.75 : 1)**		0 : 4 : 1 **(0 : 3.50 : 1)**	
Initial pH: 6.0					
SiO$_2$	83	SiO$_2$	28	SiO$_2$	10
Ca	15	Ca	14	Ca	14
Mg	6	Mg	4	Mg	5
Fe	252	Fe	76	Fe	0
Al	0	Al	0.2	Al	1
Final pH	5.1	Final pH	4.8	Final pH	7.1
Hypothetical Solid Composition Per Si$_{1.0}$		Hypothetical Solid Composition Per Si$_{1.0}$		Hypothetical Solid Composition Per Si$_{1.0}$	
Fe(II)$_{10.11}$		Fe(II)$_{1.61}$Al$_{2.56}$		Al$_{3.99}$	
Initial pH: 8.0					
SiO$_2$	12	SiO$_2$	12	SiO$_2$	4
Ca	14	Ca	14	Ca	11
Mg	5	Mg	4	Mg	4
Fe	0.1	Fe	0.1	Fe	0
Al	0	Al	1	Al	1
Final pH	6.8	Final pH	7.1	Final pH	7.7
Hypothetical Solid Composition Per Si$_{1.0}$		Hypothetical Solid Composition Per Si$_{1.0}$		Hypothetical Solid Composition Per Si$_{1.0}$	
Fe(II)$_{4.59}$		Fe(II)$_{2.29}$Al$_{2.04}$		Ca$_{0.05}$Al$_{3.74}$	
Initial pH: 10.0					
SiO$_2$	7	SiO$_2$	1	SiO$_2$	8
Ca	10	Ca	2	Ca	2
Mg	2	Mg	0	Mg	2
Fe	0.2	Fe	0	Fe	0
Al	0	Al	23	Al	47
Final pH	8.7	Final pH	9.2	Final pH	9.5
Hypothetical Solid Composition Per Si$_{1.0}$		Hypothetical Solid Composition Per Si$_{1.0}$		Hypothetical Solid Composition Per Si$_{1.0}$	
Mg$_{0.06}$Ca$_{0.07}$Fe(II)$_{4.33}$		Mg$_{0.11}$Ca$_{0.20}$Fe(II)$_{2.02}$Al$_{1.26}$		Mg$_{0.06}$Ca$_{0.21}$Al$_{2.70}$	

Effect of Ferrous and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)
Nitrogen Sparged Tap Water

Theoretical MR = (4:0:1) (2:2:1) (0:4:1)
Actual MR = (4:0:1) (2:1.75:1) (0:3.50:1)

The effect of ferrous and aluminum ions (metals:silicon MR ≅ 4), in a deoxygenated (sparged) solution on the solubility of silica in LANL tap water is graphically shown in Figure 75. Data for each solution is given in Table 76.

This high total metals:silicon mole ratio reduces the solubility of the silica to below 10 mg/L in all three solutions. The ferrous alone (4:0:1) solution had only 8 mg/L SiO_2 at a pH as low as 5.2.

A notable effect of the ferrous ion addition is that, while the aluminum ion alone will precipitate silica to below 10 mg/L at pH 7.1, the admixture with ferrous drops the silica to 4 mg/L at the same pH.

Silica concentrations are brought down to 0.4 mg/L at pH 8.6 and pH 8.9 in the ferrous alone (4:0:1) solution and the ferrous/aluminum mixture (2:2:1), respectively. At pH 8.9 in the mixed solution and pH 9.5 in the aluminum alone solution, some aluminum resolubilization is occurring (Table 76).

There is a noticeable enhancement of the effect of ferrous ion by the removal of oxygen through the nitrogen sparging.

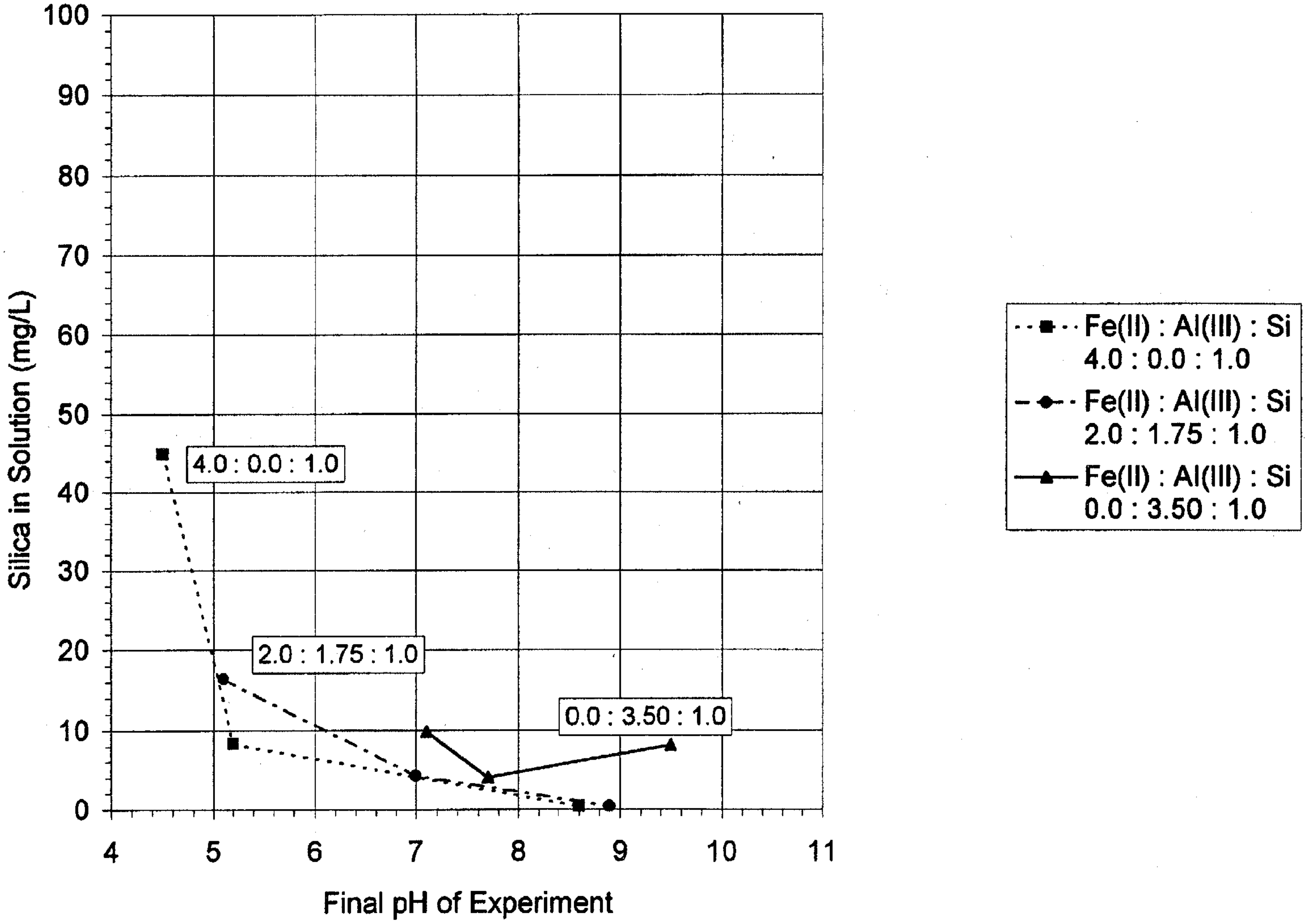

Figure 75. Effect of Ferrous, Aluminum, and pH on the Solubility of Silica in Water.
Fe(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. Nitrogen Sparged Water. Metals:SiO_2 appx. = 4

Table 76
Data from the Ferrous and Aluminum Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.
Concentration Units = mg/L.
(Nitrogen Sparged Water)

Fe(II) : Al(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**					
4 : 0 : 1 **(4 : 0 : 1)**		2 : 2 : 1 **(2 : 1.75 : 1)**		0 : 4 : 1 **(0 : 3.50 : 1)**	
Initial pH: 6.0					
SiO_2	45	SiO_2	16	SiO_2	10
Ca	13	Ca	14	Ca	14
Mg	4	Mg	4	Mg	5
Fe	163	Fe	32	Fe	0
Al	0	Al	0.1	Al	1
Final pH	4.5	Final pH	5.1	Final pH	7.1
Hypothetical Solid Composition Per $Si_{1.0}$ $Ca_{0.03}Fe(II)_{4.10}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Fe(II)_{1.97}Al_{2.17}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Al_{3.99}$	
Initial pH: 8.0					
SiO_2	8	SiO_2	4	SiO_2	4
Ca	13	Ca	13	Ca	11
Mg	4	Mg	3	Mg	4
Fe	5	Fe	0	Fe	0
Al	0	Al	0.1	Al	1
Final pH	5.2	Final pH	7.0	Final pH	7.7
Hypothetical Solid Composition Per $Si_{1.0}$ $Ca_{0.02}Fe(II)_{4.32}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.03}Ca_{0.02}Fe(II)_{2.09}Al_{1.87}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Ca_{0.05}Al_{3.74}$	
Initial pH: 10.0					
SiO_2	0.4	SiO_2	0.4	SiO_2	8
Ca	8	Ca	2	Ca	2
Mg	1	Mg	0	Mg	2
Fe	0	Fe	0	Fe	0
Al	0	Al	16	Al	47
Final pH	8.6	Final pH	8.9	Final pH	9.5
Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.08}Ca_{0.10}Fe(II)_{4.00}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.11}Ca_{0.19}Fe(II)_{2.00}Al_{1.41}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.06}Ca_{0.21}Al_{2.70}$	

Effect of Zinc and Ferric Ions and pH on Silica Solubility

Total Metals:Silica Mole Ratio $\cong$ (2:1)

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (1.88:0:1) (0.94:0.83:1) (0:1.65:1)

Figure 76 shows the effect of zinc and ferric ions (metals:silicon MR $\cong$ 2) on the silica solubility in LANL tap water. Data for each solution is given in Table 77.

The data suggested that the zinc alone (2:0:1) solution removed silica to a greater degree than the ferric ion (0:2:1) solution over the pH range 7.4-8.8. In these two solutions it should be noted that slightly more zinc to silica was added (MR = 1.88) than ferric ion to silica (MR = 1.65).

The mixed zinc and ferric iron (1:1:1) solution showed a modified pH dependence on the silica solubility. At pHs below 7.5 the silica solubility appeared to be controlled by the ferric ion. At pHs greater than 7.5 the zinc ion seemed to control the behavior of the silica solubility curve. The mixed zinc and ferric ion solution did not increase the removal of silica. No resolubilization of silica was noted in the mixed solution as the pH increased.

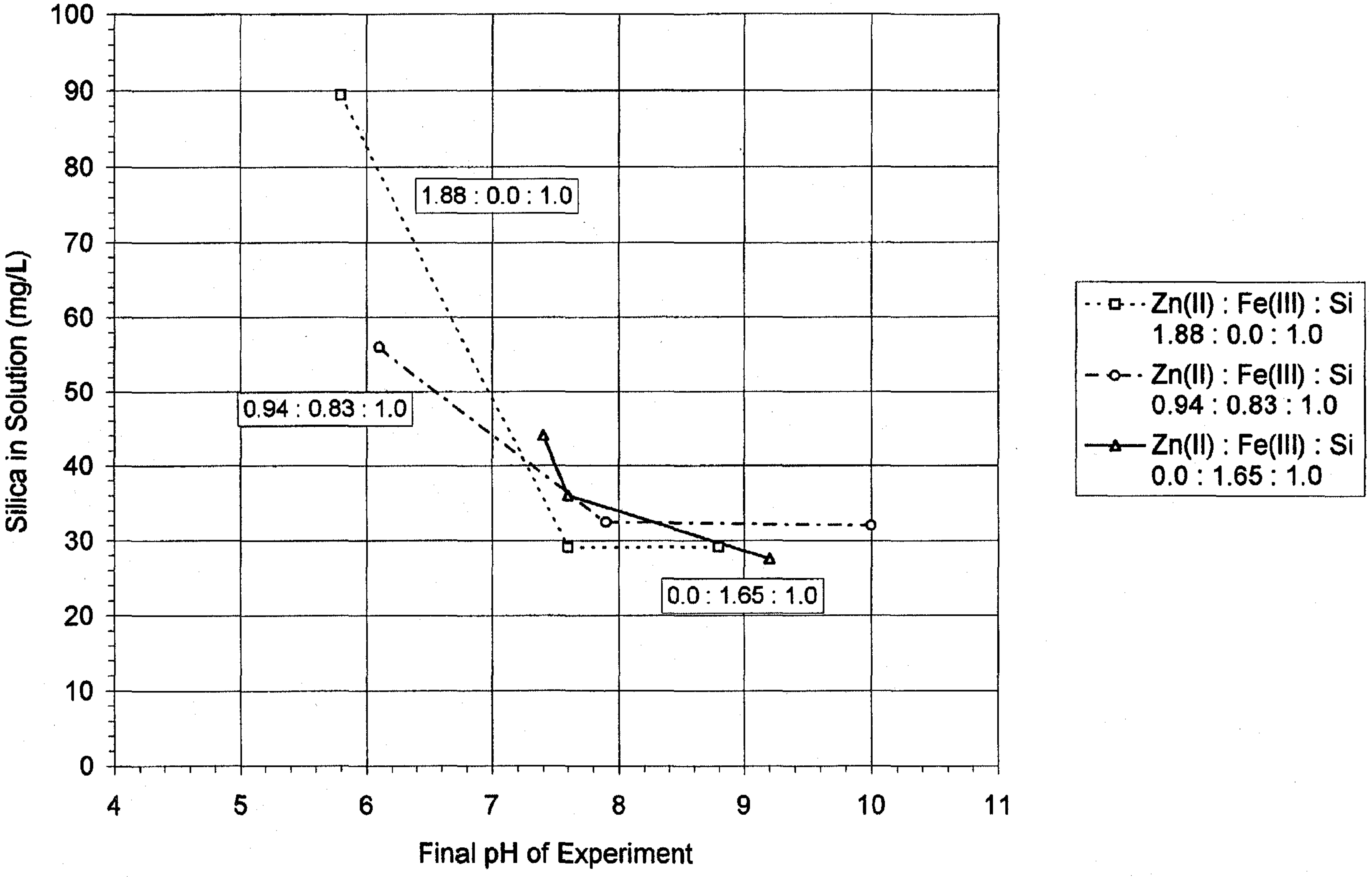

Figure 76. Effect of Zinc, Ferric, and pH on the Solubility of Silica in Water. Zn(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 2

Table 77
Data from the Zinc and Ferric Ions Mixed Valence Metals on the Solubility of Silica Work. Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1. Concentration Units = mg/L.

Zn(II) : Fe(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**					
2 : 0 : 1 **(1.88 : 0 : 1)**		1 : 1 : 1 **(0.94 : 0.83 : 1)**		0 : 2 : 1 **(0 : 1.65 : 1)**	
Initial pH: 6.0					
SiO_2	89	SiO_2	56	SiO_2	44
Ca	15	Ca	14	Ca	14
Mg	5	Mg	5	Mg	5
Fe	0	Fe	0.1	Fe	0.1
Zn	164	Zn	72	Zn	0
Final pH	5.8	Final pH	6.1	Final pH	7.4
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Zn_{6.20}$		$Zn_{0.57}Fe(III)_{2.09}$		$Fe(III)_{3.16}$	
Initial pH: 8.0					
SiO_2	29	SiO_2	32	SiO_2	36
Ca	13	Ca	12	Ca	10
Mg	4	Mg	4	Mg	4
Fe	0	Fe	0	Fe	0
Zn	1	Zn	0.4	Zn	0
Final pH	7.6	Final pH	7.9	Final pH	7.6
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Ca_{0.02}Zn_{2.73}$		$Ca_{0.05}Zn_{1.43}Fe(III)_{1.27}$		$Ca_{0.11}Fe(III)_{2.72}$	
Initial pH: 10.0					
SiO_2	29	SiO_2	32	SiO_2	28
Ca	9	Ca	6	Ca	4
Mg	2	Mg	2	Mg	2
Fe	0	Fe	0.3	Fe	0.1
Zn	0.1	Zn	0.4	Zn	0
Final pH	8.8	Final pH	10.0	Final pH	9.2
Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$		Hypothetical Solid Composition Per $Si_{1.0}$	
$Mg_{0.08}Ca_{0.12}Zn_{2.74}$		$Mg_{0.08}Ca_{0.20}Zn_{1.43}Fe(III)_{1.26}$		$Mg_{0.08}Ca_{0.23}Fe(III)_{2.38}$	

Effect of Zinc and Ferric Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)

Theoretical MR =	(4:0:1)	(2:2:1)	(0:4:1)
Actual MR =	(3.76:0:1)	(1.88:1.65:1)	(0:3.31:1)

The effect of zinc and ferric ions (metals:silicon MR ≅ 4) on the silica solubility in LANL tap water is graphically shown in Figure 77. Data for each solution is given in Table 78.

As usual, using higher mole ratios resulted in reduced concentrations of silica in solution. Silica levels were reduced to 8-16 mg/L in the pH 7.5-9.5 range.

The data suggested that the zinc alone solution (4:0:1) removed silica to a greater degree than the ferric ion (0:4:1) solution over the pH range 7.2-8.7. In these two solutions it should be noted that more zinc to silica was added (MR = 3.76) than ferric ion to silica (MR = 3.31).

The mixed zinc and ferric ion (2:2:1) solution showed a modified pH dependence on the silica solubility. The mixed zinc and ferric ion solution did not enhance the removal of silica beyond the ferric alone solutions. The curves shown resemble those obtained with ferrous ions as in Figure 70. Neither zinc nor silica resolubilized at higher pHs.

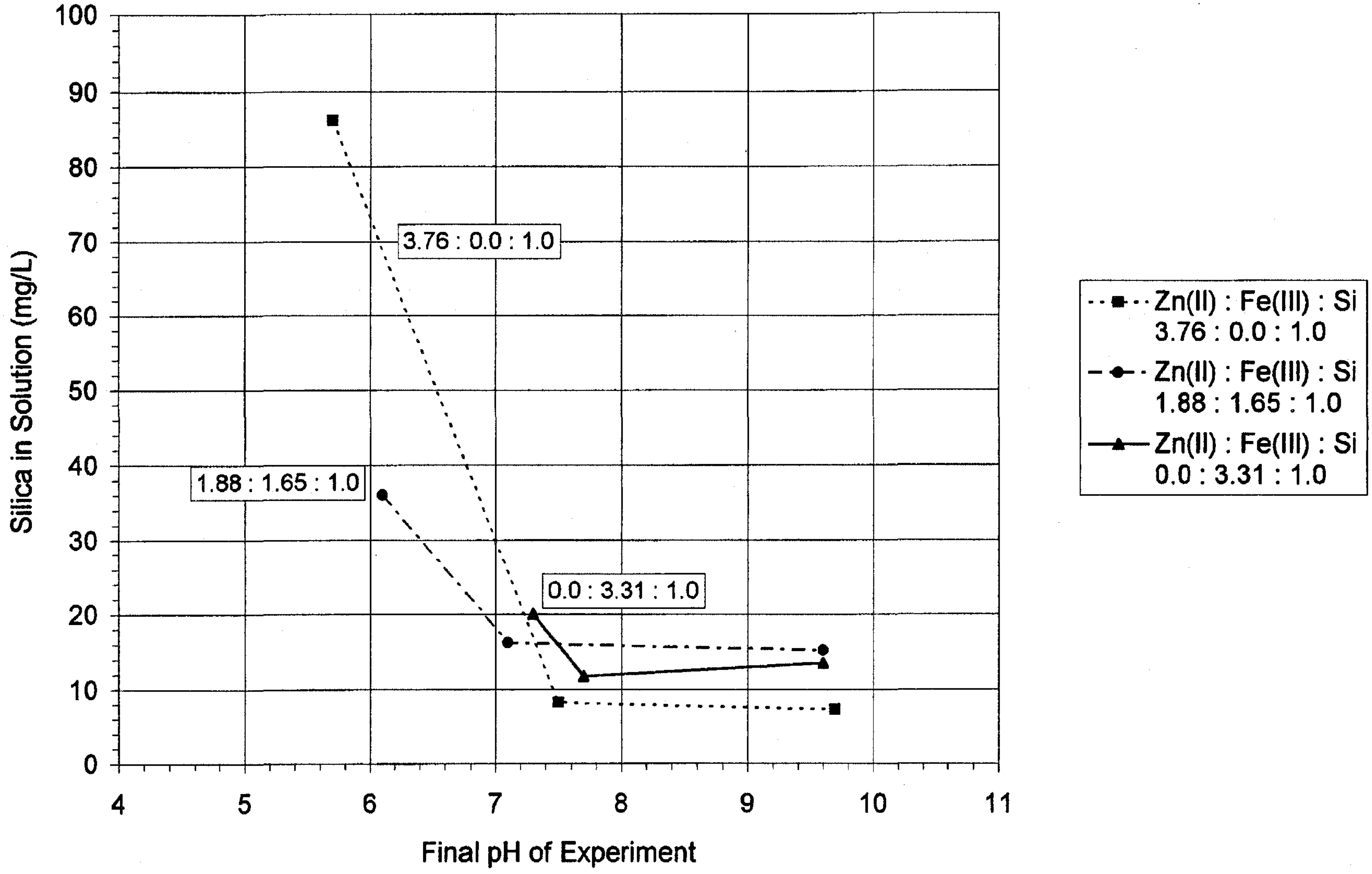

Figure 77. Effect of Zinc, Ferric, and pH on the Solubility of Silica in Water. Zn(II) : Fe(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 4

Table 78
Data from the Zinc and Ferric Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.
Concentration Units = mg/L.

Zn(II) : Fe(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**					
4 : 0 : 1 **(3.76 : 0 : 1)**		2 : 2 : 1 **(1.88 : 1.65 : 1)**		0 : 4 : 1 **(0 : 3.31 : 1)**	
Initial pH: 6.0					
SiO_2	86	SiO_2	36	SiO_2	20
Ca	14	Ca	14	Ca	13
Mg	6	Mg	5	Mg	5
Fe	0	Fe	0.1	Fe	0.1
Zn	341	Zn	157	Zn	0
Final pH	5.7	Final pH	6.1	Final pH	7.3
Hypothetical Solid Composition Per $Si_{1.0}$ $Zn_{5.38}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Zn_{0.55}Fe(III)_{2.72}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Ca_{0.02}Fe(III)_{4.23}$	
Initial pH: 8.0					
SiO_2	8	SiO_2	16	SiO_2	12
Ca	13	Ca	13	Ca	4
Mg	4	Mg	4	Mg	2
Fe	0	Fe	0	Fe	0
Zn	2	Zn	4	Zn	0
Final pH	7.5	Final pH	7.1	Final pH	7.7
Hypothetical Solid Composition Per $Si_{1.0}$ $Ca_{0.02}Zn_{4.11}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Ca_{0.02}Zn_{2.23}Fe(III)_{2.01}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.06}Ca_{0.19}Fe(III)_{3.81}$	
Initial pH: 10.0					
SiO_2	7	SiO_2	15	SiO_2	14
Ca	11	Ca	4	Ca	2
Mg	3	Mg	2	Mg	2
Fe	0	Fe	0.1	Fe	0.5
Zn	0.1	Zn	0.1	Zn	0
Final pH	9.7	Final pH	9.6	Final pH	9.6
Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.03}Ca_{0.05}Zn_{4.08}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.06}Ca_{0.19}Zn_{2.24}Fe(III)_{1.98}$		Hypothetical Solid Composition Per $Si_{1.0}$ $Mg_{0.06}Ca_{0.23}Fe(III)_{3.90}$	

Effect of Zinc and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (2:1)

Theoretical MR = (2:0:1) (1:1:1) (0:2:1)
Actual MR = (1.88:0:1) (0.94:0.87:1) (0:1.75:1)

The effect of zinc and aluminum ions (metals:silicon MR ≅ 2) on the silica solubility in LANL tap water is graphically shown in Figure 78. Data for each solution is given in Table 79.

The addition of zinc did not increase silica removal from solution compared to the removal by the aluminum alone (0:2:1) solution. In these solutions minimum silica solubilities seemed to strongly center around pH 8.0. The zinc alone solution (2:0:1) removed silica down to 29 mg/L; the zinc/aluminum (1:1:1) mixture reduced silica to 20 mg/L at pH 7.5. The mixed solution was intermediate between the pure zinc (1:0:1) solution and the pure aluminum (0:2:1) solution. The minimum silica in solution in the aluminum alone solution was 10 mg/L.

At pH 9.8 there was a slight resolubilization with the zinc/aluminum admixture. There was a greater resolubilization of silica in the aluminum alone solution. In the aluminum alone (0:2:1) solution at pH 9.8 the aluminum in solution was 26 mg/L, contrasted with 2 mg/L at pH 8.0.

