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STUDY OF SILICA SCALING FROM GEOTHERMAL BRINES

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SUMMARY

Further studies have been made of factors influencing the rate of rejection from true solution of excess silica contained in geothermal brine. Prominent influences on the course of this precursor step in silica scaling include degree of supersaturation with respect to silicic acid monomer, concentration of dissolved salt, brine pH and temperature. Most of the measurements were made at 95°C, an especially pertinent temperature because it approximates that of a hot brine after flashing.

Concurrent analyses for silicic acid monomer and total dispersed silica in a 2% brine at 95°C and pH 5 revealed a growth and decay of non-monomeric silica concentration, superimposed on the disappearance of monomer. Consistent with this behavior, the non-monomeric species eventually precipitated out of solution (as floc or as scale), while the monomer concentration approached a saturation value characteristic of the brine composition and temperature. The observed sequence suggests that monomer combines with polymeric species, and the latter grow and aggregate into flocculent silica or scale. A practical implication of these results is the possible retardation of scaling through inhibition of silica polymerization.

Simulated geothermal brines, i.e., solutions supersaturated with respect to silica at 95°C and containing Na^+, K^+ and Ca^{++} in a ratio corresponding to a commonly encountered source temperature (in the vicinity of 300°C) were prepared reproducibly. With all silicic acid in

true solution initially, simulated brines typically exhibited a period of slow reaction prior to the onset of relatively rapid monomer disappearance. The rate of decay of silica monomer concentration (i.e., rate of relief of supersaturation) increased significantly with increasing level of initial supersaturation, total salinity of the brine, and pH (relative to pH 4). Isothermal dilution of the supersaturated brine resulted, as anticipated, in a pronounced decrease in the rate of polymerization. A more complete description of the system requires a closer definition of interactions among several species of dispersed silica, the role of temperature, and specific effects of ionic solutes. Experiments to obtain this information are planned for the near term.

The introduction of additional surface for heterogeneous nucleation, in the form of glass wool or quartz powder, had no significant effect on the course of monomer disappearance. Two limiting types of adherent scale have been produced simultaneously with separation of a silica floc - a soft scale and a coherent, or hard scale. In preliminary observations, increased brine salinity and pH favor hard scale formation at 95°C.

Studies at higher temperatures, corresponding to hot brines before flashing, and requiring the use of pressure equipment, have to date provided less definitive information than tests at 95°C. The problems encountered relate to lessened controllability of silica concentration and of scaling. It is hoped to circumvent these experimental difficulties through elimination of the vapor phase, with continuous volume compensation for solution withdrawn during brine sampling. Use of autoclave techniques has the potential advantage of achieving even closer correspondence of synthetic brine to natural geothermal brines. Thus, pH can be fixed through control of the CO_2 pressure, making possible the elimination of the acetate buffer generally employed in the work at 95°C.

The program plans for the coming period include detailed characterization of scales and precipitates produced isothermally and those formed under a thermal gradient between substrate and brines. Additionally, the dependence of silica scale formation on prevailing hydrodynamic conditions and on the nature of the substrate will be studied. Also, because it is potentially fruitful from the standpoint of scale prevention, a study will be made of factors that determine whether excess silica aggregates to a floc or an adherent deposit.

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I. INTRODUCTION

In the first six months of this program, we began a detailed study of the kinetics of polymerization of silicic acid in geothermal brines for the following reasons:

(a) Monomeric silicic acid is the only thermodynamically stable silica solute species in neutral and acid brines.

(b) Silica scale formation is a mechanism by which a brine can be relieved of supersaturation with respect to dissolved monomeric silica.

(c) At two conceptual extremes, polymerization of monomer may be an essential precursor to scaling, or it may proceed in parallel with scaling; in either case, the processes are interconnected, and knowledge of the detailed relationship would indicate whether polymerization ought to be inhibited or accelerated in order to retard scaling.

(d) Purely empirical studies of silica scaling, while useful in defining practical conditions under which scale is prone to form with specific geothermal fluids, do not provide insight into the chemical mechanisms involved. An understanding of reaction mechanisms is essential to the design of new methods to alleviate scaling.

The polymerization work initiated in the previous report period was extended to include a range of conditions and brine compositions expected in plants for extracting power or heat from geothermal fluids. In addition, we examined the time-dependent distribution of SiO_2 among several species of dispersed and particulate silica: monomer, oligomer (i.e., a molecule containing a small number of monomer units), polymer, colloidal aggregates, precipitate and scale. A complementary study of scale formation and characterization was also initiated. Some further search of the pertinent technical literature on silica scaling was also made.

II. EXPERIMENTAL METHODS

1. Preparation of Simulated Geothermal Brine

As noted in the previous report, the inadvertent (initial) presence of oligomeric or polymeric silica accelerates the rate of disappearance of excess monomer. Since natural geothermal brines contain little or no oligomer or polymer when they are in equilibrium with rock (Weill and Bottinga, 1970), it is necessary in accurately simulating these brines to make sure that they do not initially contain appreciable quantities of oligomeric or polymeric silica. The reaction of silicic acid with molybdate allows the detection of small quantities of oligomeric or larger amounts of polymeric silicic acid (the latter by difference, if total silica is known). Hence, we were able to evaluate various methods of brine preparation on the basis of the amount of non-monomeric silica detected.

Five techniques for preparing simulated brines were outlined in the last report. All but the ultrafiltration were evaluated during the present reporting period.

(1) Rapid cooling of a superheated, undersaturated brine.

(2) Isothermal evaporation of water from an undersaturated solution.

(3) Rapid mixing of an alkaline solution of sodium metasilicate into an acidic chloride brine.

(4) Ultrafiltration of a solution prepared as in method (3).

(5) Acid hydrolysis of the tetramethyl ester of silicic acid.

On the basis of Baumann's (1959) experiments, we assumed that method (5) would prove superior, although it was recognized that the method would introduce unwanted methanol into the brine. In fact, however, experiments indicated that rapid acid hydrolysis of the ester produced unexpectedly large amounts of oligomer. This undesired effect can probably best be overcome by diluting the ester with excess methanol. For these reasons, it was decided to abandon method (5).

Rapid mixing of a solution of sodium metasilicate into an acidic chloride solution (method 3) was found to be the most satisfactory of the brine preparation methods evaluated. The following procedure, or a close variant, was used in all experiments carried out at 95°C with 2% brine:

(1) Three separate solutions were equilibrated at 95°C

  (a) 3.0 volumes of 0.0287M $Na_2H_2SiO_4 \cdot 8H_2O$ (to give about 1000 ppm SiO_2)

  (b) 1.0 volume of 0.250M HCl and 0.225M KCl

  (c) 1.0 volume of 0.400M NaCl, 0.350M $CaCl_2$, and 0.534M $NaC_2H_3O_2$ (sodium acetate).

  Solution (b) is brought to temperature in the Pyrex reaction vessel (a 500-ml, three-necked flask), the others in stoppered bottles.

(2) With rapid stirring of the contents of the flask, solution (a) was added to the reaction vessel over a period of about 30 sec by spraying through a nozzle.

(3) Solution (c) was then added to the reaction vessel.

Immediately following step (3), an aliquot of the solution was mixed with the molybdate reagent for silica monomer and oligomer analysis.

The concentrations of the various species in a simulated brine prepared as described are:

	M	g/l		M	g/l
Ca^{++}:	0.070	2.81	Cl^-	0.315	11.17
Na^+:	0.221	5.08	CH_3COO^-	0.091	5.37
K^+:	0.045	1.76	CH_3COOH:	0.016	0.96
H_4SiO_4:	0.017	(1034 ppm SiO_2)	pH:	5.15 ± 0.05 at 95°C	

The $Na^+/Ca^{++}/K^+$ ratio is 3.00/0.95/0.61, on a molar basis, which is close to the ratio 3/1/0.6 appropriate to a natural brine having a source temperature on the neighborhood of 300°C (Fournier and Truesdell, 1973; Helgeson, 1968). The total concentration of NaCl, $CaCl_2$ and KCl is 20.8 g/l, i.e., approximately 2% by weight.

2. Determination of Monomeric Silica

The concentration of monomeric silica in the brine at any given time was determined by a procedure similar to that reported previously. Approximately 2 ml of the brine solution is removed from the reaction vessel and cooled on a watch glass. Using a SMI micropipette, a nominal volume of 30 µl is then pipetted from the watch glass into 3.00 ml of molybdate solution that has been equilibrated at 25°C in the thermostatted spectrophotometer cell holder. The increase of optical density with time is followed at 360 nm. The molybdate reagent is prepared according to Alexander's (1953) method. A recent study (Truesdale and Smith, 1975) of the molybdate-silica reaction confirms the reliability of results with this procedure.

The logarithm of the degree of color development was typically linear with time (i.e., first-order kinetics) to at least 99% extent of reaction, indicating the absence of measurable quantities of oligomer. The calculated first-order rate constant is 1.3 min^{-1} at 25°C, in agreement with the value (1.41 ± 0.07 min^{-1}) previously reported by us for monomeric silicic acid. Silicic acid prepared by cooling a superheated, undersaturated brine had the same rate constant with molybdate.

Repeatability of delivered volume for the 30 μl micropipette was ± 1.3%. The precision of the spectrophotometric measurement of monomeric silicic acid was approximately 0.5% as determined by replicate analysis of identically prepared samples; the concentration of the sodium silicate stock solution was determined by titration with HCl. Including slight effects of evaporative losses, we estimate the accuracy of our measurements of monomeric silicic acid as ± 2%.

3. Determination of Total Dispersed Silica

Silica exists in many forms in aqueous solution. In addition to monomeric silicic acid, a solution may contain various oligomeric silicic acids, higher polymers, a colloidal dispersion of silica, flocculent material, silica gel, and scale. In most of our experiments we have attempted to distinguish among only four forms of silica: monomer, oligomer, "total dispersed silica," and precipitated material. By "oligomer" is meant silicic acid that reacts with molybdate more slowly than the monomer, yet shows some evidence of reaction within ten minutes. None was observed in the experiments reported here. By "total dispersed silica" is implied all forms of silica that are contained in a sample of solution which is removed and subjected to depolymerization preparatory to analysis.