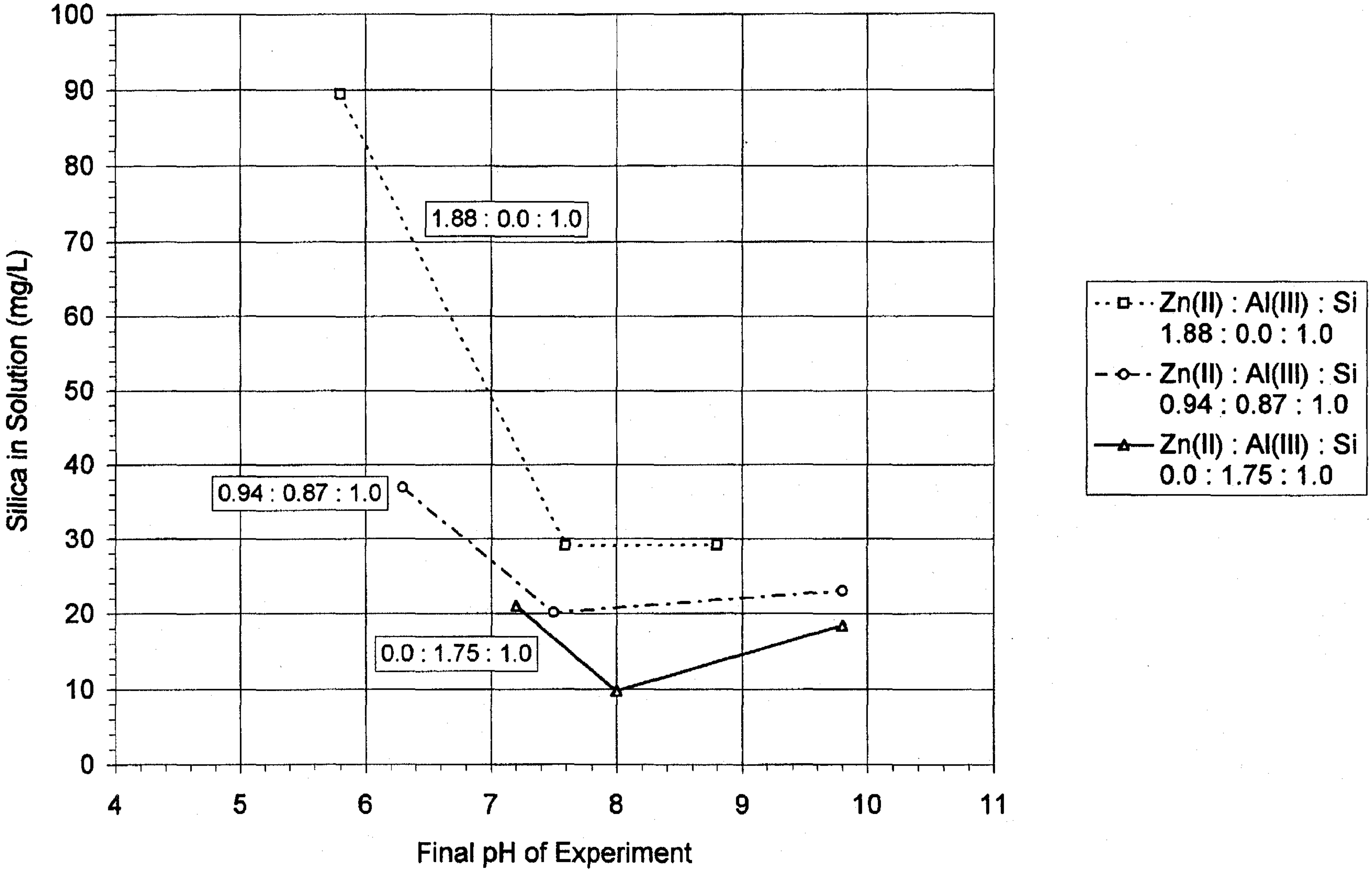

Figure 78. Effect of Zinc, Aluminum, and pH on the Solubility of Silica in Water. Zn(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 2

Table 79
Data from the Zinc and Aluminum Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 2:1.
Concentration Units = mg/L.

Zn(II) : Al(III) : SiO_2 Mole Ratios Hypothetical **(Actual)**			
	2 : 0 : 1 **(1.88 : 0 : 1)**	1 : 1 : 1 **(0.94 : 0.87 : 1)**	0 : 2 : 1 **(0 : 1.75 : 1)**
Initial pH: 6.0			
SiO_2	89	37	21
Ca	15	13	14
Mg	5	5	5
Al	0	1	1
Zn	164	63	0
Final pH	5.8	6.3	7.2
Hypothetical Solid Composition Per $Si_{1.0}$	$Zn_{6.20}$	$Ca_{0.03}Zn_{0.53}Al_{1.45}$	$Al_{2.30}$
Initial pH: 8.0			
SiO_2	29	20	10
Ca	13	12	6
Mg	4	4	2
Al	0	0	2
Zn	1	1	0
Final pH	7.6	7.5	8.0
Hypothetical Solid Composition Per $Si_{1.0}$	$Ca_{0.02}Zn_{2.73}$	$Ca_{0.04}Zn_{1.18}Al_{1.13}$	$Mg_{0.06}Ca_{0.14}Al_{1.97}$
Initial pH: 10.0			
SiO_2	29	23	18
Ca	9	5	1
Mg	2	2	0
Al	0	4	26
Zn	0.1	1	0
Final pH	8.8	9.8	9.8
Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.08}Ca_{0.11}Zn_{2.74}$	$Mg_{0.07}Ca_{0.19}Zn_{1.24}Al_{1.05}$	$Mg_{0.13}Ca_{0.26}Al_{1.45}$

Effect of Zinc and Aluminum Ions and pH on Silica Solubility
Total Metals:Silica Mole Ratio ≅ (4:1)

Theoretical MR =	(4:0:1)	(2:2:1)	(0:4:1)
Actual MR =	(3.76:0:1)	(1.88:1.75:1)	(0:3.50:1)

The effect of zinc and aluminum ions (metals:silicon MR ≅ 4) on the silica solubility in LANL tap water is shown in Figure 79. Data for each solution is given in Table 80.

The aluminum alone, the aluminum/zinc mixture, and the zinc alone mixture are all effective at these mole ratios in the removal of silica to levels below 10 mg/L in the pH range of 7.5-8.1. At pH values above 9.0 some resolubilization of silica is evident in the aluminum containing solutions.

These results reinforced the previous conclusions that aluminum alone was more effective than zinc alone or the zinc/aluminum mixture in removing silica from solution at pHs 7.5-8.1.

The MR 4:1 metals:silicon was more effective than the MR 2:1 in the removal of silica from the water.

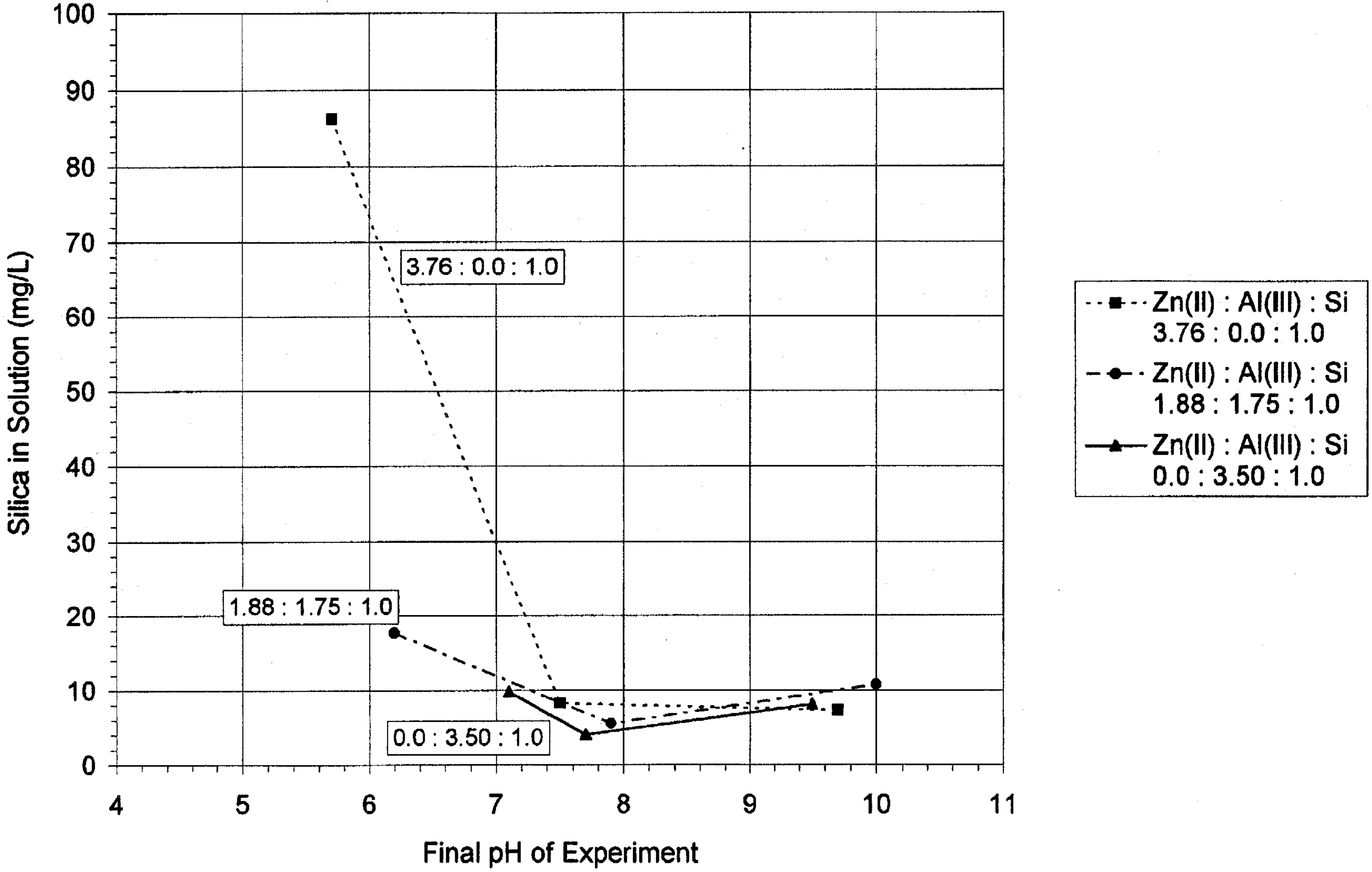

Figure 79. Effect of Zinc, Aluminum, and pH on the Solubility of Silica in Water.
Zn(II) : Al(III) : Silicon Mole Ratios Indicated in Legend. Metals:SiO_2 appx. = 4

Table 80
Data from the Zinc and Aluminum Ions Mixed Valence Metals Work.
Hypothetical Total Moles of Metals to Moles of Silica Equals 4:1.
Concentration Units = mg/L.

$Zn(II) : Al(III) : SiO_2$ Mole Ratios Hypothetical **(Actual)**			
	4 : 0 : 1 **(3.76 : 0 : 1)**	2 : 2 : 1 **(1.88 : 1.75 : 1)**	0 : 4 : 1 **(0 : 3.50 : 1)**
Initial pH: 6.0			
SiO_2	86	18	10
Ca	14	14	14
Mg	6	5	5
Al	0	1	1
Zn	341	134	0
Final pH	5.7	6.2	7.1
Hypothetical Solid Composition Per $Si_{1.0}$	$Zn_{5.38}$	$Zn_{0.70}Al_{2.21}$	$Al_{3.99}$
Initial pH: 8.0			
SiO_2	8	6	4
Ca	13	12	11
Mg	4	2	4
Al	0	0.4	1
Zn	2	0.1	0
Final pH	7.5	7.9	7.7
Hypothetical Solid Composition Per $Si_{1.0}$	$Ca_{0.02}Zn_{4.10}$	$Mg_{0.06}Ca_{0.03}Zn_{2.01}Al_{1.91}$	$Ca_{0.05}Al_{3.74}$
Initial pH: 10.0			
SiO_2	7	11	8
Ca	11	6	2
Mg	3	1	2
Al	0	21	47
Zn	0.1	0.2	0
Final pH	9.7	10.0	9.5
Hypothetical Solid Composition Per $Si_{1.0}$	$Mg_{0.03}Ca_{0.05}Zn_{4.08}$	$Mg_{0.09}Ca_{0.15}Zn_{2.14}Al_{1.47}$	$Mg_{0.06}Ca_{0.21}Al_{2.70}$

Summary - Metals Part 2

In Metals Part 1 of this study we determined the relative effectiveness of some divalent and trivalent cations in the floccing (coprecipitation) of silica. In Metals Part 2 we have attempted to determine whether spinel-type hydrous oxide flocs of mixed valence metals, such as $MgO \cdot Al_2O_3$, would increase the effectiveness of silica removal from LANL water.

The solubility of silica in the single metals work of Metals Part 2 is a marked function of pH and of mole ratio of metal:silica (Figures 60 to 79). The following tabulation (Table 81) shows the pH and silica information used to determine the characteristic pH dependence of silica in the presence of the individual metals used.

The fourth column in Table 81 shows the pH values in increasing order at which a solubility of 10 mg/L of silica is reached in the solutions. The last column shows the slope or gradient of the curve leading to the leveling off of the silica versus pH curves. The pH value, at which this leveling off of the silica concentration occurs, is what might be called the characteristic pH of the reactions.

Table 81

Effect of pH on Silica Solubility in Single Metal Solutions of Metals Part 2 Work

Metal	**Fig. #**	**MR Metals:SiO_2**	**pH at 10 mg/L SiO_2**	**Characteristic pH of the reaction**		**Slope to Level Off Point**
				pH	**mg/L SiO_2**	**mg SiO_2/pH**
$Fe^{+2}_{sparged}$	71	4.0	5.2	5.2	8	-53
Al^{+3}	63	3.5	7.1	7.7	4	-10
Zn^{+2}	77	3.76	7.5	7.5	8	-43
$Fe^{+2}_{unsparged}$	70	4.0	7.6	6.8	12	-42
Fe^{+3}	61	3.31	7.7 @12	7.7	12	-16
Mg^{+2}	61	3.84	8.8	---	near 0	-69
Ca^{+2}	65	3.78	---	---	---	---

The effectiveness of the single metals as flocculants, as a function of pH and mole ratio, was compared at the end of Metals Part 1 section (Figure 59). In Metals Part 2 we also showed the effect of the single cations, but under more standardized mixing conditions and higher mole ratios than in Metals Part 1.

The individual metals used in Metals Part 2, showed characteristic pH responses in the insolubilization of silica.

With magnesium additions, sharp drops in silica solubility occurred between pH 8.2 and 8.8 (Figures 60 through 63).

In the work with calcium addition, no effect on silica solubility was observed over the pH range from 6.2 to 9.7 (Figures 64 through 67).

Low solubility of silica was found in solutions with aluminum additions. Silica solubility was sharply dependent on the aluminum:silica mole ratio and pH. As an insolubilizer of silica, aluminum is more effective than most of the other metals at pHs below 8.0 (Figures 73 and 74).

Ferrous iron, Fe (II), had a very strong effect on the removal of silica (Figures 68 through 75). The effectiveness of the Fe (II) iron as a silica remover was increased by removal of oxygen from the solutions by sparging with nitrogen gas prior to mixing the metal ion into the water. One effect of Fe (II) iron addition alone was to lower the pH at which the desired 10 mg/L or less of silica, left in solution, was attained.

Ferric iron, Fe (III), showed a moderate effect of pH on silica insolubilization, being most effective above pH 7.7. The effect of mole ratio of Fe(III):silica is moderate as seen is Figures 68 through 71.

The effect of zinc on silica insolubilization is greatest at pH values above 7.0. Silica is removed to the 8 mg/L level, at pH 7.5, in the zinc:silica mole ratio 3.76 solution (Figure 79).

Figure 80 shows the effects, on silica solubility, of mole ratios of the individual cations, at pH 9.0. By inspection of Figure 80, the following list was developed showing the mole ratios of the metals needed to reduce the silica solubility to the required 10 mg/L level.

$\text{Ferrous}_{\text{sparged}}$	MR = 2.5
Aluminum	MR = 2.8
Magnesium	MR = 3.3
$\text{Ferrous}_{\text{non-sparged}}$	MR = 3.3
Zinc	MR = 3.6
Ferric	MR = 3.7

The values of silica remaining in solution converge on silica equal to 0 mg/L at mole ratios greater than 4.0. Figure 80 shows that silica removing capability increases with mole ratio.

The effect of mixtures of bivalent and trivalent cations on silica solubility are discussed in the following paragraphs.

Mg : Fe (III)

The mixed solutions of magnesium and ferric iron, as shown in Figures 60 and 61, showed intermediate ability to remove silica from solution. At pH values below 9.0, the trivalent ferric iron was dominant in the removal of silica. Above pH 9.0, the divalent magnesium ion controlled the silica solubility.

Mg : Al (III)

Mixed solutions of magnesium and aluminum, as seen in Figures 62 and 63, show silica contents which are intermediate between the magnesium (alone) and the aluminum (alone) solutions. At pH values above 9.0 the mixed solution lowers silica solubility below that of the aluminum (alone) with no evidence of silica resolubilization at increasing pH values.

Ca : Fe (III)

Figures 64 and 65 show the effect of varying additions of calcium and ferric iron on silica solubility as a function of pH. Calcium has essentially no effect on silica solubility. The removal of silica from the mixed solutions of calcium and ferric iron was dominated by the ferric iron.

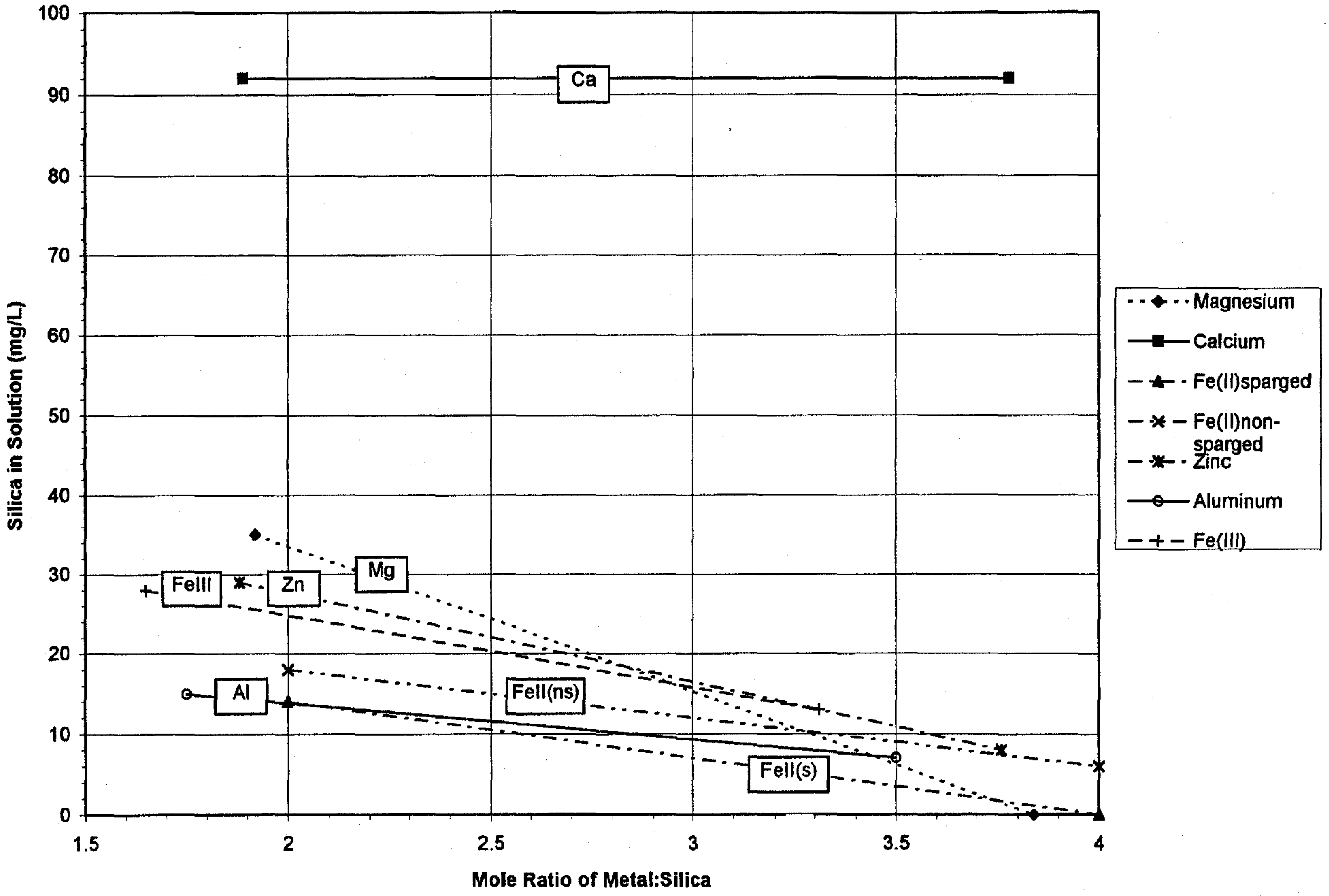

Figure 80. Effect of Valence II and III Metals at pH 9.0 As a Function of Mole Ratio of Metals to Silica.

Ca : Al (III)

The effect on silica solubility of additions of calcium and aluminum is shown is Figures 66 and 67. Aluminum dominates the removal of silica by the calcium and aluminum mixtures. Calcium had no effect. However, calcium seemed to prevent resolubilization of silica at pH values greater than 8.0.

Fe (II) : Fe (III)

Figures 68 through 71, show the effect on silica solubility of adding ferrous iron and ferric iron to solutions. In these, the divalent ferrous is dominant. The effect of sparging the solutions with nitrogen gas (Figures 69 and 71) is to markedly improve removal of silica by the mixed ions.

Fe (II) : Al (III)

The effect of using the mixed ferrous and aluminum flocculation is shown in Figures 72-75. The mixture is less effective in the oxygen containing, unsparged solutions, than in the nitrogen sparged solutions. Sparging removes dissolved oxygen, and effectively raises the ferrous content. The mixed solution in Figure 73 is more effective than the aluminum (alone) and the ferrous (alone) solutions at pH 7.8.

Zn : Fe (III)

Figures 76 and 77 show the affect of zinc and ferric iron on silica solubility. At pH values greater than 7.5 the divalent zinc ion was more effective than ferric iron in reducing the silica solubility. The silica solubility curves of the mixed solutions of zinc and ferric iron at pHs greater than 7.5 were similar to the curves obtained with the zinc alone solutions.

Zn : Al (III)

In the case of zinc and aluminum mixed solutions, as shown in Figures 78 and 79, the trivalent aluminum is dominant. The effect of the divalent zinc addition is to flatten the curves at pH values between 7.4-10.0. The effect is to minimize silica resolubilization.

The effect of the mixed valence additions, usually, is to produce silica solubilities intermediate between those with divalent (alone) and the trivalent (alone) ion. No particular advantage in silica removal is noted by using mixed valence metals except in the case of ferrous and aluminum (see Figure 73). A notable effect in the ferrous and aluminum solutions was the preventing of silica resolubilization at high pH values, where resolubilization would occur with the aluminum (alone) solutions.

The effect of pH on silica solubility in the mixed metals solutions is summarized in Table 82. In this table, the mixed metals solutions are arranged in their order of increasing pH at which the silica concentration was reduced to the 10 mg/L target level.

Table 82

Removal of Silica in Mixed Metal Solutions As a Function of pH

Mixed Metals	Figure No.	Mole Ratio Me(II):Me(III):Si	pH at 10 mg/L SiO_2
$Fe(II)_{sparged}/Al$	75	2.0/1.75/1.0	6.2
Zn/Al	79	1.88/1.75/1.0	7.2
$Fe(II)_{nonsparged}/Al$	74	2.0/1.75/1.0	7.5
Mg/Al	63	1.92/1.75/1.0	7.6
$Fe(II)_{sparged}/Fe$	71	2.0/1.65/1.0	7.6
Ca/Al	67	1.89/1.75/1.0	7.7
$Fe(II)_{nonsparged}/Fe$	70	2.0/1.65/1.0	8.5
Mg/Fe	61	1.92/1.65/1.0	8.9

IV. FINAL SUMMARY AND CONCLUSIONS

Question #1

How long a time of rest is required for silica to reach a steady state solubility following evaporation at 50° C?

Answer #1

It was determined that a minimum 50 hour time of standing was necessary for silica to reach a steady state solubility following the evaporation experiments. Appendix C details the experimental procedure used.

Question #2

What is the effect of pH on silica solubility in LANL tapwater?

Answer #2

The effect of pH on silica solubility in LANL tapwater is shown in Figure 5. Between pH values of 2.4 to 7.8, silica solubility remains relatively high. Solubility then drops sharply to 150-160 mg/L between pH 8.2 to 8.7. Solubility rises again at pH 9.0. At pH values greater than 9.0, silica solubility becomes quite erratic. This behavior may be due to the formation of silicate ions and the precipitation of silicates.

Question #3

How reproducible is data in the solubility of silica?

Answer #3

The reproducibility of silica solubility data is best shown in Figure 1K. In this figure, the measured silica found in 59 control evaporation runs (295 data points) is plotted. The data points did cluster close together for the most part. But the figure shows there are two clusters of dissolved silica values around 250 and 540 mg/L Expected Silica. These data indicate extraordinarily high occasional supersaturation of the silica.

Question #4

What is the effect of anionic additives, both inorganic and organic, on the solubility of silica is LANL tap water?

Answer #4

Inorganic anion additives:

Among inorganic anions, it was found that fluoride solubilizes silica at MR 3.3 (Figure 6). The other halides (chloride, bromide, and iodide) had little effect (Figures 7, 8, and 9). The thiocyanate ion, a pseudo halide, induces some supersaturation (Figure 10). The oxygen-bearing anions: phosphate (Figure 17), sulfate (Figure 14), bisulfite (Figure 16), sulfamate (Figure 15), and nitrate (Figure 12) either kept silica in solution or helped keep it in a supersaturated (thermodynamically unstable) condition. It was also found that anions which insolubilize or complex magnesium and calcium also increased the solubility of silica in the water. The magnesium is apparently the key element in the insolubilization of silica. The order of effectiveness of the inorganic anions on silica solubility at a concentration factor of 7.5 (Expected Silica of 600mg/L) is shown in the following series:

$$PO_4^{-3} > F^{-1} > SO_4^{-2} > HSO_3^{-1} > NH_2SO_3^{-1} > NO_3^{-1} > NO_2^{-1} >>$$
$$SCN^{-1} > Cl^{-1} = Br^{-1} = I^{-1}$$

For comparison with the inorganic anion addition work, the solubility of silica was determined in a deionized water solution of sodium metasilicate. The resulting curves, Figures 19 and 20, describing the solubility of silica in such solutions bore no resemblance to the data found with LANL tapwater controls. The solubility was much greater than in tapwater and no saturation limits were reached, within the limits of the concentration factors. These results point up the differences between the solubility of silica in LANL tapwater and those found in previous work which used silica solutions not found in nature.