To determine total dispersed silica, 1.00 ml of the solution is reacted with an equal volume of solution containing 0.5M NaOH and 0.1M EDTA. The resulting mixture is allowed to stand overnight in a stoppered plastic container. The purpose of the NaOH is to depolymerize or dissolve any oligomer, polymer, and colloidal or floc particles; the EDTA is used to complex the calcium ion and so prevent precipitation of calcium compounds. Duplicate determinations indicated that depolymerization was complete within 12 hours (i.e., overnight).

Once the silica had been converted to monomer by treatment with base, its concentration was determined in the usual manner by reaction with molybdate. However, EDTA itself reacted with molybdate to form a complex. The rate constant for the formation of this interfering complex was about the same magnitude as the rate constant for the formation of the silicomolybdate complex. Its extinction coefficient*, however, is about 15 times greater at 360 nm than at 400 nm. The corresponding ratio of extinction coefficients for the silicomolybdate complex is 2.55.

As shown in the example of Table I, it proved possible to subtract the time-varying absorption due to the formation of the EDTA complex from the time-varying absorption due to the formation of the silicomolybdate complex and, in this way, determine the concentration of total dispersed silica. Silica concentrations measured at 360 and 400 nm generally agreed within 5%. The relatively large error at both wavelengths (compared to

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*ε in the expression $D = \varepsilon C\ell$, where D is optical density, C is molar concentration and ℓ is length of light path.

Table I

A Typical Determination of Total Dispersed Silica

Time of Color Development (min)	Optical Density at 360 (400) nm	Correction due to Molybdate-EDTA Complex	Corrected Optical Density at 360 (400) nm
1	0.488	0.128	0.360
2	0.629	0.153	0.476
3	0.672	0.164	0.508
4	0.687	0.170	0.517
5	0.693	0.174	0.519
6	0.696	0.1765	0.5195
7	0.6975	0.178	0.5195
8	0.699 (0.207)	0.179 (0.010)	0.520 (0.197)*
9	0.699	0.180	0.519
10	0.700	0.181	0.519
15	0.702 (0.206)	0.184 (0.010)	0.518 (0.196)

*Estimated silica concentrations are 1061 ppm and 1024 ppm, based on the corrected optical densities at 360 and 400 nm, respectively. Based on the concentration of monomeric silicic acid initially present (i.e., prior to polymerization), the solution actually contained 1034 ppm SiO_2.

an estimated precision of 0.5% for monomeric silcic acid) is attributed to the relatively low optical densities at 400 nm and the relatively large EDTA correction at 360 nm.

III. SURVEY OF FACTORS AFFECTING RATE OF MONOMER DISAPPEARANCE AT 95°C

1. Effect of Brine Dilution

In order to simulate the effect of diluting a geothermal brine with water -- or, conversely, concentrating a brine by flashing -- the brine described in Section II.1 was diluted during preparation by adding 0.5, 1.0, or 1.5 volumes of distilled water to solution (b) before spraying it into solution (a). Dilution factors were, hence, 1.1, 1.2, and 1.3, respectively. In this way, kinetic runs were carried out at initial concentrations of silicic acid ranging from 1034 ppm (p. 4 and Table I) to 795 ppm. The results, presented in Fig. 1, show a strong dependence of rate of monomer disappearance on degree of dilution of the brine.

Experimental results reported by Baumann (1959) show that the rate of disappearance of monomeric silicic acid at 30°C depends strongly on the initial concentration of monomer. For example, at pH 5.8 the time required to reduce the initial excess monomer concentration by half increased by a factor of four when the initial concentration of monomer was reduced from 1550 ppm to 1050 ppm.

In the experiments reported here, dilution of the reference brine with respect to dissolved silica also decreased the concentration of dissolved salt. This, of course, is precisely what occurs when water is added to a hot geothermal brine in an effort to retard scale formation. The effect of varying brine salinity at fixed monomer concentration is considered in more detail in the next section.

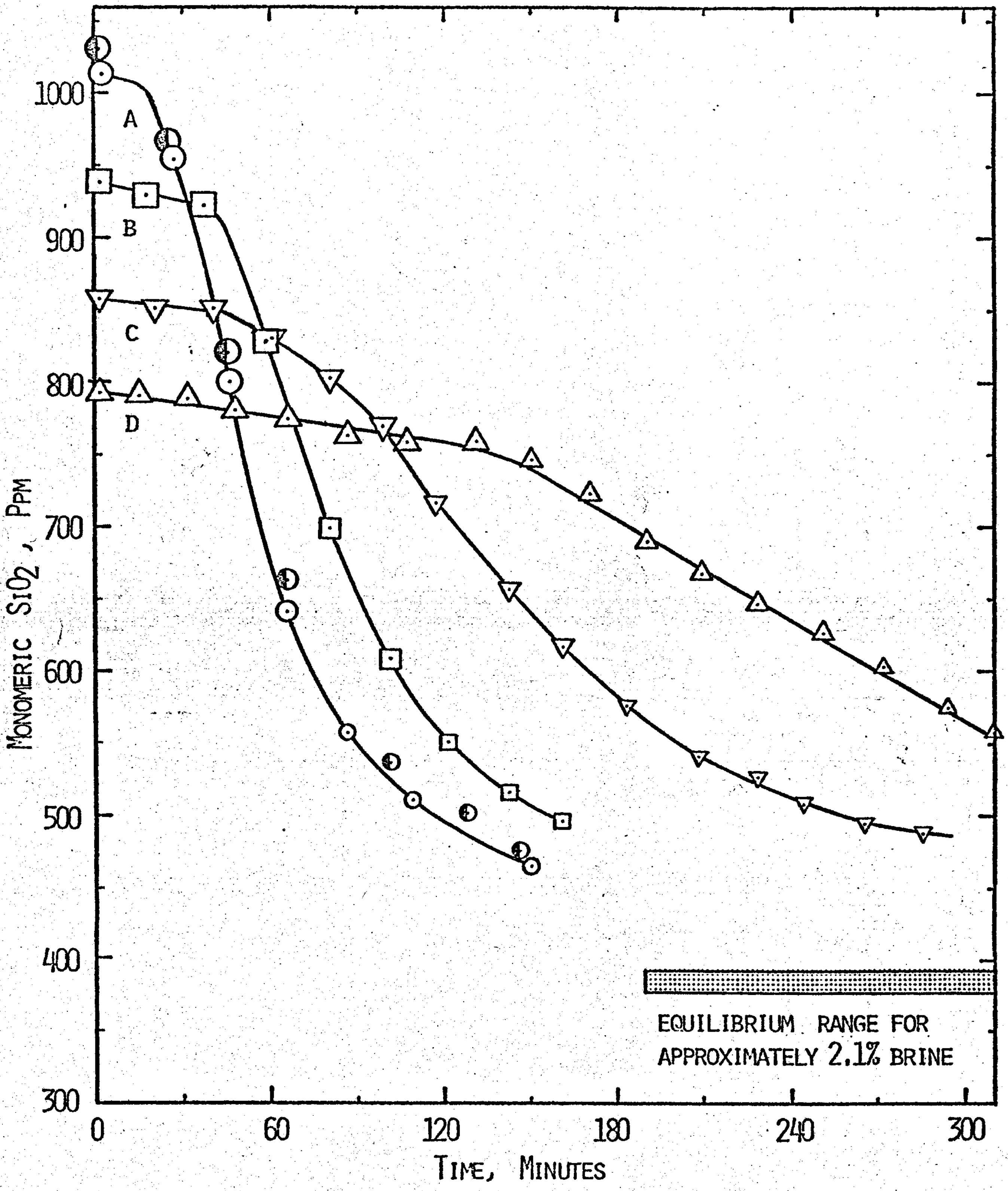

Fig. 1: Polymerization of silica at 95 ± 2° C, and pH 5.15 ± 0.10. Curve A represents a 2.1% brine. The half-shaded circles show a duplicate run. Curves B, C, and D represent the same initial brine, diluted with water by 10, 20, and 30 per cent, respectively.

The time dependence of the reaction rate is complicated. However, two measures of the rate of monomer disappearance may be used to compare different solutions: (a) the time required for relief of half the initial supersaturation, $t_{1/2}$; and (b) the first-order rate constant, k_{obs}, that fits the observed data after the initial period of slow kinetics (see next section). These measurements of the rate are shown as a function of brine dilution (on a log-log scale) in Fig. 2. The empirical relations between reaction rate and brine dilution are as follows:

$$\log(\text{half-life, min}) = 5.97 \log(\text{dilution}) + 1.75 \tag{1}$$

$$\log(\text{rate constant, min}^{-1}) = -5.41 \log(\text{dilution}) - 1.70 \tag{2}$$

Note that dilution of the reference brine by a factor of 1.3 decreased the reaction rate by a factor of four.

2. Preliminary Kinetic Analysis

As can be seen in Fig. 1, the rate of decrease of monomer concentration is initially slow. After this "induction" period, the reaction rate becomes much faster, and then slows down again as equilibrium is approached. True equilibrium, however, is not reached even after 24 hours.

The rate equation

$$-\frac{d(M)}{dt} = k_{obs}[(M) - (M)_{eq}]^n$$

$$(M) = \text{monomer concentration} \tag{3}$$

$$(M) - (M)_{eq} = \text{supersaturation}$$

has been widely used in the literature (see previous six-month report) to describe the rate of monomer disappearance. There is considerable