Organic anion additives:

The effects of various types of organic compounds (various functional groups) on silica solubility have been evaluated using the evaporative technique.

The various organic compounds (and their functional groups) are listed in decreasing order of effectiveness as solubilizers for SiO_2:

Compounds	Functional Groups
Kelig 32	lignin sulfonate
Maracell XE	lignin sulfonate
Marasperse N-22	lignin sulfonate
Catechol	1,2-dilhydroxybenzene
Oxalate	ethanedioate
Tiron	4,5-dihydroxy-1,3-benzene disulfonate
Pyrogallol	1,2,3-trihydroxydenzene
Phlorogucinol	1,3,5-trihydroxydenzene
Citrate	2-hydroxy-1,2,3,-propane tricarboxylate
Ortho-phthalate	1,2-benzene dicarboxylate
Para-phthalate	1,4-benzene dicarboxylate
EDTA	ethylenediaminetetraacetate
Maleate	cis-1,2-ethylenedicarboxylate

Some other types of compounds have considerable effects as supersaturants:

Compounds	Functional Groups
Formate	monocarboxylate
Sebacate	1,8-octanedicarboxylate
Para-toluene sulfonate	4-methylbenzene sulfonate

Other compounds that did not enhance suersaturation include:

Compounds	Functional Group
Acetate	methycarboxylate
Salicylate	2-hydroxybenzoate
Alkyl-napthalene sulfonate	alkyl-napthalene sulfonate

It was seen on the basis of this work that complexation or removing magnesium from solution is the effective method of keeping silica in solution. This does not rule out the possibility that in some cases silica is also complexed.

Question #5

Is silica above 160 mg/L in evaporated solutions in true solution or supersaturated (thermodynamically unstable)?

Answer #5

In control solutions of LANL tapwater, the silica in solution above 160 mg/L is in a supersaturated condition (Figure 1). This work has identified in both organic and inorganic anions at least two types of solubility.

One type defines an additive as a solubilizer if silica is maintained in solution to concentrations greater than 500 mg/L and the slope of the Measured Silica to Expected Silica curve is close to "one" in the original graphs. Several additives that have demonstrated solubilizing power are, for example, the lignin sulfonates, catechol, oxalate, and Tiron.

A second type of solubility, supersaturation, is defined as a region on the solubility curves above 160 mg/L silica. In this supersaturated condition, the silica may reach concentrations as great as 500 mg/L. Upon further evaporation, the silica concentrations abruptly decrease to the 160 mg/L level. Two examples are seen in solutions of sulfate and formate.

Question #6

What is the chemistry involved in the solubility of silica in the presence of anionic additives?

Answer #6

It was found that anions which complex magnesium (for example, citrate, oxalate, and EDTA) also increase the solubility of silica in the water. The magnesium is apparently the key element in the insolubilization of silica in LANL tapwater. Calcium has very little effect. This does not rule out the possibility that in some cases silica is also complexed.

Question #7

What is the effect of common flocculating cations, such as magnesium, calcium, iron, aluminum, etc., on the solubility of silica?

Answer #7

The removal of silica to levels below 10 mg/L was found to be a function of pH and mole ratios of metal additive to silica in the water. The minimum pH for various metal solutions to reach the required 10 mg/L silica content are shown below (as taken from Table 81):

Metal Additive	**MR Metal:SiO_2**	**pH (at 10 mg/L SiO_2)**
Fe^{+2} sparged	4.0	5.2
Al^{+3}	3.5	7.1
Zn^{+2}	3.76	7.5
Fe^{+2} unsparged	4.0	7.6
Fe^{+3}	3.31	7.7 (@ 12 mg/L)
Mg^{+2}	3.84	8.8

The effect of mole ratio of metal additive on the solubility of silica is shown in Figure 80. The following listing (as taken from Figure 80) demonstrates at pH 9.0, the mole ratios of metals required to remove silica below the required 10 mg/L silica content in the LANL tapwater:

Metal Additive	**MR Metal:SiO_2**
Fe^{+2} sparged	2.5
Al^{+3}	2.8
Mg^{+2}	3.3
Fe^{+2} unsparged	3.3
Zn^{+2}	3.6
Fe^{+3}	3.7

The effect of the mixed valence additions, usually, is to produce silica solubilities intermediate between those with divalent (alone) and the trivalent (alone) ion. No particular advantage in silica removal is noted by using mixed valence metals except in the case of ferrous and aluminum (Figure 73). A notable effect in the ferrous and aluminum solutions was the preventing of silica resolubilization at high pH values, where resolubilization would occur in the aluminum (alone) solutions.

V. FUTURE WORK

1. The mechanisms of magnesium's reactions with silica need to be evaluated.

2. The corrosivity of silica solubilizers needs to be investigated by literature research and by lab scale studies on various metals used in cooling systems.

3. Optimization of silica flocculation with magnesium, iron, and aluminum ions.

4. Since the removal of silica scales presently involves the use of hazardous chemicals (such as ammonium bifluoride and hydrochloric acid), the use of less hazardous solubilizers should be investigated for the possible removal of deposited silica scale.

5. Developing and evaluating light-scattering methods as a possible indicator of insoluble silica forming in solutions.

6. Determining the effects of highly turbulent liquid flow on the stability of silica solutions.

7. Evaluate various alkaline materials for their effects on silica solubility.

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VII. APPENDICES

APPENDIX A

Preparation of Solutions

Solutions for evaporation were prepared by a consistent procedure. The solutions were made with a given mole ratio of additive to silica. The various mole ratios of chemical to silica were selected depending on expected reactivity. Reagents, unless specified, were of AGS Reagent Grade. Mole ratios in the range of 0.1, 0.25, 0.5, 1.0, 2.0, and 4.0 were selected.

On the basis of analyses of a number of samples of tap water, the silicon (Si) content used in our work was set at 37 mg/L, equivalent to 79.2 mg/L silica (SiO_2). On a molar basis, these concentrations were 0.00132 mole/L silica. Therefore, to investigate the reactivity of a 1-to-1 molar ratio of a certain chemical with silica, 0.00132 moles/L of that chemical were added to the tap water. For a 0.1-to-1, or one-tenth mole ratio, 0.000132 mole/L of the chemical were added to the tap water.

Table 1A

Amount of Chemical Added to Tap Water for Various Mole Ratios (MRs) to Silica

Mole Ratio (MR) of Chemical to Silica	**Concentration of Chemical in Solution (Moles/Liter)**
0:1 = 0	0.0
0.1:1 = 0.1	0.00013
0.25:1 = 0.25	0.00033
0.5:1 = 0.5	0.00066
1:1 = 1	0.00132
2:1 = 2	0.00264
3:1 = 3	0.00396
4:1 = 4	0.00528

Step 1: The tap water was allowed to run at a fast flow for approximately three minutes, in order to purge the water line of any contaminants or particles. Four liters of the tap water were then measured, using a 1-L polypropylene volumetric flask, into a 20-L polypropylene container.

Step 2: The weighed quantity of additive was added to the water in the container with continuous stirring with a magnetic stirrer. The pH of the solution was adjusted as needed to the desired value with nitric acid or sodium hydroxide.

Since the silica content of the tap water varied at times, the actual ratio of additive to silica in the water differed from the assumed ratio. The ratio reported is the ratio of the weighed chemical to the actual (analyzed) silica present.

APPENDIX B

Evaporation of Solutions

A consistent evaporation procedure was used on the test solutions:

Step 1: Six hundred milliliters of the test solution, prepared as described in Appendix A, were poured into each of five, 600 ml Griffin low form polypropylene beakers manufactured by Nalgene™. The excess test solution was discarded.

Step 2: Beaker #1 (control sample), containing no additives, was immediately covered with Parafilm™ to prevent evaporation of the solution and contamination from the air. The other four beakers were placed on a Boekel™ stainless steel steam bath. The steam bath was boiling at 94°C (due to the elevation in Los Alamos at 7,200 ft. above sea level). Since the steam bath was located in a fume hood, room air was continuously pulled over the solutions in the beakers. This speeded the evaporation rate.

The solutions in the beakers reached a maximum temperature of about 50°C. A convection current caused by the difference in temperature between top and bottom resulted in a density gradient and an inversion of solution in the beaker approximately every minute.

Step 3: The four beakers of solutions were removed from the steam bath when they approached their target volumes. The target volume for beaker #2 was 300 ml; for beaker #3, 150 ml; for beaker #4, 100 ml; and for beaker #5, 75 ml. The steam bath times required to reach the target volumes were: 20, 24, 26, and 28 hours respectively. Upon removal from the steam bath, the beakers were immediately covered with Parafilm.

Step 4: The five beakers for a particular solution sat quiescently for 48 hours. This two-day period was required for the solutions to come to a steady state at room temperature which was generally 20-25°C.

Table 1B below shows the target volumes, concentration factors, and expected silica concentrations in the five beakers involved in one solubility experiment. In fact, actual volumes were measured cold for each concentration.

Table 1B
Evaporation Technique Used in the Solubility Studies

Beaker Number				
1	2	3	4	5
Measured Volume (ml)				
600	300	150	100	75
Concentration Factor				
1	2	4	6	8
Expected Silica (mg/L)				
90	180	360	540	720

APPENDIX C

Time of Standing to Steady State

LANL tap water is known to supersaturate after evaporation. The time required to reach a steady state silica concentration was determined in a series of experiments.

Twelve polypropylene beakers were each filled with 600 ml of LANL tap water. Six of the solutions were allowed to remain at their natural pH of 8.1. The other six solutions were adjusted to pH 3.5 with nitric acid. The solutions were evaporated in an oven at 65°C for varying periods of time to achieve required concentration. After evaporation, they were all withdrawn at the same time to cool to room temperature (23°C). Samples for analysis were taken from each solution, pressure filtered, and analyzed for SiO_2. The remainder of the solution was allowed to stand for the required time periods. The time periods were 2, 6, 25, 50, and 150 hours. At each time period, samples were taken, pressure filtered, and analyzed for SiO_2. One sample, the control, was not heated or allowed to evaporate.

The values of silica determined are plotted as a function of time of standing in Figure 1C. The first batch of solutions was at initial pH 8.1. When the same procedure was followed on solutions at initial pH 3.5, similar behavior was observed. Figure 2C shows corresponding values. Figures 1C and 2C and Table 1C and Table 2C show that in most cases, the apparent solubility was quite high but that all the values came down to a steady state at approximately 50 hours. Their shapes and levels of solubility differ considerably. This indicated the effect that the pH has on solubility.

Tables 1C and 2C, respectively, show the pertinent data for the initial pH 8.1 and pH 3.5; "time to steady state" experiments.

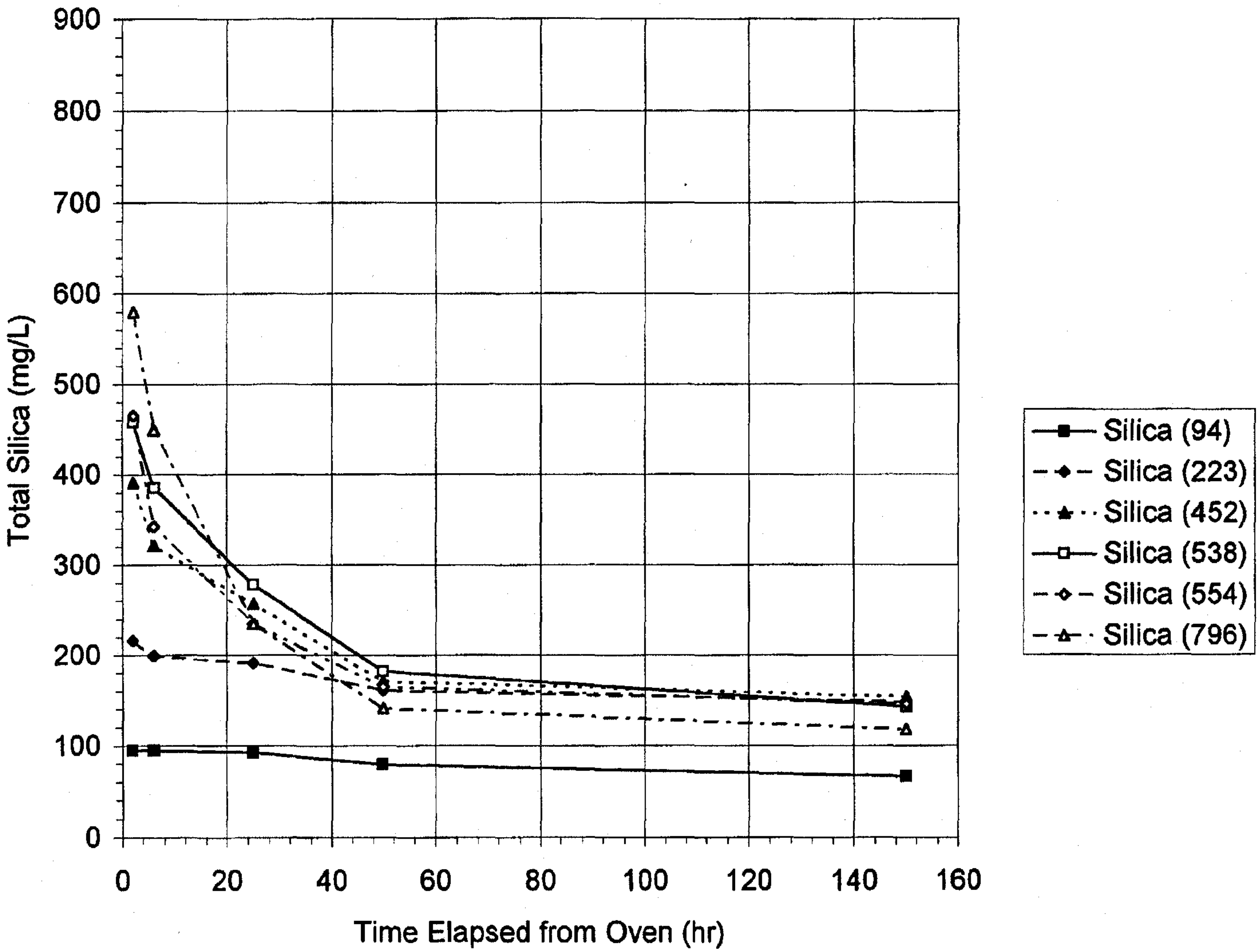

Figure 1C. Silica Solubility versus Time to Steady State. Initial pH: 8.1.
Temperature of heating: 65 Degrees Celsius
Legend: Expected Silica Concentration in Each Beaker (mg/L).

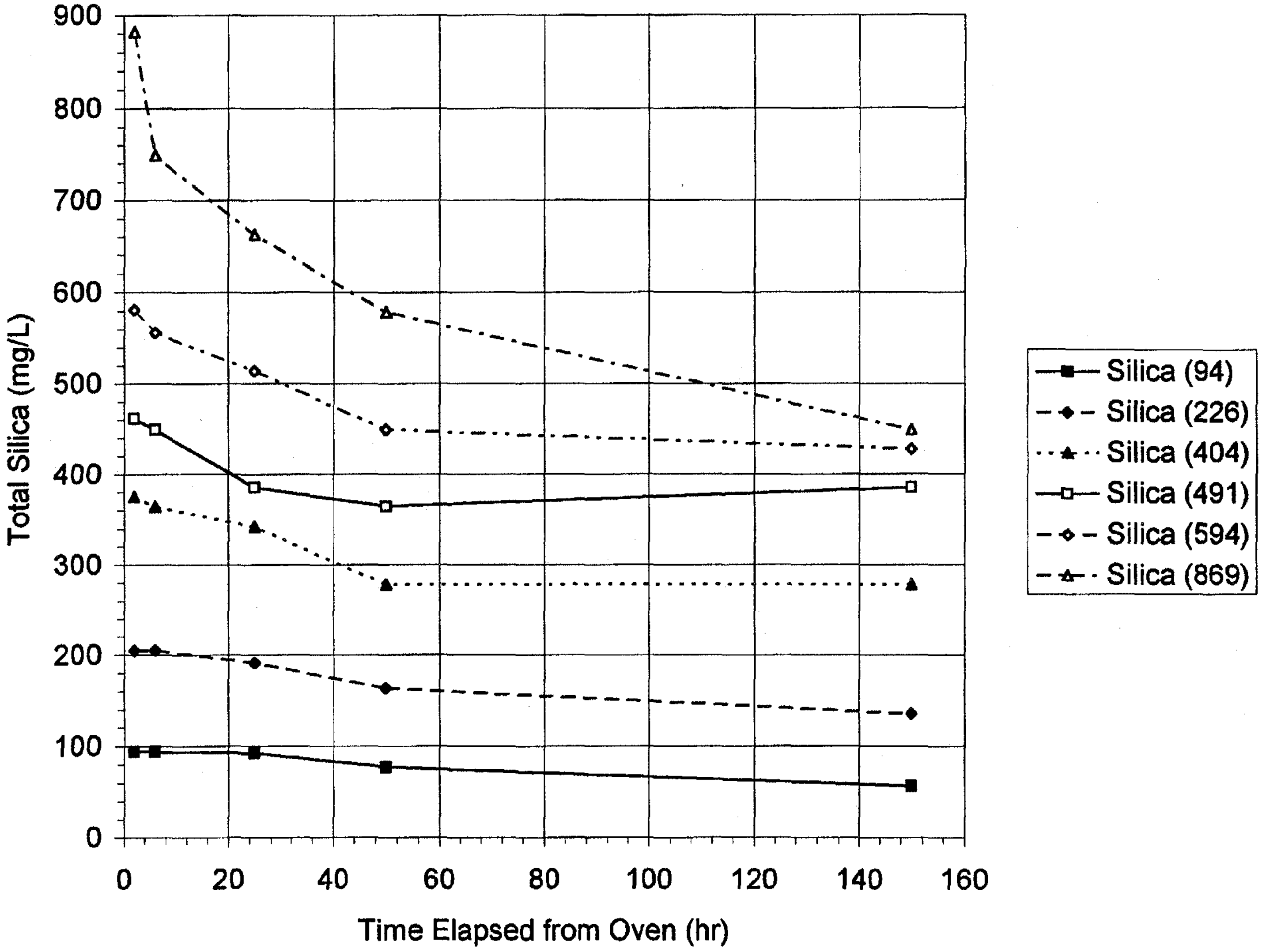

Figure 2C. Silica Solubility versus Time to Steady State. Initial pH: 3.5.
Temperature of heating: 65 Degrees Celsius
Legend: Expected Silica Concentration in Each Beaker (mg/L).

Table 1C
Data from Time to Steady State Experiment: Initial pH 8.1

Beaker	Final Volume (ml)	Expected Total Silica (mg/L)	Time of Rest (hour)	Measured Total Silica (mg/L)	pH
#1	600	94	2	94	5.9
“	“	“	6	94	
“	“	“	25	92	
“	“	“	50	79	
“	“	“	150	66	
#2	253	223	2	216	9.2
“	“	“	6	199	
“	“	“	25	191	
“	“	“	50	161	
“	“	“	150	148	
#3	125	452	2	391	9.3
“	“	“	6	321	
“	“	“	25	257	
“	“	“	50	171	
“	“	“	150	154	
#4	105	538	2	458	9.4
“	“	“	6	385	
“	“	“	25	278	
“	“	“	50	182	
“	“	“	150	143	
#5	102	554	2	465	9.4
“	“	“	6	342	
“	“	“	25	235	
“	“	“	50	165	
“	“	“	150	146	
#6	71	796	2	580	9.4
“	“	“	6	449	
“	“	“	25	235	
“	“	“	50	141	
“	“	“	150	118	

Table 2C
Data from Time to Steady State Experiment: Initial pH 3.5

Beaker	Final Volume (ml)	Expected Total Silica (mg/L)	Time of Rest (hour)	Measured Total Silica (mg/L)	pH
#1	600	94	2	94	3.1
"	"	"	6	94	
"	"	"	25	92	
"	"	"	50	77	
"	"	"	150	56	
#2	250	226	2	205	3.2
"	"	"	6	205	
"	"	"	25	191	
"	"	"	50	163	
"	"	"	150	135	
#3	140	404	2	375	2.9
"	"	"	6	364	
"	"	"	25	342	
"	"	"	50	278	
"	"	"	150	278	
#4	115	491	2	461	2.9
"	"	"	6	449	
"	"	"	25	385	
"	"	"	50	364	
"	"	"	150	385	
#5	95	594	2	581	2.8
"	"	"	6	556	
"	"	"	25	514	
"	"	"	50	449	
"	"	"	150	428	
#6	65	869	2	882	2.7
"	"	"	6	749	
"	"	"	25	663	
"	"	"	50	578	
"	"	"	150	449	

APPENDIX D

Filtration of Solutions

All solutions from the evaporation and nonevaporation flocculation experiments were filtered following the 48 to 50-hour time of standing. Pressure filtration of the solutions was used to avoid changes in concentration due to evaporation.

The pressure filter used was the Antlia Pneumatic Hand Pump System, manufactured by the Schleicher & Schuell Company. Approximately 50 ml of filtered solution from each beaker was obtained for analyses. The pressure filter was then disassembled and thoroughly rinsed twice with tap water preceding the next filtration procedure.

Supor™ membrane filters (manufactured by Gelman) were used. The pore size was 0.2 µm and the diameter of the membrane was 47 mm. Supor™ is an inherently hydrophilic polysulfone membrane that offers higher fluid flow rates, lower extractables, and greater strength than similar cellulosic (acetate, nitrate) membranes. Some membranes with noticeable solids accumulated on them were saved for further analyses. Other membranes were discarded.

The reasons for not using a finer filter were

a) less time consumption

b) less of a possibility of the filter causing coagulation of supersaturated silica through increased shearing action.

APPENDIX E

Beaker Preparation

In many instances in our work, saturated and supersaturated solutions were produced. It was decided that the beaker used should be rigorously cleaned to make certain that no nuclei were left to affect the solubility results. The following procedure yielded consistent results with experiments:

1. Rinsed with tap water and scrubbed with a paper towel.
2. Submerged for at least 24 hours.
3. Vigorously rubbed and rinsed with tap water.
4. Scrubbed with a 300 ml solution of 3 N hydrochloric acid and double rinsed with deionized water.

Beakers that maintained their hydrophobic surface character and in no way were stained by chemical additives were then inverted and allowed to dry.

APPENDIX F

Analytical Techniques

Silicon

The chemical analyses for total silicon were performed according to Standard Method 3120: "Metals by Plasma Emission Spectroscopy," in Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992, APHA, AWWA, WEF; published by APHA, Washington, D.C. The concentrations of silicon, sodium, magnesium, aluminum, calcium, titanium, manganese, iron, copper, and zinc in the experimental solutions were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) manufactured by Thermo-Jarrell Ash Corp. The instrument was a 1992, 61E Purge model. It used argon gas for the plasma and for the purge cycle.

The instrument was standardized using National Institute of Standards and Technology (NIST) Standard Reference Materials. All the spectrometric solutions were 10 μg/ml of the appropriate metal. Solutions used were as follows: #3101a for aluminum in 10% HNO_3; #3109a for calcium in 10% HNO_3; #3150 for silicon in water; #3152a for sodium in 1% HNO_3; and #3168 for zinc in 10% HCl.

An initial calibration verification of the standard solutions was performed using a 100 times dilution of Spex MultiElement Plasma Standard. This standard consisted of the metals in a 3% HNO_3 solution with a trace of hydrofluoric acid and tartaric acid in water. The undiluted Spex standard consisted of 2500 μg/ml of Al, Ca, Mg; 1000 μg/ml of Fe, K, Na; 250 μg/ml of Si; 100 μg/ml of As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, and Zn; and 25 μg/ml of Sn.

A third standard for silicon was also used in the analyses. This standard was 10 mg/L of silicon. It was the Direct Reader Setup Standard No. 4 from the Thermo-Jarrell Ash Corporation.

After the instrument was calibrated, ten samples were analyzed. The instrument calibration was then checked using the diluted Spex MultiElement Plasma Standard solution.

Carryover of signal from one sample to the next was checked using deionized water containing 3% HNO_3. When calibration checked and carry over signal was negligible, 10 more samples were analyzed.

Sodium, Magnesium, Aluminum, Calcium, Titanium, Manganese, Iron, Copper, and Zinc

The chemical analyses for sodium, magnesium, aluminum, calcium, titanium, manganese, iron, copper, and zinc were performed in accordance with Standard Method 3120: "Metals by Plasma Emission Spectroscopy," Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992, APHA, AWWA, WEF, published by APHA, Washington, D.C. The spectrometer was calibrated and the analyses were performed as described under the analytical method for silicon.

Chloride, Sulfate, Nitrate, and Fluoride

Standard Method 4110: "Determination of Anions by Ion Chromatography," in Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992, APHA, AWWA, WEF; published by APHA, Washington, D.C.

pH

Standard Method 423: "pH Value," in Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985, APHA, AWWA, WEF; published by APHA, Washington, D.C.

Alkalinity

Standard Method 403: "Alkalinity," in Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985, APHA, AWWA, WEF; published by APHA, Washington, D.C.

APPENDIX G

Metal Ion Addition Experiments (Part 1)

The detailed procedures used in the Part 1 cation work follows.

Step 1: Four 600 ml Griffin low form polypropylene Nalgene™ beakers were filled with 600 ml of tap water.

Step 2: A small, Teflon coated, magnetic stir bar was placed in the beaker and the solution was vigorously stirred on a magnetic mixer.

Step 3: Calculated mass of the desired chemicals were weighed in a closed chamber analytical balance to the third place in a plastic weighing dish. No special effort was made to avoid contact with air, but the material was transferred rapidly and weighing chamber and original container closed.

Step 4: The chemical was dissolved in the tap water by mixing for five minutes.

Step 5: The pH of the solution was adjusted to the appropriate pH of 4.0, 6.0, 8.0, and 10.0 by addition of dilute nitric acid or sodium hydroxide. The solution, at the adjusted pH, was stirred for five minutes.

Step 6: The other solutions in a series were similarly prepared to yield the desired mole ratio and pH.

Step 7: The beakers were covered with Parafilm as they came off the magnetic stirring apparatus. Twenty-four hours later, the flocculated material was resuspended in the beakers by rotating the covered beakers by hand.