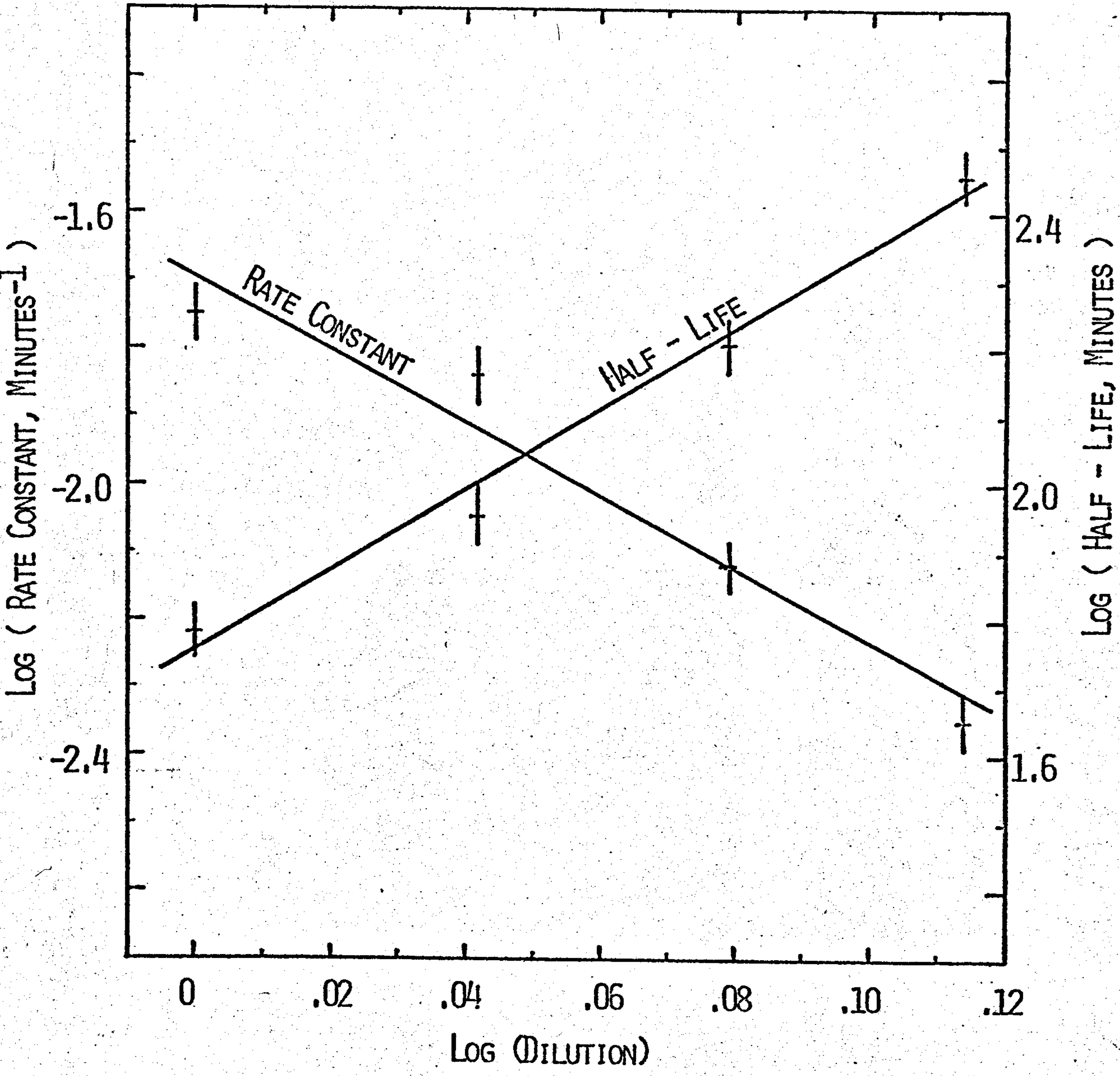

Fig. 2: Log-log dependence of polymerization rate on dilution. The composition of the undiluted reference brine is described in Section II.

disagreement over the value of n, and n equal to 1, 2 and 3 have been suggested. The data reported here are clearly inconsistent with n equal to 2 or 3. Indeed, the rate of decrease of monomer with time is nearly constant for a considerable portion of the reaction (see Fig. 1), which suggests zero-order kinetics. A somewhat better fit to the data can be obtained by assuming n equals 1 after the initial period of slow reaction.

The simplest mechanism consistent with n equals 1 is first-order reaction of monomer with polymeric product to produce a larger, but equally reactive, product. The back reaction of polymer to give monomer is assumed to be zero order:

$$M + P \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P \tag{4}$$

Then

$$-\frac{d(M)}{dt} = k_1(M)(P) - k_2(P) \tag{5}$$

At equilibrium, $d(M)/dt = 0$, so that

$$k_1(M)_{eq}(P) = k_2(P) \tag{6}$$

and

$$(M)_{eq} = k_2/k_1 \tag{7}$$

By this mechanism, the monomer concentration decays to a characteristic final value that is independent of its initial value. The rate equation may now be simplifed to give

$$-\frac{d(M)}{dt} = k_1(P)[(M) - (M)_{eq}] \tag{8}$$

which is of the same form as Eq. (3), with n = 1 and

$$k_1(P) = k_{obs} \tag{9}$$

The integrated form of Eq. (3) with n = 1 is

$$\ln\left[\frac{(M)_o - (M)_{eq}}{(M) - (M)_{eq}}\right] = k_{obs}(t - t_o) \qquad (10)$$

where $(M)_o$ is the initial concentration of monomer. Representative plots of Eq. (10) are shown in Fig. 3. Because of the initial period of slow reaction, the quantities t_o have positive values. The least-squares lines fit the data points within the one percent experimental error for values of the fraction of monomer unreacted, $[(M) - (M)_{eq}]/[(M)_o - (M)_{eq}]$, between 0.85 and 0.25. Above about 0.85 (during the "induction" period), the rate of disappearance of monomer is relatively slow; below 0.25, the rate again becomes relatively slow, perhaps due to agglomeration of polymer.

In a true first-order reaction, k_{obs} should be independent of the initial concentration of monomer. This is not true in the present case, however. As shown in the following sections, k_{obs} depends on several factors, including salt concentration, pH, and the initial concentration of monomer itself. Thus, while the reaction rate is approximately first-order with respect to monomer during a given kinetic run, the dependence of k_{obs} on initial monomer concentration indicates that the overall dependence of reaction rate on monomer concentration is greater than first order. In terms of the mechanism above, this may be explained as a dependence of the concentration of polymeric nuclei (P) on the initial concentration of monomer. These nuclei are presumed to form during the initial period of slow reaction.

3. Effects of Supersaturation and Total Salt

In the experiments just described, the total concentration of NaCl, $CaCl_2$, and KCl varied between 20,800 and 16,000 ppm. In order to determine

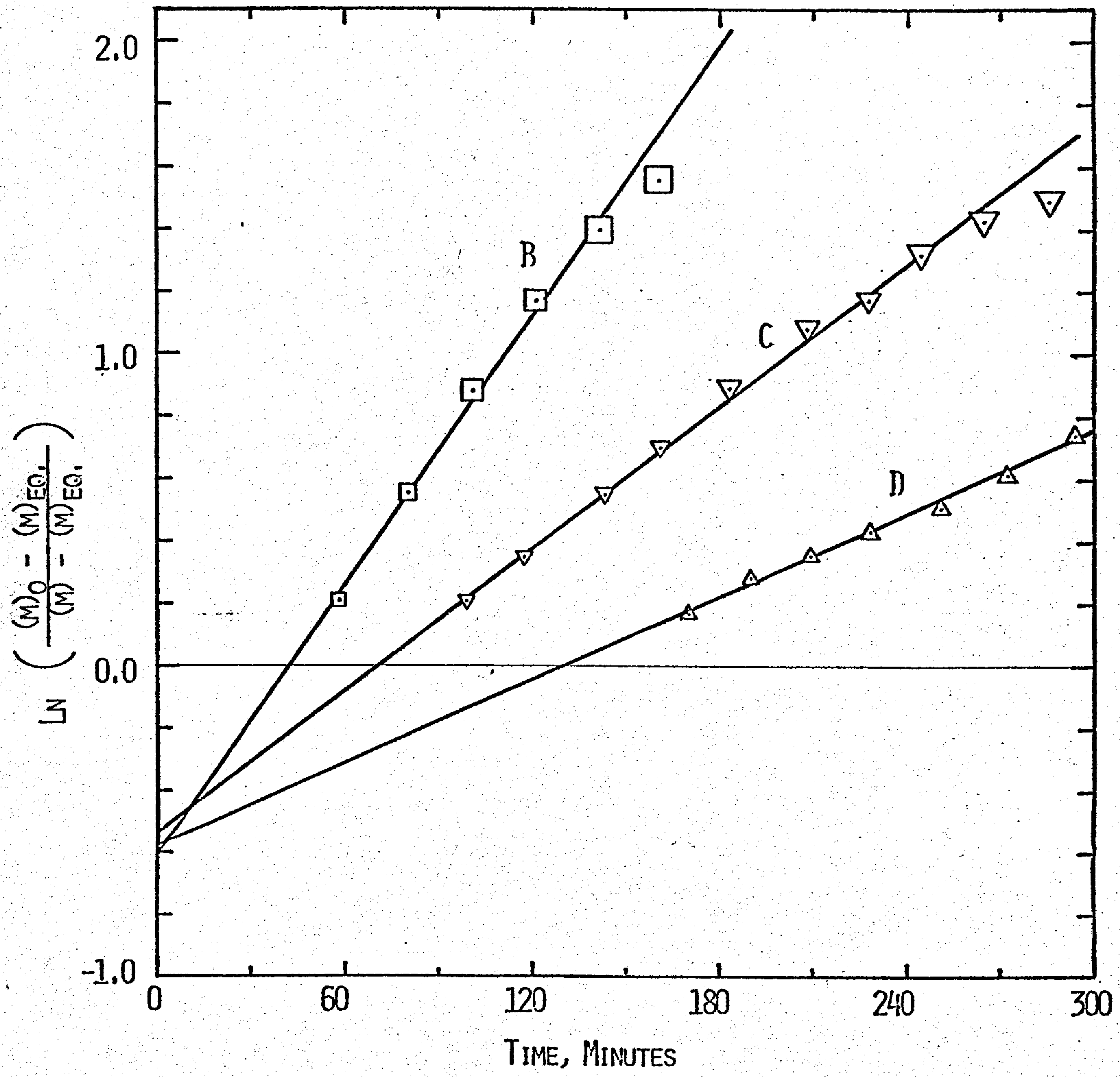

Fig 3: First-order kinetic plots for silica polymerization at 95 ± 2°C, pH 5.2 ± 0.15.

whether the salt content itself has a significant influence of the rate of disappearance of monomer, a more concentrated simulated brine was prepared. For this purpose, solution (c) in Section II.1 was replaced by 2 volumes of a solution containing 2.601M NaCl, 0.338M KCl, 0.656M $CaCl_2$, and 0.267M $NaC_2H_3O_2$. The initial concentrations of the various species in this brine were as follows:

Ca^{++}: 0.219M　　Cl^-: 1.496M

Na^+: 0.985M　　CH_3COO^-: 0.076M

K^+: 0.150M　　CH_3COOH: 0.013M

H_4SiO_4: 0.0143M (862 ppm SiO_2)　　pH: 5.28 ± 0.10 at 95°C

The total concentration of NaCl, $CaCl_2$, and KCl was 90.3 g/l.