Step 8: After a forty-eight hour total rest period, the solutions were pressure filtered through 0.2 micron polysulfone membrane filters. Samples were then taken for analysis.

APPENDIX H

Flocculation Experiments (Part 2) Cationic Additions

The detailed procedures used in the Part 2 cation work (flocculation) follows.

Preparation of Stock Solutions

The stock solutions of magnesium, calcium, ferrous iron, ferric iron, zinc, and aluminum used in the Part 2 cation experiments were of such concentrations that 10 ml added to 600 ml of tap water produced a 4:1 molar ratio of the metal to silicon. Proportionally, a 5 ml addition would produce a 2:1 MR and a 2.5 ml addition produced a 1:1 MR. The basic assumption in preparation of the stock solutions was that LANL tap water has 37 mg Si/L or 79.2 mg SiO_2/L.

The stock solutions were prepared using $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$. All the cationic chemicals were "Reagent Grade." Due to the hygroscopic nature of some of the salts, the measured concentrations of the stock solutions was somewhat different than the target theoretical concentrations. The metal ion concentrations in the actual test runs were determined spectroscopically.

Table 1H
Theoretical and Actual Amounts of Metals Added to Cations Part 2 Solutions. The Initial Silica Concentration in the Tap Water was 93 mg/L.

Metal	Theoretical Mole Ratio	Actual Mole Ratio	Actual (mg/L)
Magnesium	1	0.96	36
"	2	1.92	72
"	4	3.84	143
Calcium	1	0.95	59
"	2	1.89	117
"	4	3.78	234
Aluminum	1	0.87	37
"	2	1.75	75
"	4	3.50	150
Ferrous Iron	1	1.00	87
"	2	2.00	173
"	4	4.00	346
Ferric Iron	1	0.83	72
"	2	1.65	144
"	4	3.31	287
Zinc	1	0.94	95
"	2	1.88	191
"	4	3.76	382

Step 1: Six 600 ml Griffin low form Nalgene™ polypropylene beakers were filled to mark with tap water.

Step 2: The six beakers were placed on the Phipps & Bird™ mechanical stir unit. The stirrer was turned on and run at 30 rpm.

Step 3: The cation solutions were added to beaker #1. They were mixed for 5 minutes. A one hour timer was started.

Step 4: Following completion of Step 3, the metal ions were added to beaker #2. The pH in beaker #1 was adjusted.

Step 5: Five minutes after the addition of the metal ion solution to beaker #2; the appropriate metal ion solutions were added to beaker #3. The pH of the solution was adjusted in beaker #2.

Step 6: Repeat Step 5 until all six of the beakers had the metals added and their pHs adjusted.

Step 7: After 60 minutes of stirring the solution in beaker #1, take beaker #1 was taken off the mechanical stirrer.

Step 8: Remove beakers #2 through #6 from the stirring apparatus at 5 minute intervals thereafter.

Step 9: The beakers were covered with Parafilm as they came off the stirring apparatus. Twenty-four hours later, the flocculated material was resuspended in the beakers by rotating the covered beakers by hand.

Step 10: After a total 48-hour rest period, the solutions were filtered and samples for analyses prepared.

APPENDIX I

Effect of Filtration on Total Silica As Solutions Are Concentrated

Three evaporation experiments were performed to compare the effect of multiple filtrations on total silica remaining in solution. Unfiltered LANL tap water was concentrated. Once filtered water was the solution for a second evaporation experiment. The third evaporation experiment used water that had been filtered three times. Figure 1I shows that the amount of Measured Silica remaining in solution for the three runs is nearly the same as the Expected Silica in solution increases.

From the results shown, it was concluded that filtration did not substantially change the results obtained in the evaporation runs.

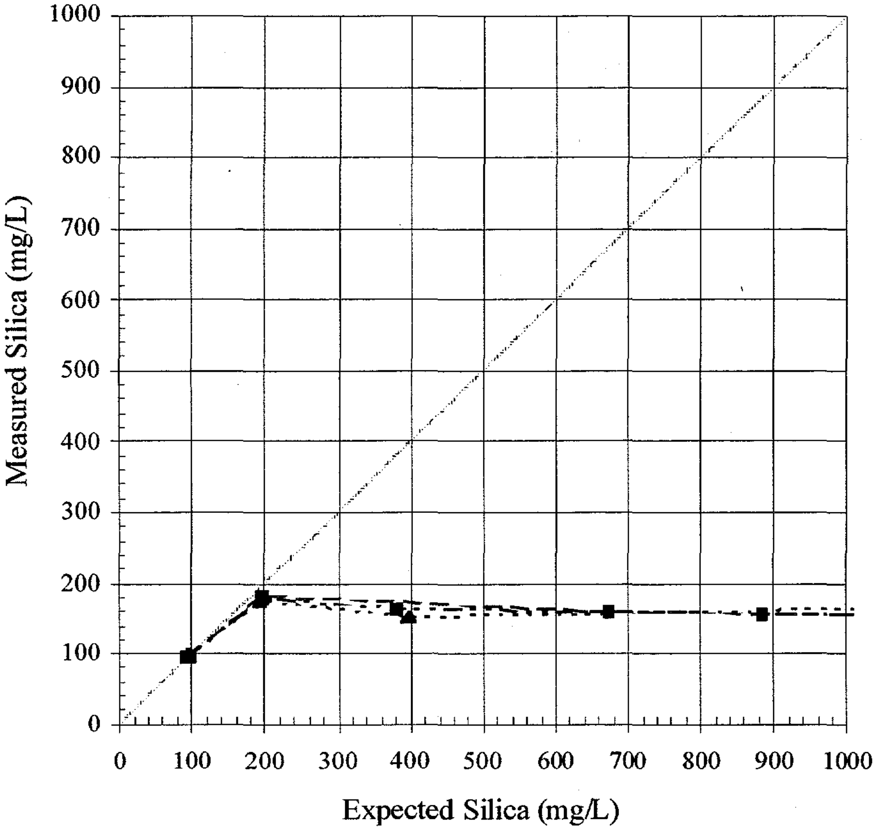

Figure 1I. Silica Remaining in Solution When Tap Water Was Unfiltered, Filtered Once, and Filtered Three Times.

APPENDIX J

Solubility Data from pH Evaporation Experiments

The following fourteen tables give the analytical data from the effect of pH on silica solubility experiments. Figures 2 through 5 in the report are plots of the silica and pH data shown in these tables.

Table 1J
Data from the Initial *p*H 3.0 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	3.4	clear, no floc	96	96
284 / *2.1*	3.0	clear, no floc	203	202
140 / *4.3*	2.6	clear, no floc	413	389
90 / *6.7*	2.5	clear, no floc	642	613
54 / 11.1	2.2	clear, no floc	1070	979

Table 1J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	15	4	5	14	14
29	30	9	9	29	28
60	56	18	16	60	54
93	86	27	26	93	91
154	140	46	41	154	135

Table 2J

Data from the Initial *p*H 4.0 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	5.4	clear, no floc	96	96
275 / *2.2*	5.1	clear, no floc	210	203
130 / *4.6*	4.1	clear, no floc	444	423
99 / *6.1*	3.9	clear, no floc	584	566
70 / *8.6*	3.7	clear, no floc	825	805

Table 2J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	14	15
30	28	9	9	30	31
64	59	19	18	64	65
84	80	25	24	84	86
119	115	35	34	119	121

Table 3J

Data from the Initial *p*H 5.0 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	6.5	clear, no floc	96	97
273 / *2.2*	7.0	clear, no floc	212	204
126 / *4.8*	7.4	clear, no floc	459	384
96 / *6.3*	7.6	clear, no floc	602	482
44 / 13.6	7.7	clear, no floc, hard to filter	1313	668

Table 3J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	15
31	29	9	9	31	32
66	62	20	18	66	68
87	76	26	22	87	80
190	163	56	47	190	179

Table 4J
Data from the Initial *p*H 5.5 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	7.0	clear, no floc	99	99
265 / *2.3*	7.6	clear, no floc	224	208
144 / *4.2*	7.8	cloudy	412	331
98 / *6.1*	8.0	cloudy	605	502
64 / *9.4*	8.0	cloudy, hard to filter	926	315

Table 4J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	14
31	29	10	9	31	29
57	52	18	16	57	53
83	75	26	23	83	77
128	115	39	34	128	122

Table 5J
Data from the Initial *p*H 6.0 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	7.3	clear, no floc	99	97
300 / *2.0*	8.1	clear, no floc	198	192
142 / *4.2*	8.4	clear, no floc	417	308
100 / *6.0*	8.5	cloudy, hard to filter	593	163
80 / 7.5	8.5	cloudy, hard to filter	741	176

Table 5J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	14	13
27	28	8	9	27	28
57	52	18	16	57	53
82	69	25	19	82	75
102	90	32	20	102	101

Table 6J
Data from the Initial *p*H 6.5 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	7.9	clear, no floc	99	98
260 / *2.3*	8.4	clear, no floc	228	212
144 / *4.2*	8.6	clear, no floc	412	175
108 / *5.6*	8.6	clear, no floc	549	175
65 / *9.2*	8.4	white floc, hard to filter	912	175

Table 6J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	13
31	29	10	9	31	29
57	48	18	14	57	51
76	65	23	13	76	73
126	62	39	15	126	112

Table 7J
Data from the Initial *p*H 7.0 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	8.0	clear, no floc	99	98
285 / *2.1*	8.5	clear, no floc	208	202
142 / *4.2*	8.7	clear, no floc	417	182
95 / *6.3*	8.8	cloudy, hard to filter	624	182
67 / 9.0	8.6	cloudy, harder to filter	885	173

Table 7J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	14
29	28	9	8	29	28
57	50	18	14	57	55
86	69	27	11	86	83
122	28	38	11	122	118

Table 8J
Data from the Initial *p*H 7.8 Evaporation Experiment

Final		Solution Description	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H		Expected	Measured
600 / *1.0*	8.2	clear, no floc	99	99
213 / *2.8*	8.7	clear, no floc	278	228
130 / *4.6*	8.5	cloudy, some grit	455	172
95 / *6.3*	8.6	cloudy, some grit	623	152
70 / *8.6*	8.7	white floc, grit	845	154

Table 8J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	14
38	35	12	10	38	36
62	49	19	11	63	56
85	27	26	10	86	71
116	14	35	9	117	99

Table 9J
Data from the Initial *p*H 8.5 Evaporation Experiment

Final		Solution Description	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H		Expected	Measured
600 / *1.0*	7.5	clear, no floc	99	98
245 / *2.4*	8.4	clear, no floc	241	234
159 / *3.8*	8.7	clear, no floc	372	174
97 / *6.2*	8.7	cloudy, hard to filter	610	157
73 / *8.2*	8.7	cloudy, hard to filter	810	157

Table 9J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	16	16
33	32	10	9	40	39
51	43	15	10	61	54
84	26	25	8	100	92
111	13	34	7	133	118

Table 10J
Data from the Initial *p*H 9.0 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	8.6	clear, no floc	99	99
235 / *2.6*	8.7	clear, some grit	252	240
155 / *3.9*	8.5	cloudy, some grit	382	171
100 / *6.0*	8.7	cloudy, some grit	592	151
25 / *24.0*	9.2	white floc, grit	2366	207

Table 10J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	23	23
34	27	10	10	59	55
52	41	16	8	89	75
81	17	25	6	138	112
324	7	98	4	552	401

Table 11J
Data from the Initial *p*H 9.5 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	9.5	clear, no floc	86	86
267 / 2.3	9.5	clear, no floc	194	175
124 / *4.8*	9.0	clear, no floc	477	342
75 / 8.0	9.4	white floc, grit	690	361
60 / *10.0*	9.5	white floc, grit	863	301

Table 11J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	27	27
28	24	9	8	61	56
65	11	20	12	169	142
100	10	32	14	216	191
125	4	40	1	270	225

Table 12J
Data from the Initial *p*H 10.0 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	9.8	clear, no floc	98	98
230 / *2.6*	9.5	clear, some grit	254	221
148 / *4.1*	9.4	clear, some grit	395	291
100 / *6.0*	9.5	clear, grit, hard to filter	585	263
70 / *8.6*	9.6	cloudy, grit, hard to filter	836	526

Table 12J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	10	4	4	55	55
34	9	10	3	144	141
52	5	16	1	223	198
77	5	23	1	330	294
111	8	33	11	471	416

Table 13J
Data from the Initial *p*H 10.5 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	*p*H	Description	Expected	Measured
600 / *1.0*	10.1	clear, no floc	98	91
248 / *2.4*	9.8	clear, some grit	236	197
153 / *3.9*	9.6	clear, some grit	382	294
105 / *5.7*	9.6	cloudy, grit	557	359
68 / *8.8*	9.7	cloudy, grit	860	607

Table 13J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	6	4	1	83	83
31	3	9	1	201	192
51	2	15	0	325	296
74	2	22	1	474	422
114	3	34	1	732	675

Table 14J
Data from the Initial pH 11.0 Evaporation Experiment

Final		Solution	Total SiO_2 (mg/L)	
Vol. (ml) / *C.F.*	pH	Description	Expected	Measured
600 / *1.0*	10.7	clear	98	91
237 / *2.5*	10.1	clear	247	212
150 / *4.0*	9.6	clear, some grit	390	285
118 / *5.1*	10.0	cloudy, grit	496	383
68 / *8.8*	9.8	cloudy, grit	860	391

Table 14J continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	5	4	0	101	101
33	2	10	0	256	247
52	3	16	0	404	351
66	3	20	0	513	474
114	3	34	0	891	824

APPENDIX K

Variability of Measured Silica, Magnesium, and Calcium in Control Evaporation Experiments

In each of the evaporation experiments to determine the reactivity of additives with silica, a control evaporation run was also performed with tap water. In the control evaporation run, a water sample with no additive was evaporated under the same conditions and subjected to the same physical processing as all the rest, but no chemicals were added. This provided a basis for comparison, plotted as the values of Measured Silica vs. Expected Silica in Figure 1. Fifty-nine of these control tap water evaporation runs were made. The "X" symbols in Figure 1K show the amount of Measured Silica remaining in solution (in each of the 295 solutions of the 59 control evaporation runs) as a function of the Expected Silica in solution. Data is shown in Table 1K.

Figure 1K shows that between 200 to 350 mg/L Expected Silica there is a definite supersaturation effect which varies between 170 to 275 mg/L Measured Silica. From an Expected Silica value of 350 to 1000 mg/L, the Measured Silica values range from 140 to 180 mg/L about a mean value, about 160 mg/L. In the course of our 59 experimental control runs some extreme variations in Measured Silica were found. The only explanation to date is supersaturation.

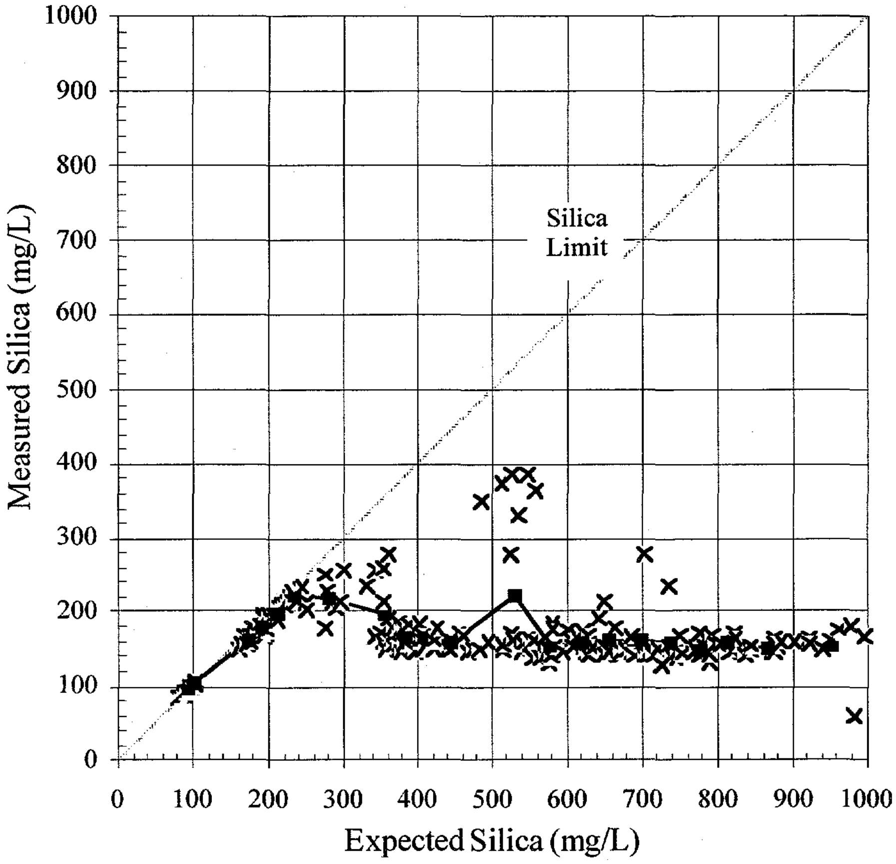

Figure 1K. Total Silica Remaining in Solution for 59 Tap Water Evaporation Runs.

Table 1K

Data Used to Generate the Average Measured Silica Curve

Range of Expected Silica Values (mg/L)	Number of Values in Range	Average of Expected Silica Values (mg/L)	Average of Measured Silica Values (mg/L)	Standard Deviation of Measured Silica Values (mg/L)
81-100	50	95	95	4
101-105	9	102	102	2
160-179	11	173	161	9
183-200	20	193	179	9
202-220	14	212	198	9
224-250	9	236	220	8
251-300	8	281	219	26
332-368	14	355	196	44
374-397	17	384	163	13
401-416	11	407	164	10
422-475	10	446	158	11
483-558	21	531	221	98
563-594	10	577	152	18
601-628	12	619	159	11
635-679	13	657	161	22
685-715	10	700	160	42
722-750	8	737	157	34
754-789	11	778	148	10
793-824	8	813	158	10
837-885	10	866	151	7
903-997	9	952	152	36

Variability of Measured Magnesium in Control Evaporation Experiments

The variation in the solubility in the control experiment is shown in Figure 2K. Although the variability of the magnesium (probably as carbonate) is considerable, it is less so than that of calcium. Solubilities are similar. This curve was generated using the data in Table 2K.

Figure 2K shows that nearly all the magnesium is soluble in solution up to an Expected Magnesium Concentration of 10 mg/L. Between Expected Magnesium concentrations of 15 to 43 mg/L the Measured Magnesium decreased gradually from 12 to 7 mg/L.

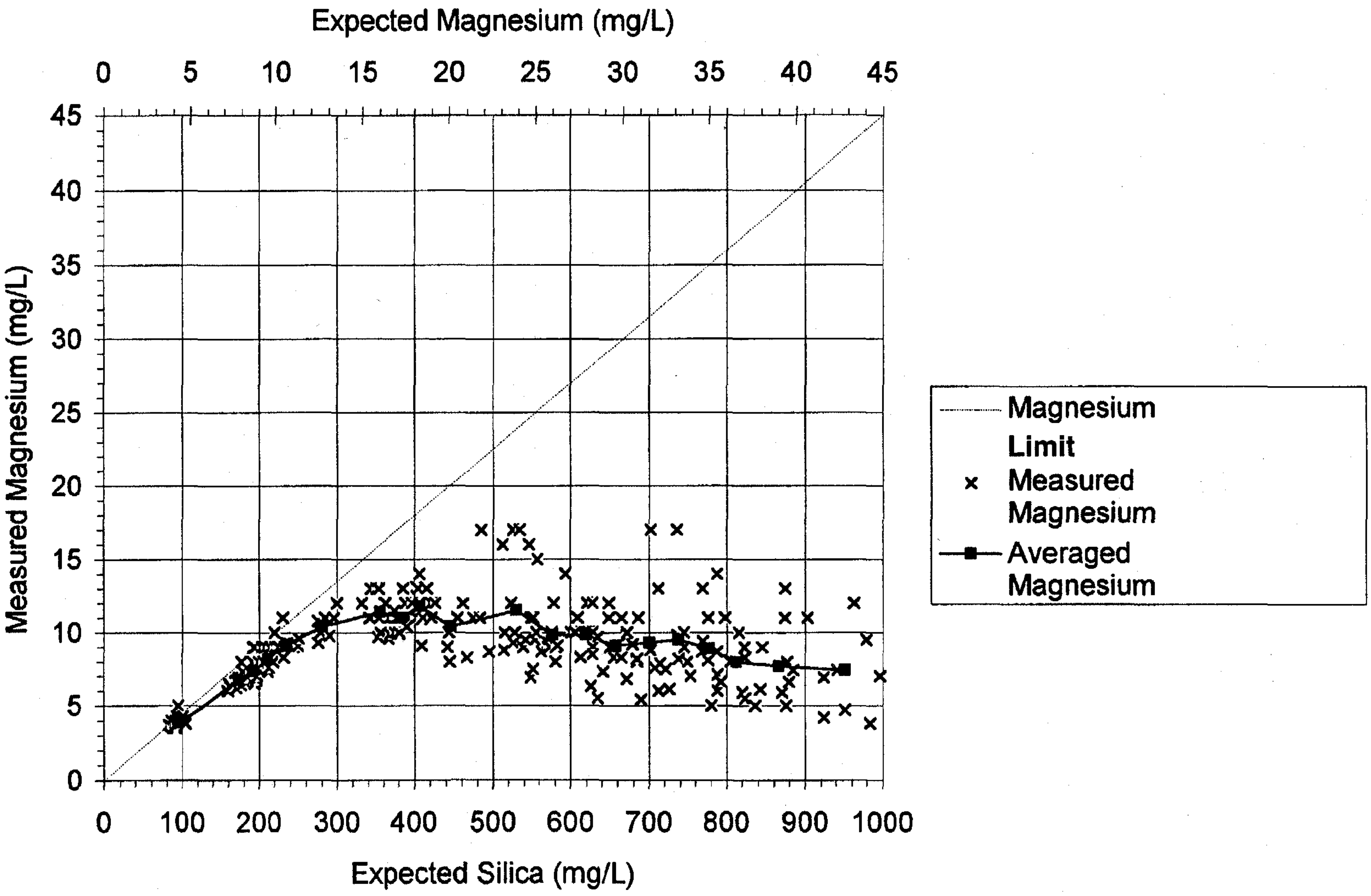

Figure 2K. Magnesium Remaining in Solution in 59 Tapwater Evaporation Runs.
Initial pHs of Solutions: 7.8 - 8.2.

Table 2K
Data Used to Generate the Average Measured Magnesium Curve

Range of Expected Silica Values (mg/L)	Number of Values in Range	Average of Expected Magnesium Values (mg/L)	Average of Measured Magnesium Values (mg/L)	Standard Deviation of Measured Magnesium Values (mg/L)
81-100	50	4	4	0.2
101-105	9	5	4	0.1
160-179	11	8	7	0.6
183-200	20	9	7	0.7
202-220	14	10	8	0.8
224-250	9	11	9	0.7
251-300	8	13	10	0.9
332-368	14	16	11	1
374-397	17	17	11	1
401-416	11	18	12	2
422-475	10	20	10	2
483-558	21	24	12	3
563-594	10	26	10	2
601-628	12	28	10	2
635-679	13	30	9	2
685-715	10	32	9	4
722-750	8	33	10	3
754-789	11	35	9	3
793-824	8	37	8	2
837-885	10	39	8	3
903-997	9	43	7	3

Variability of Measured Calcium in Control Evaporation Experiments

Calcium and, to some extent, magnesium have often been deemed to be essential contributors to silica precipitation. Therefore, it seemed advisable to show the behavior of these elements as part of the preliminary work. This provided comparison of the effects of calcium on SiO_2 to the behavior of the silica in the original water.

Figure 3K shows the amount of Measured Calcium remaining in solution, in each of the 295 solutions of the 59 control evaporation runs, as a function of the Expected Silica in solution. The average values of the Measured Calcium as a function of the Expected Silica is shown by the heavy line. This line was generated using the data in Table 3K.

Figure 3K shows that nearly all the calcium is found in solution up to an Expected Calcium concentration of 40 mg/L. Between Expected Calcium concentrations of 45 to 95 mg/L. The Measured Calcium leveled off to 40 to 45 mg/L. At concentrations above 100 mg/L of Expected Calcium, the Measured Calcium concentrations dropped sharply to 15 mg/L. The effects of calcium on the solubility of SiO_2 will be discussed further in sections on the effects of cation. But, the rather random solubility of calcium is striking.