As can be seen in Table II and Fig. 4, the effect of increased salt content was dramatic: the rate of disappearance of monomer in Run E was much faster than in Run C, in which the initial concentration of monomer was comparable. This result suggests that one or more of the ions* — Ca^{++}, Na^+, K^+, or Cl^- — has a strong accelerating effect on the reaction rate. On the other hand, the final concentration of monomer (276 ppm) was depressed below the equilibrium value (ca. 400 ppm) appropriate to dilute brines. Thus, the apparent supersaturation in Run E (594 ppm) was intermediate between those of Runs A and B (Table II). If the rate constant, k_{obs}, for disappearance of monomer depends on supersaturation, $(M) - (M)_{eq}$,

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*Recent preliminary experiments, not complete at the time of this report, suggest that the accelerating effect is due to Cl^-.

Table II

Rates of Monomer Disappearance at pH 5.2 and 95°C

Run*	Initial Monomer Concentration (ppm)	Apparent Supersaturation (ppm)	Total Salt Concentration (g/l)	Half Life of Excess Monomer (min)	First Order Rate Constant (k_{obs}, min^{-1})
A	1034	656	20.8	60	0.0178
B	940	561	18.9	90	0.0144
C	862	482	17.3	160	0.0076
D	795	414	16.0	286	0.0045
E	870	594	90.3	19	0.034
F	946	605	42.6	45	0.0307
G	860	482	20.8	128	0.0109

*Runs A-D are shown in Fig. 1

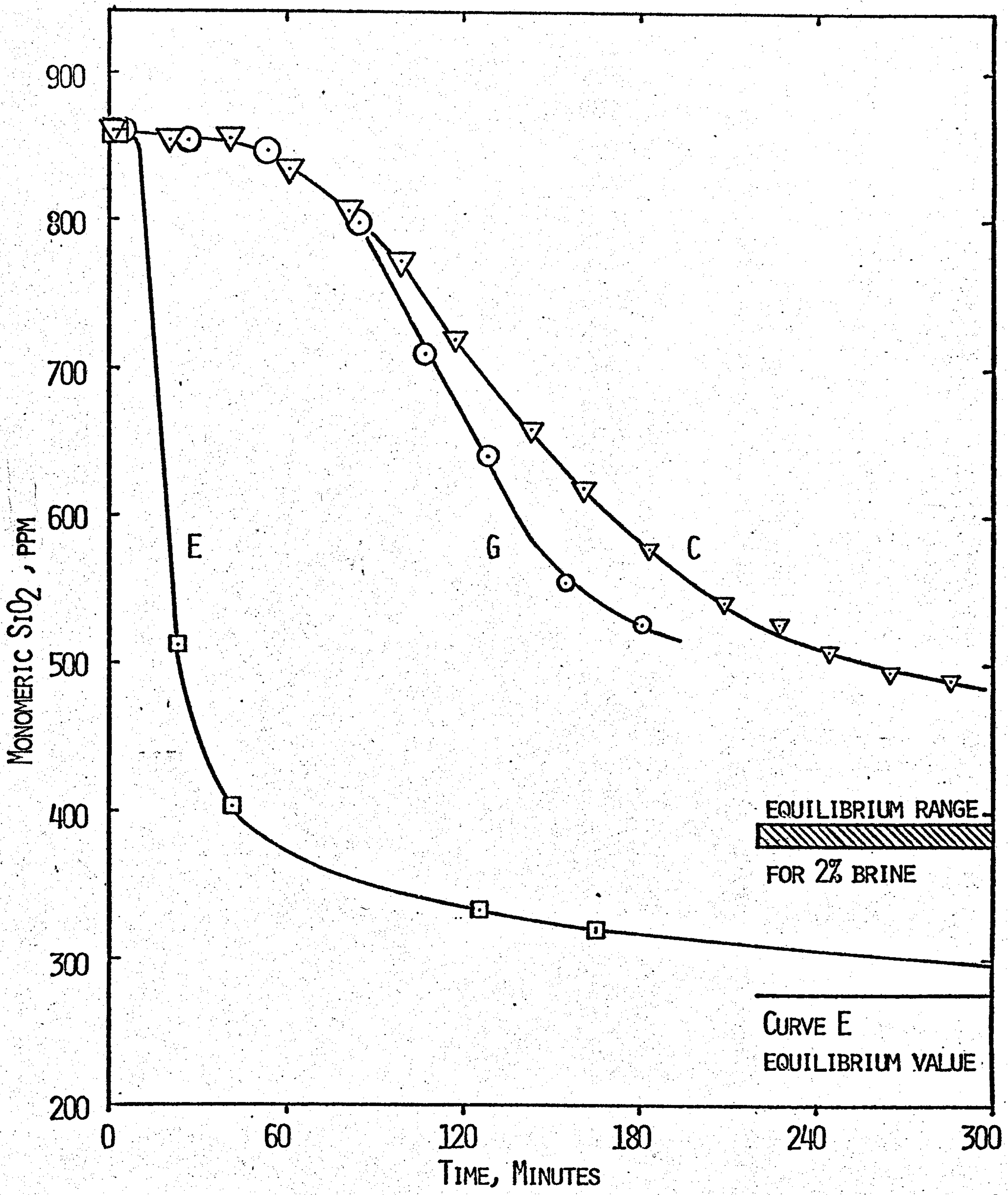

Fig. 4: The effect of salt concentration on silica polymerization at 95 ± 2° C and pH 5.15 ± 0.10. Curve C represents a brine containing a total of 17.3 g/l of NaCl, KCl, and $CaCl_2$. Curves G and E show brines with 20.8 and 90.3 g/l of total salt, respectively.

then the accelerating effect of salt may, in part, be due to its effect on final monomer concentration.