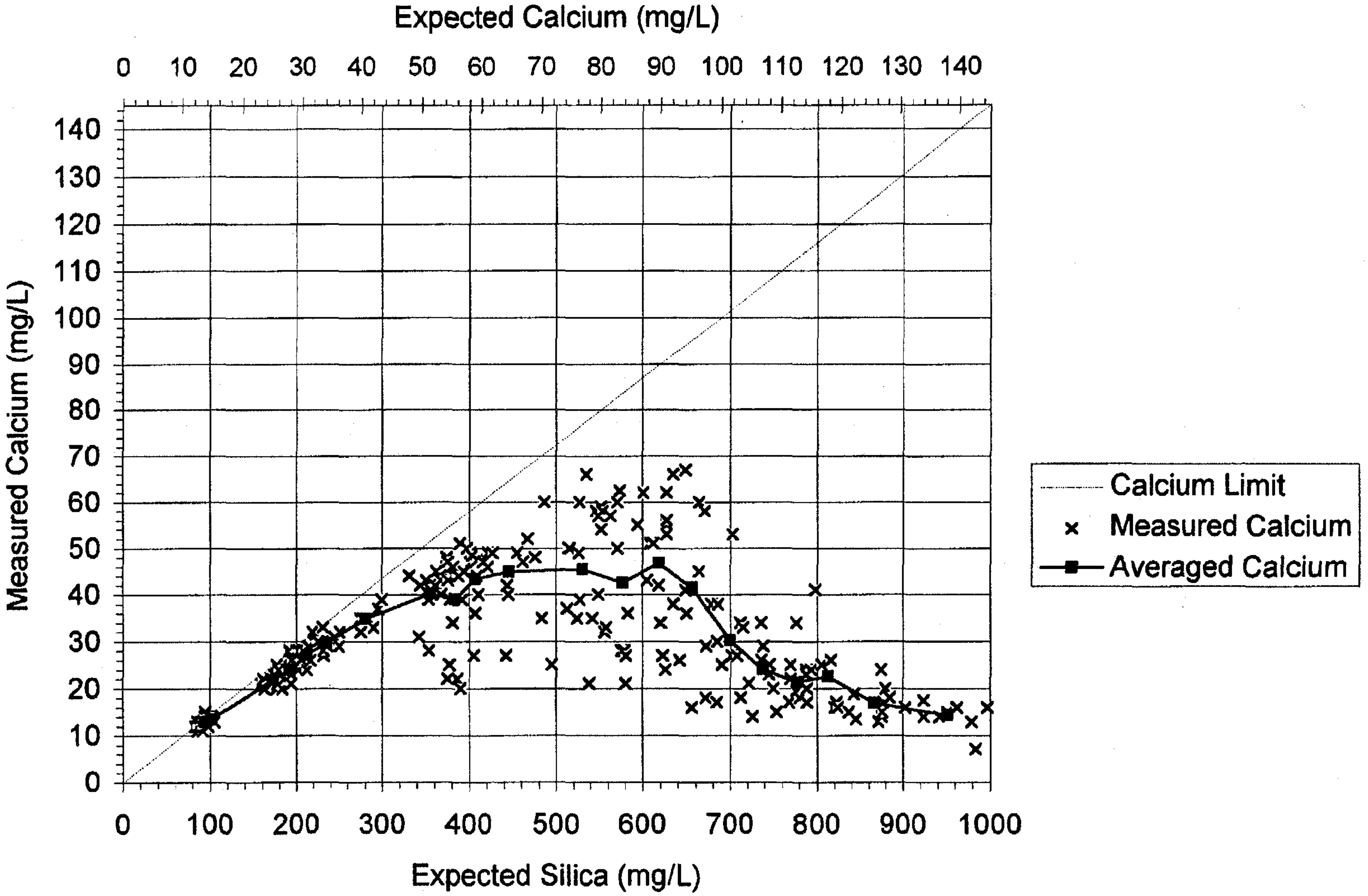

Figure 3K. Calcium Remaining in Solution in 59 Tapwater Evaporation Runs.
Initial pHs of Solutions: 7.8 - 8.2.

Table 3K
Data Used to Generate the Average Measured Calcium Curve

Range of Expected Silica Values (mg/L)	Number of Values in Range	Average of Expected Calcium Values (mg/L)	Average of Measured Calcium Values (mg/L)	Standard Deviation of Measured Calcium Values (mg/L)
81-100	50	14	13	1
101-105	9	15	14	1
160-179	11	25	22	2
183-200	20	28	24	2
202-220	14	31	27	3
224-250	9	34	30	2
251-300	8	41	35	2
332-368	14	52	40	5
374-397	17	56	39	10
401-416	11	59	43	7
422-475	10	65	45	7
483-558	21	77	45	13
563-594	10	84	43	16
601-628	12	90	47	13
635-679	13	95	41	17
685-715	10	102	30	10
722-750	8	107	24	6
754-789	11	113	21	5
793-824	8	118	23	9
837-885	10	126	17	4
903-997	9	138	14	3

APPENDIX L

Variability of Magnesium As a Function of pH

Figure 1L demonstrates that in solutions with low initial pHs of 3.0, 4.0, 5.0, and 5.5 nearly all of the magnesium remains in solution.

Evaporation runs at initial pHs of 6.0, 6.5, 7.0, 7.8, 8.5, and 9.0 yield results, as shown in Figures 1L and 2L, which show the attainment of a maximum magnesium concentration beyond which the magnesium in solution levels off. The magnitude of the maximum Measured Magnesium concentration decreased with increasing pH.

Magnesium concentrations measured in the initial pH 9.5 evaporation run, as seen in Figure 3L, showed a strong solubilization of magnesium. Higher pH evaporation experiments at initial pHs 10.0, 10.5, and 11.0, also seen in Figure 3L, reveal a removal of magnesium from the water prior to the evaporation of the solutions. A curious resolubilization of magnesium is noted in initial pH 10.0 evaporation run for solutions with greater than 600 mg/L of Expected Silica. For these three high pH evaporation runs the magnesium concentrations decreased very slightly from their initial concentrations as the evaporation experiments progressed.

The effect of pH on magnesium solubility can be visualized as in Figure 4L. Vertical slices, at Expected Magnesium concentrations of 10, 15, 20, 25, 30, and 35 mg/L, were made through Figures 1L, 2L, 3L. For each Expected Magnesium concentration, the Measured Magnesium remaining in solution and final pH at its intersection with each pH evaporation run was determined.

From pH 2.5 to 4.0, greater than 86% of the Expected Magnesium was found in solution at all the iso-expected magnesium concentration levels. Between pH 4.0 and 7.5 there is a gradual drop in the Measured Magnesium along each of the iso-expected magnesium concentration lines. This drop in Measured Magnesium is more pronounced in the 25, 30, and 35 iso-expected magnesium concentration lines. A slight resolubilization of magnesium appears to occur between pH 7.5 and 8.0. From pH 8.0 to 8.6 a sharp decrease in magnesium solubility occurs. A dramatic resolubilization occurs at pH 9.0 to 9.2 followed by a precipitous drop in magnesium to

2 mg/L levels for pHs greater than 9.6. We do not offer an explanation for these seeming anomalies but include these results as they may be of interest in plant operations.

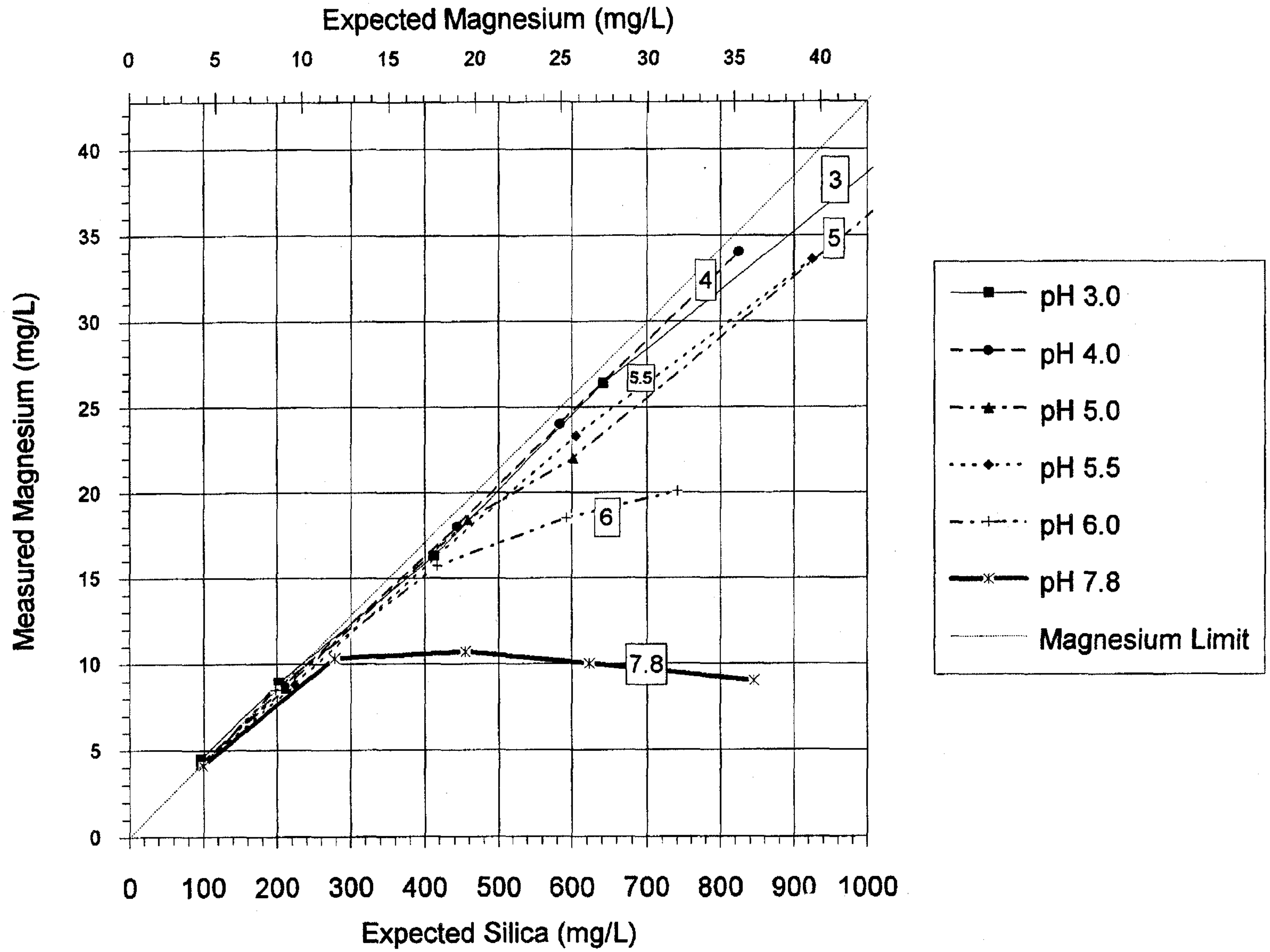

Figure 1L. Magnesium Solubility As a Function of Expected Silica.
Initial Solution pHs: 3.0, 4.0, 5.0, 5.5, 6.0, and 7.8.

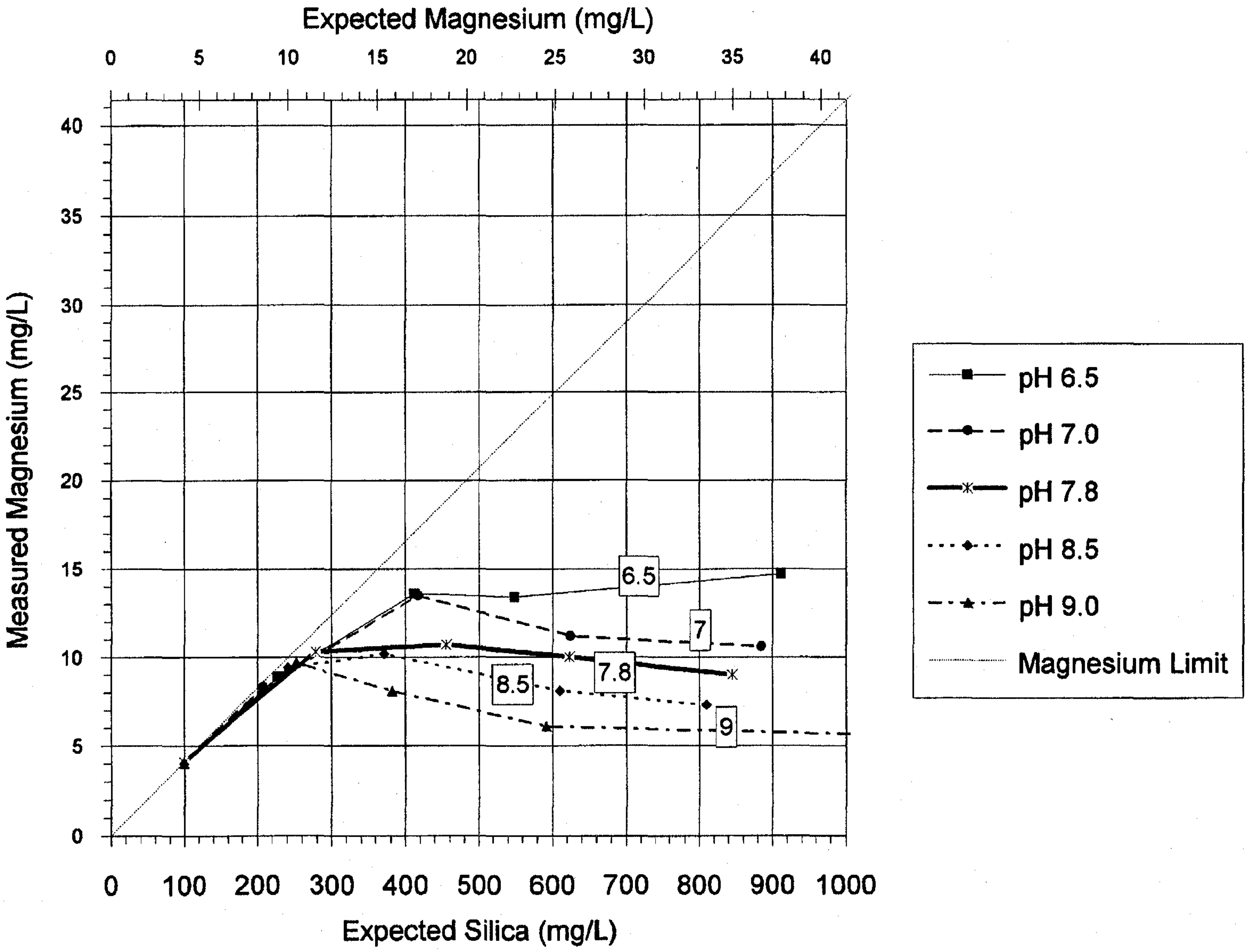

Figure 2L. Magnesium Solubility As a Function of Expected Silica. Initial Solution pHs: 6.5, 7.0, 7.8, 8.5, and 9.0.

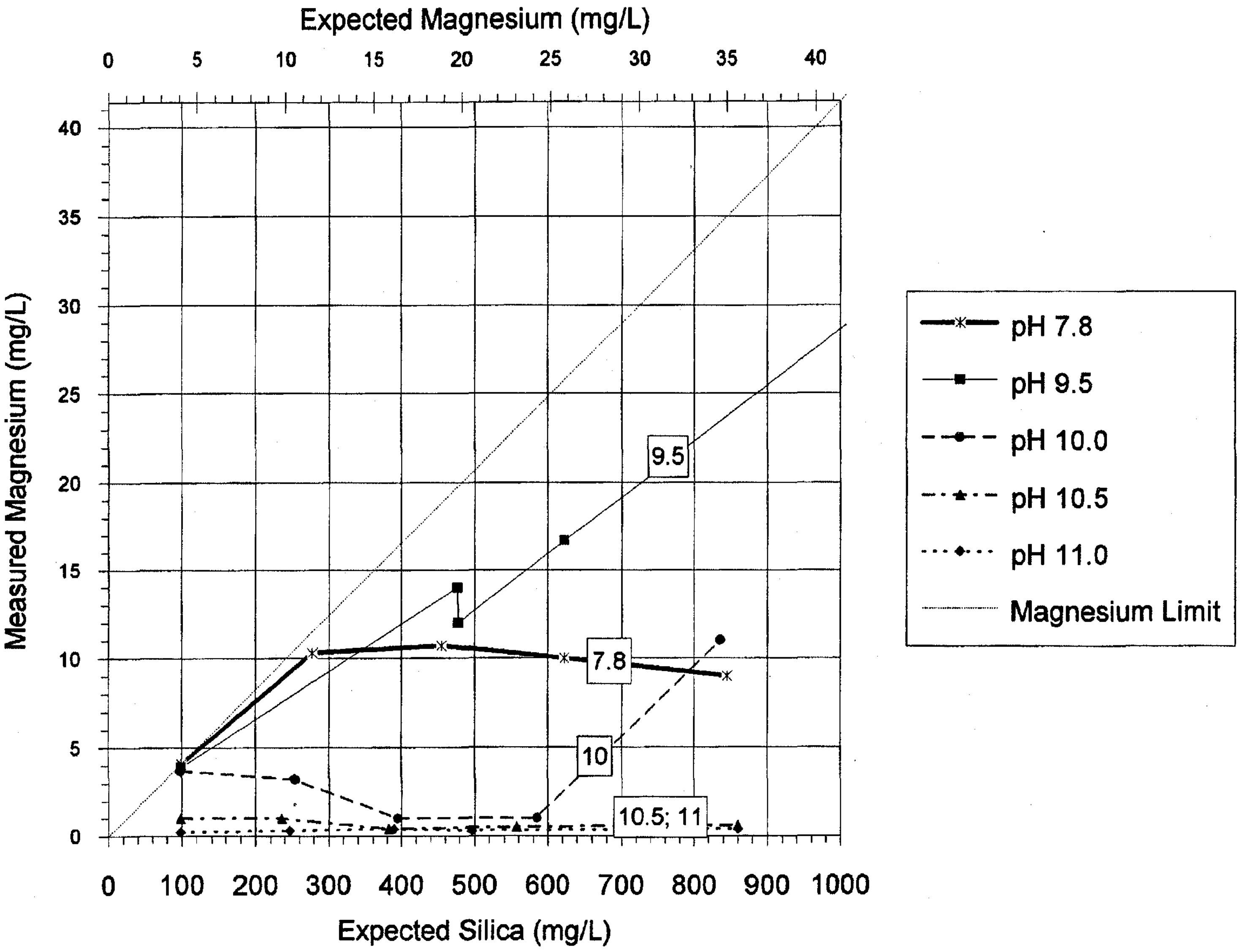

Figure 3L. Magnesium Solubility As a Function of **Expected Silica.**
Initial Solution pHs: 7.8, 9.5, 10.0, 10.5, and 11.0.

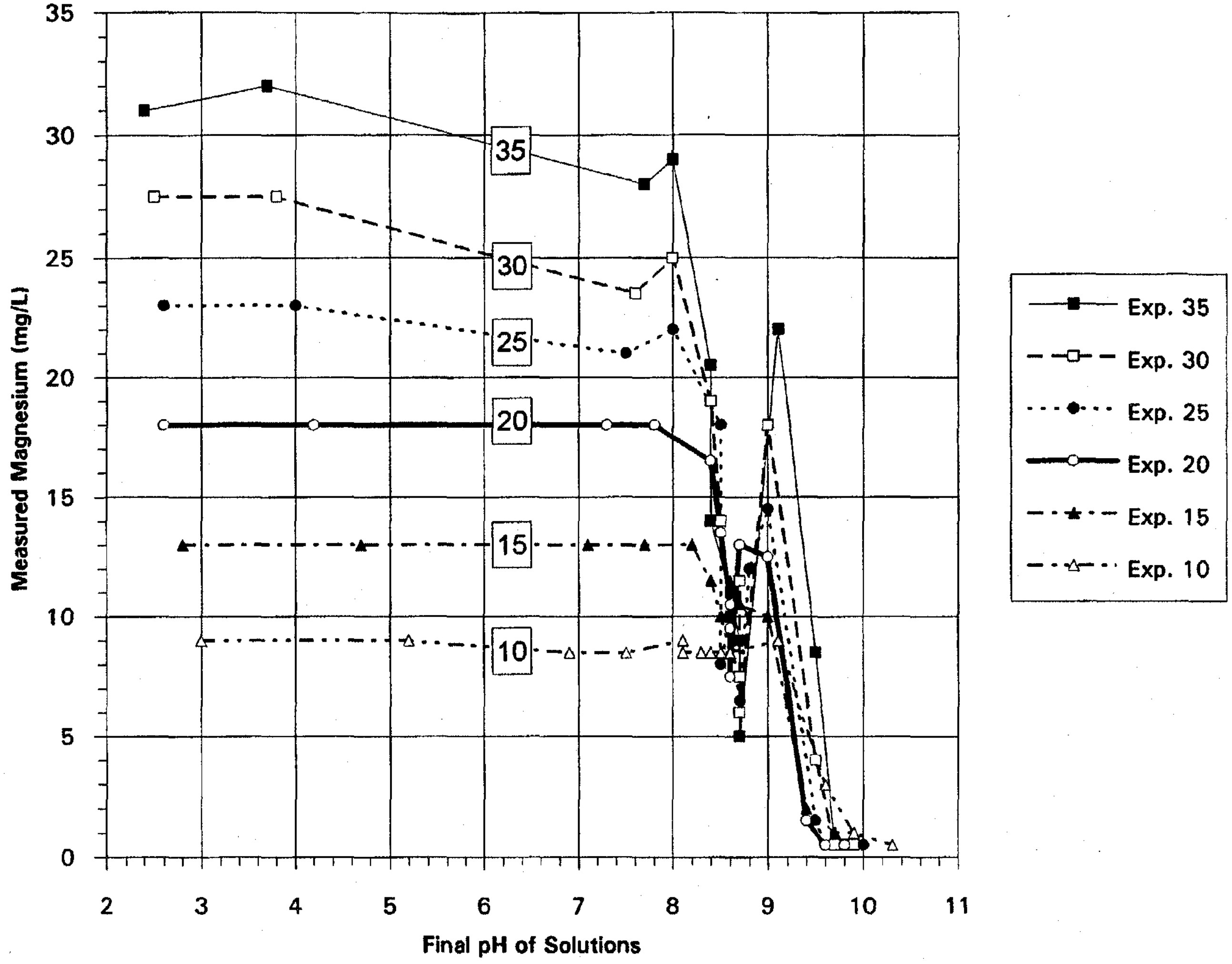

Figure 4L. Solubility of Magnesium at Iso-Expected Magnesium Concentrations As a Function of Final Solution pH.

APPENDIX M

Variability of Calcium As a Function of pH

Figure 1M demonstrates that in solutions with low initial pHs of 3.0, 4.0, 5.0, 5.5, and 6.0 nearly all of the calcium remains in solution up to fairly high Expected Calcium concentrations of 110 to 140 mg/L.

Evaporation runs at initial pHs of 6.5, 7.0, 7.8, 8.5, and 9.0 yield results, as shown in Figure 2M. This figure shows the attainment of a maximum calcium concentration beyond which the calcium in solution decreases dramatically. The magnitude of the maximum Measured Calcium concentration decreased with increasing pH.

Evaporation experiments were done at higher initial pH values such as pH 9.5, 10.0, 10.5, and 11 are shown in Figure 3M. For these four high pH evaporation runs the calcium concentrations decreased very slightly from their initial concentrations as the evaporation experiments progressed.

The effect of pH on calcium solubility can be visualized as in Figure 4M. Vertical slices, at Expected Calcium concentrations of 30, 40, 50, 60, 70, 80, 90, 100, and 110 mg/L, were made through Figures 1M, 2M, and 3M. For each Expected Calcium concentration, the Measured Calcium remaining in solution and final pH at its intersection with each pH evaporation run was determined.

From pH 2.5 to 4.0, greater than 93% of the Expected Calcium was found in solution at all the iso-expected calcium concentration levels. Between pH 4.0 and 8.5 there is a gradual drop in the Measured Calcium along each of the iso-expected calcium concentration lines. This drop in Measured Calcium is more pronounced in the 60, 70, 80, 90, 100, and 110 iso-expected calcium concentration lines. A dramatic drop in Measured Calcium begins at pH 8.4 and by pH 9.8 all the solutions had calcium concentrations no greater than 4 mg/L.

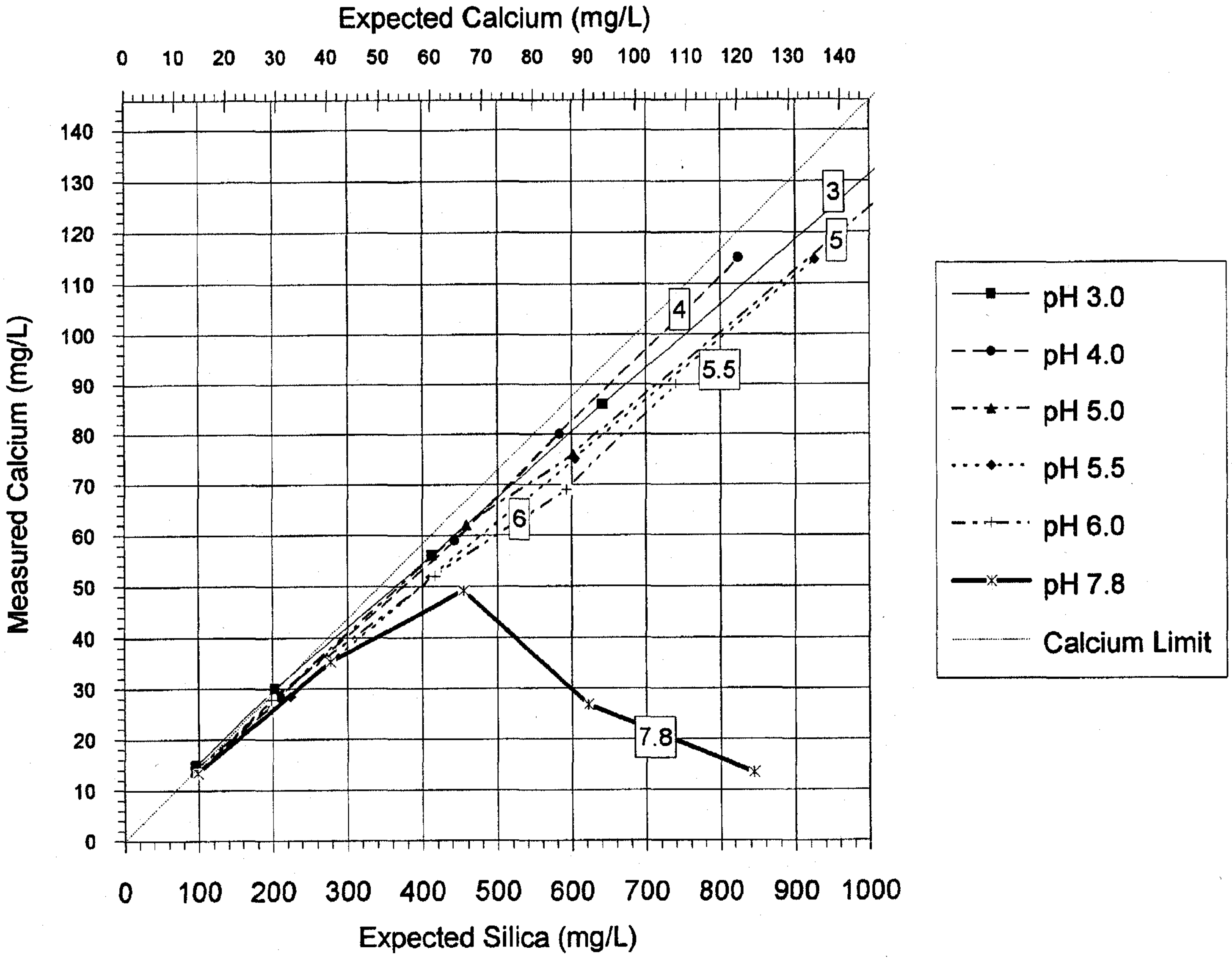

Figure 1M. Calcium Solubility As a Function of Expected Silica.
Initial Solution pHs: 3.0, 4.0, 5.0, 5.5, 6.0, and 7.8.

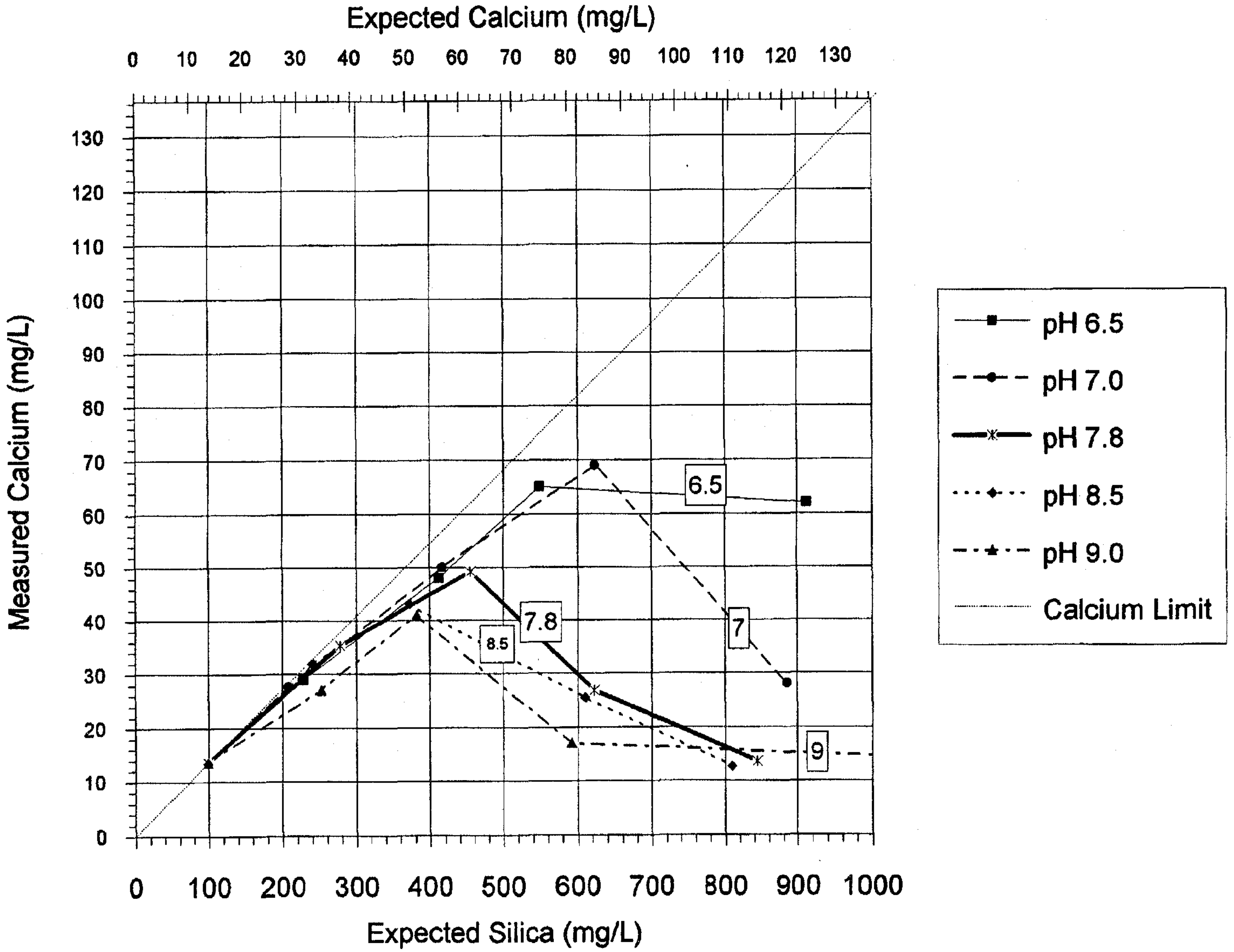

Figure 2M. Calcium Solubility As a Function of Expected Silica.
Initial Solution pHs: 6.5, 7.0, 7.8, 8.5, and 9.0.

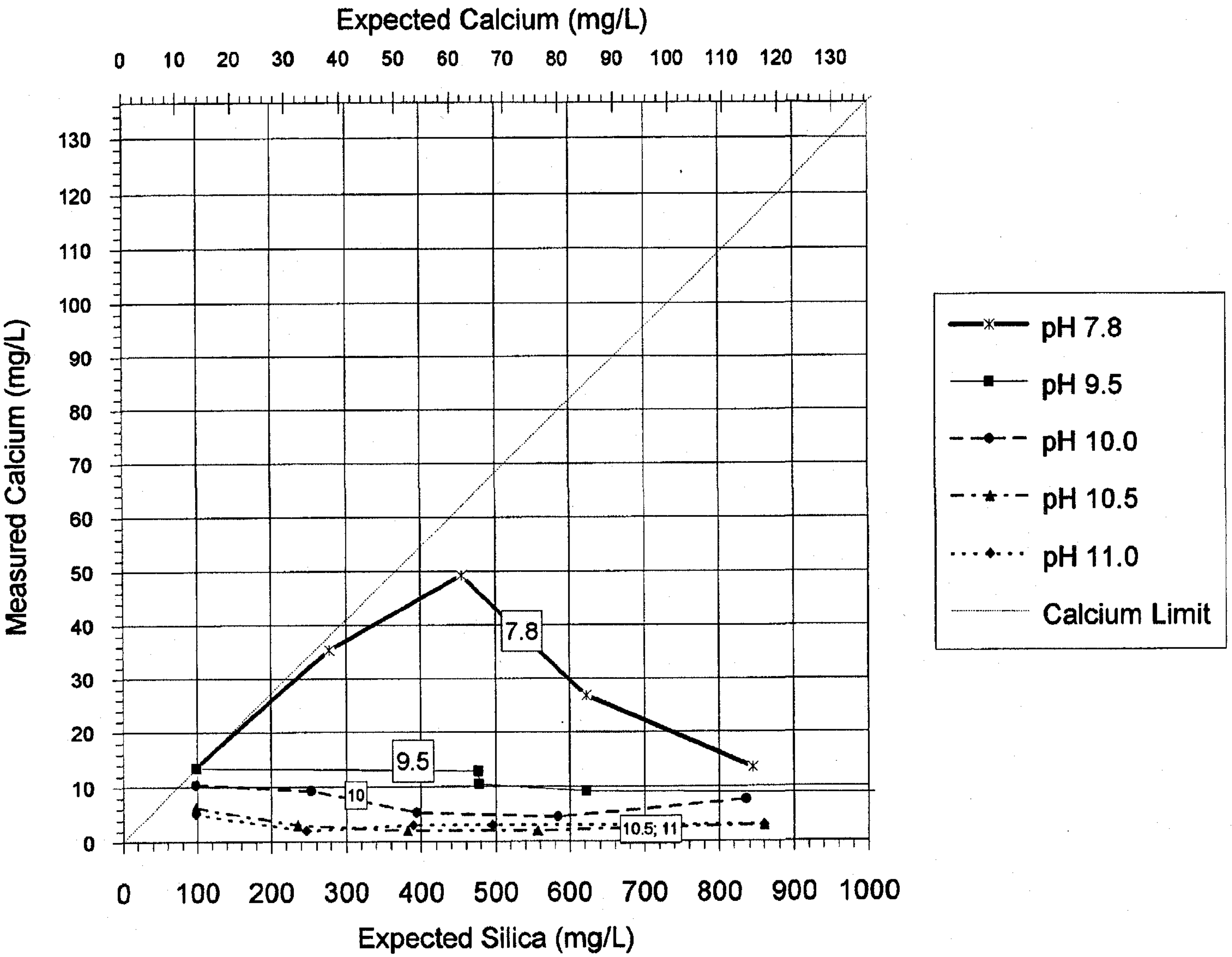

Figure 3M. Calcium Solubility As a Function of Expected Silica.
Initial Solution pHs: 7.8, 9.5, 10.0, 10.5, and 11.0.

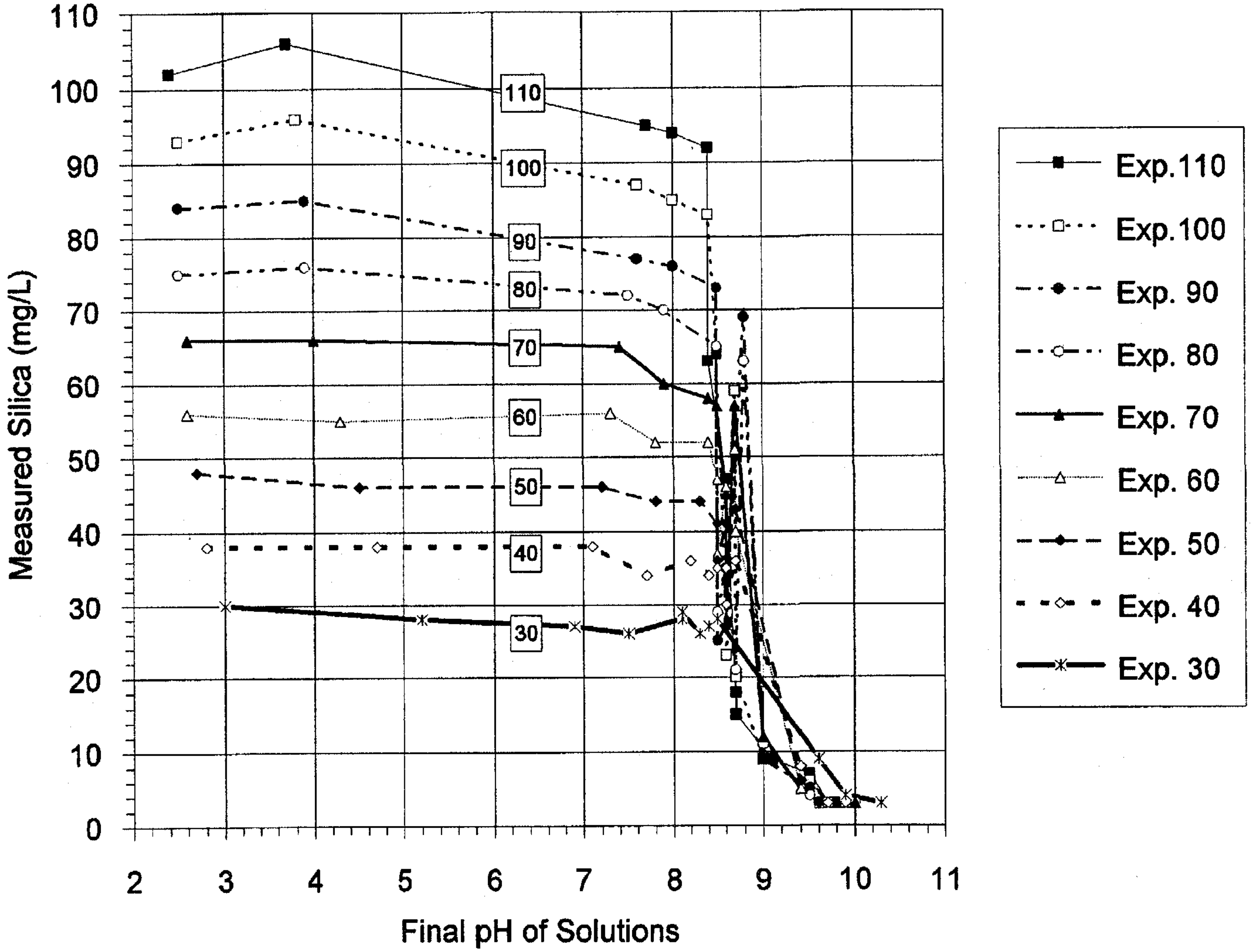

Figure 4M. Solubility of Calcium at Iso-Theoretical (Expected) Calcium Concentrations As a Function of Final Solution pH.

APPENDIX N

Data Tables of Evaporation Experiments

INORGANICS

NaF **MR 0.00**

Table 1N Data for the NaF Addition Solution. Mole Ratio of NaF:SiO_2 = 0.0.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	96	96
295	2.0	8.8	196	188
149	4.0	9.2	388	165
92	6.5	9.1	628	154
80	7.5	8.8	722	150

Table 1N continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.7	-----	-----
26	24	8	7.2	-----	-----
52	44	15	11	-----	-----
85	62	24	9.2	-----	-----
98	21	28	7.5	-----	-----

MR 0.21

Table 2N Data for the NaF Addition Solution. Mole Ratio of NaF:SiO_2 = 0.21.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	96	96
304	2.0	8.8	190	186
154	3.9	9.2	375	167
97	6.2	9.2	596	193
76	7.9	9.3	760	156

Table 2N continued:

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.8	-----	-----
26	24	7	7.2	-----	-----
51	45	14	11	-----	-----
80	65	23	9.6	-----	-----
103	72	29	6.1	-----	-----

Table 3N Data for the NaF Addition Solution. Mole Ratio of NaF:SiO_2 = 0.83.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	96	96
290	2.1	8.8	199	188
150	4.0	9.2	385	278
105	5.7	9.2	550	364
77	7.8	9.2	750	163

Table 3N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.7	-----	-----
27	25	8	7.2	-----	-----
52	46	15	13	-----	-----
74	35	21	14	-----	-----
101	7	29	3.7	-----	-----

MR 3.3

Table 4N Data for the NaF Addition Solution. Mole Ratio of NaF:SiO_2 = 3.3.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	96	94
287	2.1	8.8	201	197
144	4.2	9.3	401	364
94	6.4	9.2	615	535
42	14.3	9.5	1376	1134

Table 4N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	5.3	4	3.4	-----	-----
27	5.5	8	6.3	-----	-----
54	1.1	15	7.5	-----	-----
83	0.8	24	8.9	-----	-----
186	3.2	53	4.5	-----	-----

MR 0.0

Table 5N Data for the NaCl Addition Solution. Mole Ratio of NaCl:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	101	101
293	2.0	8.8	206	195
164	3.7	9.2	368	178
110	5.5	9.2	549	163
75	8.0	9	805	156

Table 5N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4.1	-----	-----
27	26	8	7.8	-----	-----
48	40	15	11	-----	-----
71	57	22	11	-----	-----
104	25	33	8	-----	-----

MR 0.2

Table 6N Data for the NaCl Addition Solution. Mole Ratio of NaCl:SiO_2 = 0.2.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	101	98
329	1.8	8.9	183	171
158	3.8	9.1	382	180
105	5.7	9.1	575	167
85	7.1	9	710	152

Table 6N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	-----	-----
24	23	7	6.9	-----	-----
49	44	16	12	-----	-----
74	61	23	10	-----	-----
92	29	29	6.2	-----	-----

Table 7N Data for the NaCl Addition Solution. Mole Ratio of NaCl:SiO_2 = 0.78.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	101	101
315	1.9	8.9	192	178
155	3.9	9.2	389	178
98	6.1	9.2	616	235
84	7.1	9	718	158

Table 7N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	-----	-----
25	23	8	7.2	-----	-----
50	43	16	11	-----	-----
80	66	25	12	-----	-----
93	42	29	8.7	-----	-----

MR 3.1

Table 8N Data for the NaCl Addition Solution. Mole Ratio of NaCl:SiO_2 = 3.1.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	101	101
305	2.0	8.9	198	175
144	4.2	9.2	419	173
85	7.1	9.2	710	169
77	7.8	9.1	784	165

Table 8N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	-----	-----
26	24	8	7.1	-----	-----
54	48	17	13	-----	-----
92	72	29	9.6	-----	-----
101	78	32	10	-----	-----

MR 0.0

Table 9N Data for the NaBr Addition Solution. Mole Ratio of NaBr:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	95	95
297	2.0	8.8	192	181
140	4.3	9	407	167
94	6.4	8.9	606	161
65	9.2	9	877	157

Table 9N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
15	15	5	5	17	17
30	28	10	9	34	29
64	47	21	14	73	61
96	43	32	10	109	86
138	17	46	8	157	119

MR 0.21

Table 10N Data for the NaBr Addition Solution. Mole Ratio of NaBr:SiO_2 = 0.21.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	95	96
307	2.0	8.7	186	181
136	4.4	9	419	169
106	5.7	8.7	538	153
44	13.6	9	1295	160

Table 10N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
15	14	5	4	17	22
29	26	10	8	33	41
66	52	22	11	75	92
85	55	28	10	96	108
205	16	68	6	232	264

NaBr **MR 0.83**

Table 11N Data for the NaBr Addition Solution. Mole Ratio of NaBr:SiO_2 = 0.83.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	95	96
302	2.0	8.7	189	186
142	4.2	8.9	401	169
102	5.9	8.9	559	152
74	8.1	8.8	770	147

Table 11N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
15	14	5	4	17	47
30	26	10	8	34	88
63	50	21	13	72	178
88	63	29	10	100	243
122	31	41	8	138	328

MR 3.3

Table 12N Data for the NaBr Addition Solution. Mole Ratio of NaBr:SiO_2 = 3.3.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	95	96
296	2.0	8.6	193	188
136	4.4	8.9	419	163
100	6.0	9	570	155
69	8.7	8.9	826	158

Table 12N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
15	14	5	4	17	138
30	27	10	8	34	271
66	54	22	15	75	579
90	67	30	12	102	754
130	53	43	11	148	1201

MR 0.0

Table 13N Data for the NaI Addition Solution. Mole Ratio of NaI:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	96	96
284	2.1	8.5	203	188
148	4.1	8.9	389	182
93	6.5	8.6	619	163
70	8.6	8.6	823	172

Table 13N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	15	15
30	28	8	9	32	28
57	51	16	12	61	55
90	42	26	10	97	88
120	17	34	9	129	129

MR 0.21

Table 14N Data for the NaI Addition Solution. Mole Ratio of NaI:SiO_2 = 0.21.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	96	96
286	2.1	8.6	201	183
139	4.3	8.6	414	187
92	6.5	8.8	626	165
63	9.5	8.8	914	170

Table 14N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	15	26
29	27	8	8	31	50
60	50	17	12	65	109
91	30	26	8	98	164
133	15	38	5	143	244

Table 15N Data for the NaI Addition Solution. Mole Ratio of NaI:SiO_2 = 0.83.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.6	96	97
278	2.2	8.6	207	194
153	3.9	8.5	376	183
94	6.4	8.4	613	188
53	11.3	8.8	1087	168

Table 15N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	15	50
30	29	9	9	32	100
55	50	16	12	59	186
89	56	26	12	96	339
158	19	45	6	170	461

MR 3.3

Table 16N Data for the NaI Addition Solution. Mole Ratio of NaI:SiO_2 = 3.3.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	96	95
297	2.0	8.6	194	180
145	4.1	8.6	397	189
107	5.6	8.3	538	168
75	8.0	8.5	768	173

Table 16N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	15	141
28	27	8	8	30	274
58	54	17	13	62	577
79	66	22	11	84	735
112	46	32	9	120	1129

Table 17N Data for the NaSCN Addition Solution. Mole Ratio of NaSCN:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	92	92
254	2.4	8.9	217	210
124	4.8	9.1	445	161
95	6.3	9.1	581	184
63	9.5	8.9	876	163

Table 17N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.6	13	13
28	26	9	7.8	31	27
58	40	17	8.2	63	52
76	27	23	7.6	82	67
114	15	34	5	124	110

MR 0.22

Table 18N Data for the NaSCN Addition Solution. Mole Ratio of NaSCN:SiO_2 = 0.22.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	92	92
228	2.6	8.9	242	214
152	3.9	8.9	363	167
93	6.5	9.1	594	180
46	13.0	9	1200	165

Table 18N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	13	20
32	28	9	8.3	34	47
47	38	14	10	51	73
77	24	23	6.3	84	110
157	15	47	5.9	170	250

NaSCN **MR 0.86**

Table 19N Data for the NaSCN Addition Solution. Mole Ratio of NaSCN:SiO_2 = 0.86.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	92	92
250	2.4	8.9	221	208
135	4.4	9.1	409	171
99	6.1	9.1	558	471
45	13.3	9	1227	158

Table 19N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	13	40
29	27	9	7.8	31	91
53	38	16	8.9	58	170
73	67	22	18	79	230
160	20	48	6	173	500

MR 3.44

Table 20N Data for the NaSCN Addition Solution. Mole Ratio of NaSCN:SiO_2 = 3.44.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	92	92
242	2.5	8.9	228	214
132	4.5	9.1	418	195
95	6.3	9	581	492
66	9.1	8.9	837	165

Table 20N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	13	130
30	28	9	8.1	32	310
55	50	16	12	59	570
76	70	23	19	82	760
109	31	33	10	118	1100

MR 0.0

Table 21N Data for the $NaNO_3$ Addition Solution. Mole Ratio of $NaNO_3$:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	98	98
215	2.8	9	275	178
157	3.8	9.1	376	156
102	5.9	8.8	579	139
83	7.2	8.8	712	148

Table 21N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	-----	-----
36	32	11	9.3	-----	-----
50	43	15	11	-----	-----
76	28	24	12	-----	-----
94	34	29	13	-----	-----

MR 0.2

Table 22N Data for the $NaNO_3$ Addition Solution. Mole Ratio of $NaNO_3$:SiO_2 = 0.2.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	98	98
235	2.6	8.9	251	197
150	4.0	9.1	394	152
103	5.8	9	573	385
71	8.5	9	832	143

Table 22N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	-----	-----
33	30	10	8.6	-----	-----
52	45	16	11	-----	-----
76	40	23	17	-----	-----
110	20	34	7.3	-----	-----

Table 23N Data for the $NaNO_3$ Addition Solution. Mole Ratio of $NaNO_3$:SiO_2 = 0.81.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	98	98
224	2.7	9	264	184
167	3.6	9	354	201
113	5.3	9	523	165
82	7.3	9	720	197

Table 23N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.9	-----	-----
35	32	11	9.2	-----	-----
47	41	14	11	-----	-----
69	56	21	8.2	-----	-----
95	44	29	10	-----	-----

MR 3.23

Table 24N Data for the $NaNO_3$ Addition Solution. Mole Ratio of $NaNO_3$:SiO_2 = 3.23.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	98	96
293	2.0	8.9	202	178
160	3.8	9.1	369	214
130	4.6	9.1	454	321
108	5.6	9.2	547	321

Table 24N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.8	-----	-----
27	24	8	7.1	-----	-----
49	45	15	12	-----	-----
60	56	18	14	-----	-----
72	65	22	15	-----	-----

MR 0.0

Table 25N Data for the NaNO$_2$ Addition Solution. Mole Ratio of NaNO$_2$:SiO$_2$ = 0.0.

Final			**Total SiO$_2$ (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	96	96
277	2.2	8.7	208	187
145	4.1	8.9	397	146
100	6.0	8.8	576	129
53	11.3	8.9	1087	141

Table 25N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	15	15
30	28	9	9	32	29
58	50	17	12	62	55
84	28	24	10	90	75
158	15	45	6	170	155

MR 0.21

Table 26N Data for the NaNO$_2$ Addition Solution. Mole Ratio of NaNO$_2$:SiO$_2$ = 0.21.

Final			**Total SiO$_2$ (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	96	92
280	2.1	8.8	206	185
150	4.0	9	384	135
100	6.0	8.9	576	136
30	20.0	9.3	1920	120

Table 26N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	15	23
30	27	9	8	32	47
56	44	16	10	60	81
84	33	24	9	90	128
280	7	80	3	300	338

Table 27N Data for the $NaNO_2$ Addition Solution. Mole Ratio of $NaNO_2$:SiO_2 = 0.83.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	96	91
287	2.1	8.8	201	180
153	3.9	9	376	155
110	5.5	8.7	524	132
35	17.1	9	1646	129

Table 27N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	15	47
29	26	8	8	31	91
55	48	16	12	59	178
76	57	22	10	82	227
240	12	69	4	257	678

MR 3.3

Table 28N Data for the $NaNO_2$ Addition Solution. Mole Ratio of $NaNO_2$:SiO_2 = 3.3.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	96	89
295	2.0	8.7	195	176
160	3.8	9	360	209
110	5.5	9	524	226
28	21.4	9	2057	135

Table 28N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	15	134
28	26	8	8	31	266
53	48	15	14	56	510
76	65	22	15	82	712
300	26	86	7	321	2696

Table 29N Data for the Sodium Sulfate Addition Solution. Mole Ratio of Na_2SO_4:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	95	95
260	2.3	8.6	219	207
142	4.2	8.8	401	176
108	5.6	8.6	528	162
73	8.2	8.6	781	153

Table 29N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	13	13
32	32	9	8	30	31
59	49	17	11	55	53
78	39	22	10	72	72
115	18	33	5	107	104

MR 0.21

Table 30N Data for the Sodium Sulfate Addition Solution. Mole Ratio of Na_2SO_4:SiO_2 = 0.21.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	95	95
258	2.3	8.7	221	207
144	4.2	8.9	396	174
92	6.5	8.7	620	249
88	6.8	8.7	648	197

Table 30N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	13	32
33	31	9	8	30	74
58	50	17	10	54	124
91	35	26	9	85	202
95	40	27	10	89	216

Na_2SO_4 **MR 0.83**

Table 31N Data for the Sodium Sulfate Addition Solution. Mole Ratio of Na_2SO_4:SiO_2 = 0.83.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	95	97
180	3.3	8.8	317	226
147	4.1	9	388	306
88	6.8	8.9	648	444
60	10.0	8.9	950	363

Table 31N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	12	4	4	13	88
47	42	13	13	43	284
57	52	16	15	53	307
95	82	27	19	89	489
140	34	40	15	130	739

MR 3.33

Table 32N Data for the Sodium Sulfate Addition Solution. Mole Ratio of Na_2SO_4:SiO_2 = 3.33.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	95	96
250	2.4	8.6	228	218
131	4.6	9	435	337
94	6.4	9.1	606	550
59	10.2	9.1	966	188

Table 32N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	15	4	4	13	261
34	31	10	8	31	580
64	58	18	16	60	1091
89	87	26	24	83	1705
142	103	41	10	132	2619

Table 33N Data for the Ammonium Sulfamate Addition Solution. Mole Ratio of $NH_2SO_3NH_4$:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.7	101	101
305	2.0	8.1	198	175
127	4.7	8.7	475	150
82	7.3	8.6	736	235
81	7.4	8.5	745	137

Table 33N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	0	0
28	25	8	7.1	0	0
66	48	19	11	0	0
102	34	29	17	0	0
104	25	30	10	0	0

MR 0.2

Table 34N Data for the Ammonium Sulfamate Addition Solution. Mole Ratio of $NH_2SO_3NH_4$:SiO_2 = 0.2.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	101	101
295	2.0	8.2	205	169
139	4.3	8.8	434	154
99	6.1	8.8	610	154
62	9.7	8.6	973	141

Table 34N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4.2	0	0
28	24	8	6.9	0	0
60	50	17	13	0	0
85	62	24	13	0	0
135	38	39	17	0	0

Table 35N Data for the Ammonium Sulfamate Addition Solution. Mole Ratio of $NH_2SO_3NH_4$:SiO_2 = 0.78.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	101	101
307	2.0	8.1	197	173
218	2.8	8	277	180
78	7.7	8.1	774	407
71	8.5	8.5	850	599

Table 35N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4.1	0	0
27	25	8	7	0	0
39	34	11	9.6	0	0
108	94	31	27	0	0
118	120	34	34	0	0

MR 3.14

Table 36N Data for the Ammonium Sulfamate Addition Solution. Mole Ratio of $NH_2SO_3NH_4$:SiO_2 = 3.14.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	101	101
297	2.0	7.6	203	180
200	3.0	6.9	302	278
100	6.0	6.5	603	492
61	9.8	6.2	989	706

Table 36N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	15	4	4.2	0	0
28	26	8	7.3	0	0
42	40	12	11	0	0
84	74	24	21	0	0
138	130	39	35	0	0

$NaHSO_3$ **MR 0.0**

Table 37N Data for the Sodium Bisulfite Addition Solution. Mole Ratio of $NaHSO_3$:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.5	100	100
280	2.1	8.3	214	205
140	4.3	8.3	427	177
90	6.7	8.2	665	179
60	10.0	8.5	997	166

Table 37N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14.1	4	4.2	14	14.4
30	29	9	8.6	31	28.8
60	48.7	18	11.7	62	54
94	44.8	28	10.9	96	90
141	15.6	42	7	144	130

MR 0.2

Table 38N Data for the Sodium Bisulfite Addition Solution. Mole Ratio of $NaHSO_3$:SiO_2 = 0.2.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.1	100	100
290	2.1	8.3	206	195
149	4.0	8.2	401	178
101	5.9	8	592	168
98	6.1	8.4	610	163

Table 38N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	13.8	4	4.2	14	33.5
29	27.4	9	8.2	30	65.2
57	47.7	17	11.5	58	120.2
84	64.2	25	10.4	86	175
86	31.6	26	7.6	88	247

Table 39N Data for the Sodium Bisulfite Addition Solution. Mole Ratio of $NaHSO_3$:SiO_2 = 0.79.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	100	97
279	2.2	8.3	214	192
135	4.4	8.7	443	307
94	6.4	8.8	636	480
66	9.1	8.3	906	177

Table 39N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	13.8	4	4.2	14	80.4
30	27.6	9	8.2	31	161
63	55.4	19	15.3	64	333
90	80.9	27	21.8	92	484
128	67.8	38	9.7	131	702

MR 3.2

Table 40N Data for the Sodium Bisulfite Addition Solution. Mole Ratio of $NaHSO_3$:SiO_2 = 3.2.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	100	96
292	2.1	8.2	205	71
140	4.3	8.6	427	313
95	6.3	8.9	630	497
74	8.1	8.9	808	441

Table 40N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14.4	4	4.1	14	260.7
29	10.3	9	3	30	196.9
60	52	18	15.2	62	1020
89	82	27	23.9	91	1680
114	95.8	34	24.6	117	1989

Na_2HPO_4 **MR 0.0**

Table 41N Data for the Disodium Phosphate Addition Solution. Mole Ratio of Na_2HPO_4:SiO_2 = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.1	86	86
290	2.1	8.3	177	165
150	4.0	9	342	165
98	6.1	8.9	524	278
80	7.5	8.8	642	190

Table 41N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4.4	0	0
27	25	9	8	0	0
52	31	18	11	0	0
80	35	27	12	0	0
98	26	33	7	0	0

MR 0.23

Table 42N Data for the Disodium Phosphate Addition Solution. Mole Ratio of Na_2HPO_4:SiO_2 = 0.23.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	86	86
287	2.1	8.6	179	169
142	4.2	9	362	300
103	5.8	9.3	499	471
88	6.8	9.2	584	492

Table 42N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	12	4	3.5	0	0
27	8.6	9	5.2	0	0
55	5.1	19	8.4	0	0
76	4.1	26	10	0	0
89	4.2	30	11	0	0

Na_2HPO_4 **MR 0.92**

Table 43N Data for the Disodium Phosphate Addition Solution. Mole Ratio of Na_2HPO_4:SiO_2 = 0.92.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	86	86
253	2.4	8.7	203	167
130	4.6	9.1	395	321
90	6.7	9.3	571	514
74	8.1	9.4	694	599

Table 43N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	12	4	3.4	0	0
31	3.8	10	4.6	0	0
60	2	20	8.3	0	0
87	1.5	29	12	0	0
105	1.2	36	12	0	0

MR 3.68

Table 44N Data for the Disodium Phosphate Addition Solution. Mole Ratio of Na_2HPO_4:SiO_2 = 3.68.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	86	81
294	2.0	8.6	175	158
140	4.3	8.9	367	278
102	5.9	9	504	449
79	7.6	9.1	650	578

Table 44N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	10	4	3.3	0	0
27	4.1	9	4.7	0	0
56	2.7	19	8.8	0	0
76	2.4	26	11	0	0
99	2.2	33	14	0	0

$Na_2SiO_3 \cdot 9H_2O$

Table 45N Data for 113 mg/L $Na_2SiO_3 \cdot 9H_2O$ Addition Solutions,Run #1. Initial pH 8.0.

Final			Total Silica (mg/L)		Reactive Silica (mg/L)
Vol. (ml)	C.F.	pH	Expected	Measured	Measured
600	1	6.6	113	113	110
270	2.2	7	252	235	-
165	3.6	8	412	364	-
87	6.9	8.1	782	663	-
62	9.7	8.1	1098	877	-

Table 46N Data for 113 mg/L $Na_2SiO_3 \cdot 9H_2O$ Addition Solutions,Run #2. Initial pH 8.0.

Final			Total Silica (mg/L)		Reactive Silica (mg/L)
Vol. (ml)	C.F.	pH	Expected	Measured	Measured
600	1	-	113	113	-
265	2.3	-	257	235	-
150	4	-	454	407	175
85	7.1	-	801	663	-
65	9.2	-	1047	942	-

Table 47N Data for 113 mg/L $Na_2SiO_3 \cdot 9H_2O$ Addition Solutions,Run #3. Initial pH 8.0.

Final			Total Silica (mg/L)		Reactive Silica (mg/L)
Vol. (ml)	C.F.	pH	Expected	Measured	Measured
600	1	-	113	113	-
265	2.3	-	257	235	-
143	4.2	-	476	428	-
88	6.8	-	773	663	-
66	9.1	-	1031	877	115

Table 48N Data for 113 mg/L $Na_2SiO_3 \cdot 9H_2O$ Addition Solutions,Run #4. Initial pH 8.0.

Final			Total Silica (mg/L)		Reactive Silica (mg/L)
Vol. (ml)	C.F.	pH	Expected	Measured	Measured
600	1	-	113	113	-
263	2.3	-	259	235	225
140	4.3	-	486	449	-
88	6.8	-	773	621	118
75	8	-	907	749	-

Table 49N Data for 111 mg/L $Na_2SiO_3 \cdot 9H_2O$ Addition Solutions. Initial pH 3.0.

Final			Total Silica (mg/L)		Reactive Silica (mg/L)
Vol. (ml)	C.F.	pH	Expected	Measured	Measured
600	1	3	111	111	107
297	2	2.8	224	197	175
142	4.2	2.5	469	449	370
85	7.1	2.3	784	749	546
70	8.6	2.2	951	920	609

Table 50N Data for 111 mg/L $Na_2SiO_3 \cdot 9H_2O$ Addition Solutions. Initial pH 6.0.

Final			Total Silica (mg/L)		Reactive Silica (mg/L)
Vol. (ml)	C.F.	pH	Expected	Measured	Measured
600	1	6	111	111	107
302	2	4.9	221	210	190
155	3.9	6.1	430	342	129
98	6.1	6.3	680	599	119
60	10	6.3	1110	920	108

Table 51N Data for 111 mg/L $Na_2SiO_3 \cdot 9H_2O$ Addition Solutions. Initial pH 9.0.

Final			Total Silica (mg/L)		Reactive Silica (mg/L)
Vol. (ml)	C.F.	pH	Expected	Measured	Measured
600	1	9	111	111	107
285	2.1	7.7	234	214	220
135	4.4	8.7	493	449	152
88	6.8	8.8	757	621	147
50	12	9.1	1332	1134	166

Table 52N Data for 111 mg/L $Na_2SiO_3 \cdot 9H_2O$ Addition Solutions. Initial pH 10.5.

Final			Total Silica (mg/L)		Reactive Silica (mg/L)
Vol. (ml)	C.F.	pH	Expected	Measured	Measured
600	1	10.5	111	111	107
304	2	9.9	219	208	205
160	3.8	9.9	416	385	365
91	6.6	10	732	685	336
75	8	10.1	888	856	334

Organics

HCOONa **MR 0.0**

Table 53N Data for the Sodium Formate Addition Solution. Mole Ratio of HCOONa = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.7	98	98
330	1.8	8.4	179	178
197	3.0	9	300	257
94	6.4	9.1	628	156
75	8.0	8.8	788	154

Table 53N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	0	0
24	24	7	7.3	0	0
40	39	12	12	0	0
83	55	26	12	0	0
104	24	32	14	0	0

MR 0.2

Table 54N Data for the Sodium Formate Addition Solution. Mole Ratio of HCOONa = 0.2.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	98	94
314	1.9	8.7	188	178
180	3.3	9.1	328	278
105	5.7	9.1	563	449
76	7.9	8.9	777	150

Table 54N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	12	4	3.9	0	0
25	23	8	7.4	0	0
43	41	13	13	0	0
74	60	23	20	0	0
103	27	32	13	0	0

HCOONa **MR 0.81**

Table 55N Data for the Sodium Formate Addition Solution. Mole Ratio of HCOONa = 0.81.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	98	98
317	1.9	8.8	186	180
200	3.0	9	295	257
118	5.1	9.2	501	407
80	7.5	9	738	167

Table 55N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4.1	0	0
25	24	8	7.5	0	0
39	37	12	12	0	0
66	46	20	18	0	0
98	31	30	14	0	0

MR 2.43

Table 56N Data for the Sodium Formate Addition Solution. Mole Ratio of HCOONa = 2.43.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	98	96
325	1.8	8.7	182	180
185	3.2	9.1	319	278
97	6.2	9.3	609	492
87	6.9	9.2	679	278

Table 56N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	0	0
24	24	7	7.4	0	0
42	42	13	13	0	0
80	78	25	22	0	0
90	66	28	16	0	0

Table 57N Data for the Sodium Acetate Addition Solution. Mole Ratio of CH_3COONa = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	101	101
287	2.1	8.9	210	193
160	3.8	9.3	377	178
88	6.8	8.9	686	165
82	7.3	8.8	736	154

Table 57N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.9	0	0
27	25	8	7.6	0	0
49	25	15	11	0	0
89	38	27	11	0	0
95	26	29	9.8	0	0

MR 0.2

Table 58N Data for the Sodium Acetate Addition Solution. Mole Ratio of CH_3COONa = 0.2.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.6	101	105
342	1.8	8.9	176	169
145	4.1	9.2	410	175
107	5.6	–	564	–
85	7.1	8.9	710	152

Table 58N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	15	4	5	0	0
23	22	7	7	0	0
54	48	16	12	0	0
73	–	22	–	0	0
92	28	28	7	0	0

Table 59N Data for the Sodium Acetate Addition Solution. Mole Ratio of CH_3COONa = 0.78.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	101	101
300	2.0	9	201	182
154	3.9	9.3	392	175
103	5.8	9.2	586	169
65	9.2	9.1	928	165

Table 59N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	0	0
26	24	8	7.2	0	0
51	22	15	11	0	0
76	49	23	8.8	0	0
120	22	36	9	0	0

MR 2.35

Table 60N Data for the Sodium Acetate Addition Solution. Mole Ratio of CH_3COONa = 2.35.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	101	103
275	2.2	9	219	203
137	4.4	9.2	440	163
118	5.1	9.2	511	163
70	8.6	9.1	862	163

Table 60N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	0	0
28	27	9	8	0	0
57	47	17	12	0	0
66	31	20	12	0	0
111	30	33	12	0	0

MR 0.0

Table 61N Data for the Sodium Oxalate Addition Solution. Mole Ratio of NaOOCCOONa = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	93	93
330	1.8	8.5	169	167
143	4.2	8.9	390	158
83	7.2	8.6	672	141
64	9.4	8.6	871	144

Table 61N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	11.81102362	4	3.802281369	14	14.14141414
21	21	7	6.653992395	26	25
50	20.2020202	16	10.45627376	59	55.44554455
85	18.36734694	27	6.844106464	102	93.1372549
111	13.26530612	36	5.893536122	133	116.5048544

MR 0.11

Table 62N Data for the Sodium Oxalate Addition Solution. Mole Ratio of NaOOCCOONa = 0.11.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	93	97
335	1.8	8.6	166	163
148	4.1	9	377	338
93	6.5	9	599	486
85	7.1	9	656	549

Table 62N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	7.8	4	3.9	14	23.1
21	12.5	7	6.4	25	40
48	26.3	15	13.2	57	89.6
76	36.2	25	18.9	91	132.1
83	24.5	27	20.8	100	150.9

NaOOCCOONa **MR 0.43**

Table 63N Data for the Sodium Oxalate Addition Solution. Mole Ratio of NaOOCCOONa = 0.43.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	93	95
255	2.4	8.7	219	215
133	4.5	9.1	419	364
94	6.4	9.2	593	556
74	8.1	9.2	753	642

Table 63N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	1.6	4	3.6	14	44.3
28	1	9	7.9	33	103
53	2.5	17	14.9	64	187
75	2.2	24	21.5	90	280
96	2.5	31	24.3	115	321

MR 1.7

Table 64N Data for the Sodium Oxalate Addition Solution. Mole Ratio of NaOOCCOONa = 1.7.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	93	98
250	2.4	8.7	223	235
149	4.0	9.2	374	321
85	7.1	9.4	656	642
81	7.4	9.4	688	685

Table 64N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	0.2	4	3.7	14	142
28	0.2	9	8.5	34	330
48	1	15	14	57	500
83	1.4	27	25.2	100	943
87	1.5	28	26.1	105	943

Oxalate **Initial pH 3.5**

Table 65N Data for the Sodium Oxalate Addition Solution. Mole Ratio = 0.44.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	5.1	90	88
302	2.0	3.6	179	163
129	4.7	3.1	419	385
81	7.4	2.9	667	578
58	10.3	2.6	931	899

Table 65N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
11	2.3	4	3.5	0	0
22	2.3	7	6.4	0	0
51	2.6	16	15	0	0
81	2.6	26	23	0	0
114	3.1	36	35	0	0

Initial pH 4.5

Table 66N Data for the Sodium Oxalate Addition Solution. Mole Ratio = 0.44

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	6.3	90	90
303	2	5.6	178	167
129	4.7	4.7	419	385
87	6.9	4.4	621	578
47	12.8	4.2	1149	1049

Table 66N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
11	0.9	4	3.5	-	-
22	0.8	7	6.5	-	-
51	0.7	16	15	-	-
76	0.6	24	23	-	-
140	0.8	45	41	-	-

Initial pH 5.5

Table 67N Data for the Sodium Oxalate Addition Solution. Mole Ratio = 0.44

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	7	90	90
297	2	7.7	182	167
135	4.4	8	400	342
105	5.7	8.1	514	471
75	8	8.2	720	621

Table 67N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
11	0.7	4	3.5	-	-
22	3.9	7	6.4	-	-
49	0.5	16	14	-	-
63	0.6	20	18	-	-
88	0.7	28	25	-	-

Initial pH 6.5

Table 68N Data for the Sodium Oxalate Addition Solution. Mole Ratio = 0.44

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	8	90	92
313	1.9	8.6	173	161
140	4.3	9	386	342
87	6.9	9.1	621	556
56	10.7	9.2	964	856

Table 68N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
11	0.8	4	3.6	-	-
21	1.5	7	6.1	-	-
47	0.9	15	14	-	-
76	1	24	22	-	-
118	1.2	38	33	-	-

Initial pH 7.2

Table 69N Data for the Sodium Oxalate Addition Solution. Mole Ratio of = 0.44.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	90	90
292	2.1	8.9	185	169
140	4.3	9.3	386	321
120	5.0	9.2	450	407
67	9.0	9.3	806	728

Table 69N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
11	0.7	4	3.4	0	0
23	0.7	7	6.4	0	0
47	0.9	15	13	0	0
55	1	18	16	0	0
99	1.1	31	28	0	0

Initial pH 8.2

Table 70N Data for the Sodium Oxalate Addition Solution. Mole Ratio = 0.44

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	8.6	90	88
300	2	8.9	180	163
140	4.3	9.2	386	342
95	6.3	9.3	568	492
71	8.5	9.3	761	706

Table 70N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
11	0.8	4	3.4	-	-
22	0.7	7	6.3	-	-
47	1	15	13	-	-
69	1.1	22	19	-	-
93	1.2	30	27	-	-

Initial pH 9.0

Table 71N Data for the Sodium Oxalate Addition Solution. Mole Ratio = 0.44

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	8.9	90	88
275	2.2	9	196	178
125	4.8	9.3	432	385
98	6.1	9.3	551	492
61	9.8	9.4	885	813

Table 71N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
11	0.7	4	3.4	-	-
24	0.7	8	6.9	-	-
53	1.1	17	15	-	-
67	1.1	21	19	-	-
108	1.4	34	31	-	-

Initial pH 10.0

Table 72N Data for the Sodium Oxalate Addition Solution. Mole Ratio = 0.44

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	9.5	90	88
307	2	9.4	176	158
138	4.3	9.4	391	342
100	6	9.6	540	449
64	9.4	9.7	844	792

Table 72N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
11	0.9	4	3.3	-	-
21	0.8	7	5.8	-	-
48	1.7	15	11	-	-
66	2.1	21	16	-	-
103	2.7	33	26	-	-

Calcium:Oxalate MR = 1.25

Oxalate:Silica MR = 0.0

Table 73N Data for the Sodium Oxalate Plus Calcium Addition Solution.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	8.1	103	103
313	1.9	8.5	197	171
150	4	8.8	411	152
87	6.9	8.8	708	141
70	8.6	8.8	880	152

Table 73N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
14	14	4	4	13	13
27	24	7	6.7	25	22
56	40	16	11	52	46
97	27	27	8	90	79
120	20	33	7	111	110

Oxalate:Silica MR = 0.19

Table 74N Data for the Sodium Oxalate Plus Calcium Addition Solution.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	8.3	103	98
265	2.3	8.7	233	199
163	3.7	8.8	378	146
69	8.7	8.7	893	141
46	13	8.9	1340	139

Table 74N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
31	18	4	4	29	29
69	37	9	8	67	59
113	33	14	10	107	97
265	25	34	8	252	240
398	16	51	9	377	350

Oxalate:Silica MR = 0.38

Table 75N Data for the Sodium Oxalate Plus Calcium Addition Solution.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	pH	Expected	Measured
600	1	8.4	103	98
240	205	8.6	257	197
145	4.1	8.6	425	139
74	8.1	8.6	833	128
70	8.6	8.8	880	143

Table 75N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
47	21	4	4	43	43
128	46	10	8	108	97
195	35	16	12	176	160
382	35	32	11	348	320
403	59	33	12	370	360

Oxalate and Ca **Oxalate: Silica MR = 0.77**

Table 76N Data for the Sodium Oxalate + Calcium Addition Solution. Mole Ratio of = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	103	101
258	2.3	8.6	239	197
124	4.8	8.7	497	131
77	7.8	8.8	800	171
75	8.0	8.8	822	188

Table 76N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
80	29	4	4	75	75
186	54	9	8.1	173	160
387	70	19	14	360	310
623	93	30	19	585	510
640	76	31	21	600	550

Sebacic **MR 0.0**

Table 77N Data for the Sebacic Acid Addition Solution. Mole Ratio of 1,8-octanedicarboxylic acid = 0.0.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	97	97
265	2.3	8.9	220	211
166	3.6	9.1	351	172
108	5.6	8.7	539	146
85	7.1	8.7	685	143

Table 77N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	14
32	30	9	10	32	30
51	43	14	13	51	47
78	21	22	9	78	66
99	30	28	8	99	88

MR 0.21

Table 78N Data for the Sebacic Acid Addition Solution. Mole Ratio of 1,8-octanedicarboxylic acid = 0.21.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	97	94
294	2.0	8.5	198	186
134	4.5	8.5	434	157
114	5.3	8.5	511	147
84	7.1	8.9	693	276

Table 78N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	56
29	28	8	8	29	111
63	20	18	9	63	237
74	17	21	10	74	265
100	25	29	12	100	411

Table 79N Data for the Sebacic Acid Addition Solution. Mole Ratio of 1,8-octanedicarboxylic acid = 0.82.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	97	92
240	2.5	8.8	243	213
124	4.8	9.2	469	289
100	6.0	9.1	582	377
80	7.5	8.7	728	165

Table 79N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	211
35	34	10	10	35	482
68	62	19	14	68	924
84	86	24	19	84	1246
105	33	30	9	105	1525

MR 2.45

Table 80N Data for the Sebacic Acid Addition Solution. Mole Ratio of 1,8-octanedicarboxylic acid = 2.45.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	97	81
307	2.0	8.7	190	205
150	4.0	9.2	388	338
111	5.4	9.2	524	265
85	7.1	9.1	685	247

Table 80N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	14	214
27	32	8	9	27	547
56	64	16	18	56	1135
76	76	22	19	76	1401
99	61	28	13	99	1672

Table 81N Data for the Maleic Acid Addition Solution. Mole Ratio of cis-1,2-ethylenedicarboxylic acid = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.7	99	99
215	2.8	8.5	275	250
64	9.4	8.6	924	163
64	9.4	8.5	924	156
53	11.3	8.5	1116	163

Table 81N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13.1	4	4.2	14	14.3
37	35.3	12	10.8	40	36.8
123	13.8	39	4.2	134	118.2
123	17.5	39	6.9	134	111.6
148	13.6	48	5.7	162	144.6

MR 0.1

Table 82N Data for the Maleic Acid Addition Solution. Mole Ratio of cis-1,2-ethylenedicarboxylic acid = 0.1.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	99	102
207	2.9	8.6	286	231
100	6.0	8.7	592	197
58	10.3	8.5	1020	164
56	10.7	8.5	1056	168

Table 82N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13.4	4	4.2	14	24.6
38	33.9	12	11	41	67.5
79	20.4	25	7.4	86	129.7
136	15.1	43	7.1	148	235
140	15.4	45	4.7	153	242

Maleic **MR 0.4**

Table 83N Data for the Maleic Acid Addition Solution. Mole Ratio of cis-1,2-ethylenedicarboxylic acid = 0.4.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	99	101
230	2.6	8.5	257	245
107	5.6	8.7	553	438
74	8.1	8.8	799	498
60	10.0	8.6	986	168

Table 83N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13.5	4	4.1	14	45.4
34	33.5	11	10.1	37	113.2
73	68.2	24	18.6	80	233
106	46.7	34	20.7	116	344
131	26.7	42	7.9	143	400

MR 1.6

Table 84N Data for the Maleic Acid Addition Solution. Mole Ratio of cis-1,2-ethylenedicarboxylic acid = 1.6.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	99	100
218	2.8	8.6	271	235
89	6.7	8.85	665	563
55	10.9	8.9	1076	639
52	11.5	8.9	1138	255

Table 84N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13.8	4	4.1	14	135
36	35.1	12	10.3	39	352
88	86	28	24	96	882
143	113.8	46	29	156	1335
151	60.3	48	16.7	165	1561

Table 85N Data for the Citric Acid Addition Solution. Mole Ratio of 2-Hydoxy-1,2,3-propane tricarboxylic acid = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.1	96	96
305	2.0	8.6	189	182
195	3.1	8.8	296	214
93	6.5	9	621	173
75	8.0	8.8	770	148

Table 85N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.8	0	0
24	24	7	7.3	0	0
37	37	12	11	0	0
77	34	25	12	0	0
96	22	30	9.4	0	0

MR 0.21

Table 86N Data for the Citric Acid Addition Solution. Mole Ratio of 2-Hydoxy-1,2,3-propane tricarboxylic acid = 0.21.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	96	96
304	2.0	8.4	190	184
210	2.9	8.6	275	235
100	6.0	8.9	578	492
74	8.1	8.9	781	685

Table 86N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	13	4	3.9	0	0
24	24	8	7.4	0	0
34	35	11	11	0	0
72	71	23	21	0	0
97	100	31	30	0	0

Table 87N Data for the Citric Acid Addition Solution. Mole Ratio of 2-Hydoxy-1,2,3-propane tricarboxylic acid = 0.83.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	96	98
284	2.1	8.4	203	197
203	3.0	8.6	285	235
130	4.6	8.7	444	407
90	6.7	8.9	642	599

Table 87N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	13	4	4	0	0
25	26	8	7.8	0	0
35	37	11	11	0	0
55	56	18	17	0	0
80	82	25	25	0	0

MR 2.48

Table 88N Data for the Citric Acid Addition Solution. Mole Ratio of 2-Hydoxy-1,2,3-propane tricarboxylic acid = 2.48.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.1	96	98
283	2.1	8.3	204	199
198	3.0	8.5	292	235
93	6.5	8.9	621	514
84	7.1	9.1	688	535

Table 88N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	13	4	3.9	0	0
25	26	8	7.9	0	0
36	37	12	11	0	0
77	76	25	23	0	0
86	83	27	26	0	0

Table 89N Data for the EDTA Addition Solution. Mole Ratio of Ethylenediaminetetra-acetic acid = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.5	99	99
257	2.3	8.5	231	227
154	3.9	8.7	386	168
71	8.5	8.4	837	141
49	12.2	8.5	1212	156

Table 89N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	14
33	33	9	11	33	32
55	22	16	13	55	53
118	15	34	5	118	109
171	12	49	6	171	153

MR 0.08

Table 90N Data for the EDTA Addition Solution. Mole Ratio of Ethylenediaminetetra-acetic acid = 0.08.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	99	96
240	2.5	8.5	248	227
155	3.9	8.8	383	243
75	8.0	8.8	792	507
64	9.4	8.7	928	316

Table 90N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	55
35	33	10	11	35	134
54	49	15	13	54	193
112	67	32	24	112	390
131	70	38	24	131	445

MR 0.4

Table 91N Data for the EDTA Addition Solution. Mole Ratio of Ethylenediaminetetra-acetic acid = 0.4.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	99	94
330	1.8	8.3	180	170
162	3.7	8.8	367	263
110	5.5	9	540	445
55	10.9	9.4	1080	871

Table 91N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	97
25	25	7	8	25	176
52	51	15	15	52	344
76	69	22	22	76	499
153	146	44	48	153	1077

MR 0.8

Table 92N Data for the EDTA Addition Solution. Mole Ratio of Ethylenediaminetetra-acetic acid = 0.8.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	99	96
252	2.4	8.5	236	208
165	3.6	8.8	360	247
90	6.7	9	660	547
45	13.3	9.3	1320	984

Table 92N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	14	120
33	32	10	10	33	262
51	48	15	16	51	423
93	84	27	27	93	742
187	173	53	56	187	1542

Table 93N Data for the o-Phthalic Acid Addition Solution. Mole Ratio of 1,2-benzenedicarboxylic acid = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	100	100
268	2.2	8.5	224	214
148	4.1	8.5	405	168
108	5.6	8.4	556	161
80	7.5	8.5	750	167

Table 93N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	17	17
31	30	9	9	38	30
57	27	16	13	69	54
78	32	22	10	94	76
105	20	30	8	128	109

MR 0.1

Table 94N Data for the o-Phthalic Acid Addition Solution. Mole Ratio of 1,2-benzenedicarboxylic acid = 0.1.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	100	100
298	2.0	8.2	201	195
150	4.0	8.5	400	170
104	5.8	8.6	577	166
84	7.1	8.5	714	169

Table 94N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	14	4	4	17	28
28	27	8	8	34	55
56	32	16	13	68	107
81	30	23	10	98	160
100	21	29	9	121	207

Table 95N Data for the o-Phthalic Acid Addition Solution. Mole Ratio of 1,2-benzenedicarboxylic acid = 0.4.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.7	100	98
310	1.9	8.1	194	182
143	4.2	8.5	420	167
118	5.1	8.4	508	232
109	5.5	8.4	550	418

Table 95N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	17	45
27	24	8	8	33	86
59	40	17	13	71	182
71	56	20	15	86	229
77	64	22	20	94	251

MR 1.6

Table 96N Data for the o-Phthalic Acid Addition Solution. Mole Ratio of 1,2-benzenedicarboxylic acid = 1.6.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.8	100	99
310	1.9	8	194	176
135	4.4	8.5	444	339
103	5.8	8.5	583	476
80	7.5	8.5	750	567

Table 96N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
14	13	4	4	17	139
27	22	8	8	33	258
62	50	18	17	76	608
82	68	23	22	99	792
105	90	30	27	128	999

p-Phthalic **MR 0.0**

Table 97N Data for the p-Phthalic Acid Addition Solution. Mole Ratio of 1,4-benzenedicarboxylic acid = 0.0.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	90	90
276	2.2	8.8	195	178
144	4.2	9.1	375	171
109	5.5	9	495	158
68	8.8	8.9	793	167

Table 97N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.6	0	0
28	26	8	6.9	0	0
54	22	15	10	0	0
72	25	20	8.7	0	0
115	24	32	6.6	0	0

MR 0.22

Table 98N Data for the p-Phthalic Acid Addition Solution. Mole Ratio of 1,4-benzenedicarboxylic acid = 0.22.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	90	92
284	2.1	8.8	190	186
140	4.3	9	385	165
96	6.3	0	562	385
65	9.2	0	830	156

Table 98N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.5	0	0
27	26	8	6.9	0	0
56	49	15	11	0	0
81	75	23	16	0	0
120	35	33	7	0	0

p-Phthalic **MR 0.88**

Table 99N Data for the p-Phthalic Acid Addition Solution. Mole Ratio of 1,4-benzenedicarboxylic acid = 0.88.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.8	90	94
290	2.1	0	186	178
135	4.4	8.9	399	364
91	6.6	0	593	492
69	8.7	0	782	642

Table 99N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.4	0	0
27	25	7	6.6	0	0
58	58	16	15	0	0
86	79	24	20	0	0
113	110	31	30	0	0

MR 2.64

Table 100N Data for the p-Phthalic Acid Addition Solution. Mole Ratio of 1,4-benzenedicarboxylic acid = 2.64.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	5.5	90	94
295	2.0	0	183	180
146	4.1	5.1	369	364
124	4.8	0	435	449
56	10.7	0	963	963

Table 100N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.5	0	0
26	26	7	6.7	0	0
53	52	15	13	0	0
63	64	17	17	0	0
139	79	39	38	0	0

Table 101N Data for the Catechol Addition Solution. Mole Ratio of 1,2-dihydroxybenzene = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	86	86
315	1.9	8.7	163	156
205	2.9	9	251	203
90	6.7	9	571	141
75	8.0	8.8	685	154

Table 101N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
11	11	4	3.6	0	0
21	20	7	6.3	0	0
32	32	11	9.6	0	0
73	50	24	9.3	0	0
88	17	29	8.2	0	0

MR 0.09

Table 102N Data for the Catechol Addition Solution. Mole Ratio of 1,2-dihydroxybenzene = 0.09.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.1	86	86
325	1.8	8.4	158	146
200	3.0	8.7	257	257
105	5.7	9	489	214
60	10.0	9.2	856	154

Table 102N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
11	11	4	3.5	0	0
20	18	7	5.8	0	0
33	31	11	10	0	0
63	53	21	13	0	0
110	82	36	12	0	0

Catechol **MR 0.46**

Table 103N Data for the Catecho; Addition Solution. Mole Ratio of 1,2-dihydroxybenzene = 0.46.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.8	86	83
320	1.9	7.8	161	146
205	2.9	7.8	251	235
92	6.5	8	558	514
70	8.6	8.1	734	749

Table 103N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
11	11	4	3.4	0	0
21	18	7	5.8	0	0
32	29	11	9.4	0	0
72	57	23	20	0	0
94	94	31	34	0	0

MR 1.84

Table 104N Data for the Catechol; Addition Solution. Mole Ratio of 1,2-dihydroxybenzene = 1.84.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.5	86	81
317	1.9	7.5	162	148
190	3.2	7.4	270	235
100	6.0	7.5	514	471
60	10.0	7.5	856	770

Table 104N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
11	11	4	3.3	0	0
21	19	7	5.9	0	0
35	30	11	9.7	0	0
66	58	22	19	0	0
110	91	36	30	0	0

Table 105N Data for the Pyrogallol Addition Solution. Mole Ratio of 1,2,3-trihydroxybenzene = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	86	86
295	2.0	8.9	174	165
140	4.3	9	367	154
110	5.5	8.9	467	146
72	8.3	8.7	713	150

Table 105N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.6	0	0
24	23	7	6.9	0	0
51	44	15	9.6	0	0
65	52	20	8.3	0	0
100	18	30	6	0	0

MR 0.09

Table 106N Data for the Pyrogallol Addition Solution. Mole Ratio of 1,2,3-trihydroxybenzene = 0.09.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	86	86
270	2.2	8.8	190	173
140	4.3	9	367	143
103	5.8	9	499	146
69	8.7	8.9	744	146

Table 106N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.6	0	0
27	23	8	7.3	0	0
51	40	15	11	0	0
70	54	21	12	0	0
104	70	31	9	0	0

Table 107N Data for the Pyrogallol Addition Solution. Mole Ratio of 1,2,3-trihydroxybenzene = 0.46.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.8	86	86
295	2.0	8.3	174	161
142	4.2	8.5	362	300
94	6.4	8.6	546	471
58	10.3	8.7	886	685

Table 107N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	9.4	4	3.5	0	0
24	18	7	6.5	0	0
51	34	15	13	0	0
77	50	23	19	0	0
124	85	37	34	0	0

MR 1.84

Table 108N Data for the Pyrogallol Addition Solution. Mole Ratio of 1,2,3-trihydroxybenzene = 1.84.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.6	86	83
305	2.0	7.4	168	156
140	4.3	7	367	364
80	7.5	6.7	642	449
67	9.0	6.8	767	449

Table 108N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	8.7	4	3.4	0	0
24	11	7	5.6	0	0
51	19	15	13	0	0
90	30	27	19	0	0
107	35	32	23	0	0

Phloroglucinol **MR 0.0**

Table 109N Data for the Phloroglucinol Addition Solution. Mole Ratio of 1,3,5-trihydroxybenzene = 0.0.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.8	94	94
282	2.1	8.7	200	184
164	3.7	9.2	344	257
94	6.4	9.1	601	175
60	10.0	8.9	942	150

Table 109N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.9	0	0
28	25	8	7.5	0	0
48	42	14	13	0	0
83	62	25	10	0	0
130	14	39	7.4	0	0

MR 0.08

Table 110N Data for the Phloroglucinol Addition Solution. Mole Ratio of 1,3,5-trihydroxybenzene = 0.08.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	94	94
262	2.3	8.6	216	184
165	3.6	9	342	235
95	6.3	9	595	385
60	10.0	9.1	942	139

Table 110N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.9	0	0
30	25	9	7.7	0	0
47	39	14	12	0	0
82	66	25	18	0	0
130	86	39	12	0	0

Phloroglucinol **MR 0.42**

Table 111N Data for the Phloroglucinol Addition Solution. Mole Ratio of 1,3,5-trihydroxybenzene = 0.42.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	94	92
269	2.2	7.9	210	180
162	3.7	8.5	349	278
100	6.0	8.8	565	449
62	9.7	8.8	911	749

Table 111N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.8	0	0
29	25	9	7.5	0	0
48	41	14	12	0	0
78	64	23	19	0	0
126	110	38	33	0	0

MR 1.7

Table 112N Data for the Phloroglucinol Addition Solution. Mole Ratio of 1,3,5-trihydroxybenzene = 1.7.

Final			Total SiO_2 (mg/L)	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.4	94	92
277	2.2	7.5	204	184
194	3.1	7.5	291	257
102	5.9	7.4	554	471
72	8.3	7.6	785	621

Table 112N continued

Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)	
Expected	Measured	Expected	Measured	Expected	Measured
13	14	4	5.1	0	0
28	25	8	7.9	0	0
40	35	12	11	0	0
76	65	23	20	0	0
108	86	33	26	0	0

Sodium Salicylate **MR 0.0**

Table 113N Data for the Sodium Salicylate Addition Solution. Mole Ratio of 2-hydroxybenzoic monosodium salt = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	98	98
236	2.5	8.8	250	214
167	3.6	9.1	354	214
90	6.7	8.5	656	146
75	8.0	8.8	788	150

Table 113N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	0	0
33	29	10	9.1	0	0
47	28	14	11	0	0
87	16	27	8.3	0	0
104	23	32	8.7	0	0

MR 0.2

Table 114N Data for the Sodium Salicylate Addition Solution. Mole Ratio of 2-hydroxybenzoic monosodium salt = 0.2.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	98	96
240	2.5	8.9	246	214
195	3.1	9	303	235
105	5.7	8.8	563	158
75	8.0	8.9	788	158

Table 114N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.9	0	0
33	29	10	8.9	0	0
40	36	12	11	0	0
74	17	23	9	0	0
104	22	32	9.6	0	0

Table 115N Data for the Sodium Salicylate Addition Solution. Mole Ratio of 2-hydroxybenzoic monosodium salt = 0.81.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.6	98	94
237	2.5	8.9	249	214
190	3.2	9.1	311	214
145	4.1	9.1	407	173
79	7.6	8.7	748	158

Table 115N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	3.8	0	0
33	29	10	8.9	0	0
41	36	13	10	0	0
54	26	17	12	0	0
99	23	30	8.7	0	0

MR 3.23

Table 116N Data for the Sodium Salicylate Addition Solution. Mole Ratio of 2-hydroxybenzoic monosodium salt = 3.23.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	98	96
243	2.5	8.9	243	214
165	3.6	9.1	358	214
105	5.7	9.3	563	150
85	7.1	8.6	695	163

Table 116N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	14	4	4	0	0
32	30	10	8.9	0	0
47	41	15	12	0	0
74	37	23	14	0	0
92	34	28	13	0	0

Table 117N Data for the p-Toluene Sulfonic Acid Addition Solution.
Mole Ratio of 4-methylbenzene sulfonic acid = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.7	88	88
285	2.1	8.7	185	175
145	4.1	9.1	363	161
95	6.3	9.3	554	137
75	8.0	8.9	702	139

Table 117N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	0	0
25	23	7	6.9	0	0
50	45	14	12	0	0
76	58	22	9.5	0	0
96	27	28	8.8	0	0

MR 0.09

Table 118N Data for the p-Toluene Sulfonic Acid Addition Solution.
Mole Ratio of 4-methylbenzene sulfonic acid = 0.09.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.8	88	88
265	2.3	8.8	199	190
140	4.3	9.1	376	143
95	6.3	9.1	554	139
67	9.0	9	786	137

Table 118N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	0	0
27	25	8	7.6	0	0
51	42	15	11	0	0
76	61	22	9.3	0	0
107	25	31	8.5	0	0

Table 119N Data for the p-Toluene Sulfonic Acid Addition Solution.
Mole Ratio of 4-methylbenzene sulfonic acid = 0.45.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.4	88	86
283	2.1	8.7	186	180
135	4.4	9	390	133
95	6.3	8.9	554	342
73	8.2	9	721	143

Table 119N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	11	4	3.4	0	0
25	24	7	7.2	0	0
53	45	16	12	0	0
76	67	22	18	0	0
99	80	29	13	0	0

MR 1.8

Table 120N Data for the p-Toluene Sulfonic Acid Addition Solution.
Mole Ratio of 4-methylbenzene sulfonic acid = 1.8.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	88	86
263	2.3	8.6	200	175
155	3.9	8.8	340	278
95	6.3	8.9	554	428
80	7.5	8.9	658	133

Table 120N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	11	4	3.4	0	0
27	23	8	7	0	0
46	41	14	12	0	0
76	68	22	20	0	0
90	70	26	14	0	0

Table 121N Data for the Alkyl Naphthalene Sulfonic Acid Addition Solution.
Mole Ratio of = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	96	96
305	2.0	8.7	189	178
125	4.8	8.7	462	167
75	8.0	8.7	770	154
64	9.4	8.7	903	158

Table 121N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4.1	13	13
26	24	8	7.3	26	23
62	47	20	12	62	56
104	25	33	13	104	93
122	16	38	11	122	110

MR 0.03

Table 122N Data for the Alkyl Naphthalene Sulfonic Acid Addition Solution.
Mole Ratio of = 0.03.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.1	96	98
300	2.0	8.1	193	175
130	4.6	8.5	444	171
100	6.0	8.7	578	165
59	10.2	8.7	979	165

Table 122N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	13	16
26	24	8	7.2	26	28
60	40	19	12	60	68
78	61	25	10	78	90
132	18	42	12	132	150

Table 123N Data for the Alkyl Naphthalene Sulfonic Acid Addition Solution.
Mole Ratio of = 0.16.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	96	98
300	2.0	8.6	193	178
110	5.5	9	525	165
96	6.3	9.1	602	154
67	9.0	8.8	862	126

Table 123N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4.1	13	23
26	23	8	7.3	26	41
71	57	22	11	71	110
81	57	26	9.7	81	120
116	23	37	7.6	116	140

MR 0.62

Table 124N Data for the Alkyl Naphthalene Sulfonic Acid Addition Solution.
Mole Ratio of = 0.62.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.8	96	94
290	2.1	8.4	199	175
135	4.4	8.8	428	169
102	5.9	8.9	566	161
79	7.6	8.9	731	199

Table 124N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	12	4	3.8	13	51
27	23	8	7.2	27	85
58	46	18	13	58	180
76	58	24	14	76	240
99	82	31	16	99	350

Table 125N Data for the Tiron Addition Solution. Mole Ratio of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	92	92
285	2.1	9	194	182
150	4.0	9.2	368	169
87	6.9	9	635	154
67	9.0	8.9	824	156

Table 125N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	0	0
25	23	7	6.7	0	0
48	43	14	9.9	0	0
83	38	24	5.5	0	0
107	16	31	5.5	0	0

MR 0.017

Table 126N Data for the Tiron Addition Solution. Mole Ratio of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt = 0.017.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	92	94
290	2.1	8.9	190	178
145	4.1	9.1	381	163
76	7.9	9.1	726	158
60	10.0	9	920	161

Table 126N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	0	0
25	23	7	6.7	0	0
50	43	14	10	0	0
95	54	28	5.7	0	0
120	24	35	7.6	0	0

MR 0.09

Table 127N Data for the Tiron Addition Solution. Mole Ratio of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt = 0.09.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	92	94
290	2.1	8.7	190	178
145	4.1	9	381	321
73	8.2	9.2	756	342
66	9.1	9.1	837	161

Table 127N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	0	0
25	23	7	6.6	0	0
50	46	14	13	0	0
99	74	29	16	0	0
109	74	32	12	0	0

MR 0.17

Table 128N Data for the Tiron Addition Solution. Mole Ratio of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt = 0.17.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.1	92	94
300	2.0	8.6	184	169
140	4.3	9	394	364
103	5.8	9	536	492
63	9.5	9	876	770

Table 128N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	0	0
24	21	7	6.2	0	0
51	48	15	15	0	0
70	63	20	19	0	0
114	95	33	31	0	0

Table 129N Data for the Tiron Addition Solution. Mole Ratio = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.95	92	92
284	2.1	8.6	194	190
125	4.8	8.9	442	151
95	6.3	8.8	581	176
70	8.6	8.6	789	142

Table 129N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	15	15
27	27	8	9	32	29
62	27	19	9	72	62
82	21	25	9	95	83
111	20	34	6	129	109

MR 0.13

Table 130N Data for the Tiron Addition Solution. Mole Ratio = 0.13.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	92	90
324	1.9	8.4	170	171
150	4.0	8.9	368	329
94	6.4	8.9	587	506
65	9.2	9	849	284

Table 130N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	13	4	4	15	30
24	26	7	8	28	57
52	47	16	16	60	123
83	69	26	24	96	186
120	64	37	17	138	256

MR 0.17

Table 131N Data for the Tiron Addition Solution. Mole Ratio = 0.17.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	92	90
320	1.9	8.4	173	166
124	4.8	8.9	445	402
102	5.9	8.9	541	453
82	7.3	8.9	673	571

Table 131N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	14	4	4	15	35
24	25	8	8	28	64
63	54	19	20	73	167
76	61	24	22	88	190
95	71	29	27	110	234

MR 0.43

Table 132N Data for the Tiron Addition Solution. Mole Ratio = 0.43.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.2	92	93
308	1.9	8.3	179	176
150	4.0	8.6	368	341
91	6.6	8.8	607	532
55	10.9	9.05	1004	844

Table 132N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
13	14	4	4	15	62
25	27	8	8	29	117
52	43	16	17	60	243
86	63	26	26	99	376
142	113	44	46	164	675

Table 133N Data for the Kelig 32 Addition Solution. Mole Ratio = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	92	92
287	2.1	8.8	192	180
145	4.1	9.1	381	171
135	4.4	9.1	409	163
58	10.3	8.9	952	161

Table 133N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.5	0	0
25	24	7	6.7	0	0
50	46	14	9.9	0	0
53	44	16	9.1	0	0
124	15	36	4.7	0	0

MR 0.03

Table 134N Data for the Kelig 32 Addition Solution. Mole Ratio = 0.03.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	92	92
295	2.0	8.5	187	171
135	4.4	8.8	409	407
77	7.8	8.9	717	449
57	10.5	9	969	169

Table 134N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
16	16	5	4.7	0	0
33	31	10	8.7	0	0
71	73	21	21	0	0
125	140	37	34	0	0
168	160	49	34	0	0

Table 135N Data for the Kelig 32 Addition Solution. Mole Ratio = 0.06.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.1	92	94
270	2.2	8.3	204	193
145	4.1	8.4	381	364
98	6.1	8.5	563	535
59	10.2	8.7	936	578

Table 135N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
21	21	6	6	0	0
47	42	13	12	0	0
87	82	25	24	0	0
129	120	37	35	0	0
214	200	61	57	0	0

MR 0.11

Table 136N Data for the Kelig 32 Addition Solution. Mole Ratio = 0.11.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	92	96
245	2.4	8	225	195
145	4.1	8	381	342
95	6.3	8.2	581	514
54	11.1	8.2	1022	899

Table 136N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
29	29	9	8.5	0	0
71	58	21	17	0	0
120	110	35	33	0	0
183	160	54	48	0	0
322	310	94	93	0	0

Table 137N Data for the Marasperse N-22 Addition Solution. Mole Ratio = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.6	92	92
310	1.9	8.7	178	167
238	2.5	8.9	232	214
90	6.7	9	613	165
67	9.0	8.9	824	163

Table 137N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.9	12	12
23	21	8	6.9	23	23
30	27	10	8.9	30	29
80	51	26	8.3	80	80
107	16	35	8.3	107	98

MR 0.017

Table 138N Data for the Marasperse N-22 Addition Solution. Mole Ratio = 0.017.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8	92	90
305	2.0	8.4	181	163
244	2.5	8.5	226	205
92	6.5	8.9	600	556
74	8.1	9	746	749

Table 138N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	16	4	4.7	12	77
24	28	8	8.4	24	140
30	35	10	11	30	180
78	99	25	30	78	510
97	140	32	40	97	680

MR 0.034

Table 139N Data for the Marasperse N-22 Addition Solution. Mole Ratio = 0.034.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.9	92	92
302	2.0	8.1	183	167
257	2.3	8.3	215	195
99	6.1	8.7	558	471
94	6.4	8.6	587	514

Table 139N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	20	4	5.6	12	140
24	37	8	10	24	260
28	43	9	12	28	310
73	110	24	30	73	790
77	120	25	33	77	870

MR 0.068

Table 140N Data for the Marasperse N-22 Addition Solution. Mole Ratio = 0.068.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	7.7	92	88
309	1.9	7.9	179	158
256	2.3	8	216	186
100	6.0	8.2	552	278
88	6.8	8.3	627	471

Table 140N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	28	4	7	12	260
23	50	8	13	23	470
28	59	9	15	28	560
72	95	23	24	72	920
82	160	27	40	82	1500

Table 141N Data for the Maracell XE Addition Solution. Mole Ratio = 0.0.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	83	83
295	2.0	8.8	170	156
142	4.2	9.1	353	158
80	7.5	8.8	626	143
61	9.8	8.8	821	148

Table 141N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.7	12	12
24	22	8	6.7	24	22
51	39	16	9.7	51	44
90	24	28	6.3	90	74
118	16	36	5.9	118	97

MR 0.11

Table 142N Data for the Maracell XE Addition Solution. Mole Ratio = 0.11.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.3	83	83
280	2.1	8.6	179	158
140	4.3	8.8	358	321
92	6.5	8.9	544	492
71	8.5	9	705	663

Table 142N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.7	12	200
26	23	8	7	26	370
51	43	16	14	51	770
78	58	24	22	78	1200
101	71	31	29	101	1600

Table 143N Data for the Maracell XE Addition Solution. Mole Ratio = 0.21.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.5	83	83
280	2.1	8.6	179	165
140	4.3	8.8	358	300
102	5.9	8.9	491	407
62	9.7	9	808	599

Table 143N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	12	4	3.7	12	320
26	24	8	7.3	26	640
51	35	16	14	51	1200
71	42	22	18	71	1600
116	52	36	27	116	2500

MR 0.43

Table 144N Data for the Maracell XE Addition Solution. Mole Ratio = 0.43.

Final			**Total SiO_2 (mg/L)**	
Vol. (ml)	C.F.	*p*H	Expected	Measured
600	1.0	8.8	83	83
295	2.0	8.9	170	141
145	4.1	9.1	345	321
96	6.3	9.1	522	428
77	7.8	9.2	650	514

Table 144N continued

Calcium (mg/L)		**Magnesium (mg/L)**		**Sodium (mg/L)**	
Expected	Measured	Expected	Measured	Expected	Measured
12	13	4	4	12	620
24	22	8	6.6	24	1000
50	44	15	15	50	2400
75	45	23	21	75	3300
94	50	29	25	94	4100

APPENDIX O

Silica Bibliography by Topic Area

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