In order to estimate separately the reaction order with respect to salt content and supersaturation, additional experiments (Runs F and G, Table II) were performed. The proportions of the three chloride constituents of the brine were kept the same. A rough estimate of the reaction order with respect to salt concentration can be obtained by comparing Runs C and G, in which the supersaturations are the same. If k_{obs} is expressed as a function of total salt concentration, (S),

$$k_{obs} = k'(S)^p \qquad (11)$$

where p is the order of the reaction with respect to salt, then

$$\log k_{obs} = \log k' + p \log(S) \qquad (12)$$

A comparison of the rate constants for Runs C and G gives p = 2.0. Similarly, a comparison of the rate constants for Runs F and B or F and A (here the supersaturations are not quite the same) gives p = 0.9 and p = 0.8, respectively.

It is clear that pairwise comparisons of this sort cannot be used to obtain accurate estimates of the reaction order. A better approach is to fit all the measurements of k_{obs} to a suitable kinetic equation. Two equally simple expressions are

$$k_{obs} = k(S)^p \, [(M)_o - (M)_{eq}]^q \qquad (13)$$

$$k_{obs} = k(S)^p \, [(M)_o^q - (M)_{eq}^q] \qquad (14)$$

Only the second equation has been used to fit the data, since it is more nearly consistent with the assumption that the dependence of k_{obs} on initial monomer concentration is related to the formation of polymeric nuclei from monomer during the "induction" period, when the back reaction of polymer to monomer should be negligible.

Integral values of p (0-2) and q (1-6) have been used to fit the observed rate constants by trial and error. A fit within the expected maximum error (± 20%) was not possible with $p = 0$ or $p = 2$. However, by assuming that the reaction is first order with respect to salt concentration ($p = 1$), it was found that all seven measured values of the rate constant could be fitted to the same expression, within error, with $q = 4$. The standard deviation is 15%, and all calculated values of k_{obs} agree with those given in Table II within 21%. If smaller or larger values of q are assumed ($q = 3$ or $q = 5$), the standard deviation is still below 20%, but more than one value of k_{obs} exceeds the expected maximum deviation. Runs A and E show the largest deviations, perhaps because the reaction rates in these runs are too large for accurate determinations of k_{obs}. If these runs are excluded, the reaction orders $p = 1$ and $q = 5$ or 6 fit the remaining five values of k_{obs} with a standard deviation of only 10%.

These results indicate that the effect of brine flashing on the rate of reaction should be substantial. Flashing has several consequences: the salt concentration and monomer concentration increase, due to loss of water, and the equilibrium concentration of monomer decreases due to the changes in temperature and salinity. The decrease in temperature may also affect the rate constant directly, although our data (Section IV-1) and those of Rothbaum and Wilson (1975) indicate that this effect is relatively small. In addition, flashing of CO_2 would increase the brine pH. Each of these consequences of brine flashing has the same result, namely, an increase in the rate of disappearance of excess monomer.

The strong accelerating effect of added salt is unexpected, since the literature (e.g., Baumann, 1959) indicates that no ion has as great a catalytic effect on the rate of disappearance of monomer as hydroxide, for which a tenfold increase in concentration produces about a tenfold increase in rate.

To summarize our results with 95°C, pH 5 brines having a fixed proportion of chlorides, the rate of disappearance of excess monomeric silica is approximately proportional to total salinity. The rate is also proportional to a high power (3 to 6) of the initial monomer concentration. At the present time, it is not possible to be more precise with regard to reaction orders but, clearly, further definition of the rate of monomer disappearance on initial monomer concentration and salinity is a worthwhile experimental goal.

4. Silica Solubility Versus Brine Concentration

A potentially useful by-product of our work with various salt concentrations is a set of preliminary values of final monomer concentration at 95°C. Insofar as equilibrium had been reached at the times of last sampling (approximately 24 hrs at 95°C), the measurements represent the dependence of amorphous silica solubility on brine composition. As a mimimum, since monomer disappearance had essentially ceased in each case, the measured final concentrations permit an estimate of apparent monomer supersaturation, the driving force for silica scaling and precipitation.

Depression of apparent silica solubility by added salt was appreciable. Results to date are given in Table III and Fig. 5, which also include data from the literature for the solubility of amorphous silica in water at 95°C. The observed salting out of silica monomer is much larger than the probable contribution of the decrease in activity of water with increase in salt concentration. Although Iler (1973) indicates that the state of hydration of monosilicic acid in water is unknown, it is customary to represent the dissolution of amorphous silica in water by

$$SiO_2 \text{ (amorphous)} + 2H_2O\ (\ell) \rightleftarrows H_4SiO_4 \text{ (aq.)} \tag{15}$$

hence

$$K_{eq} = a_{H_4SiO_4}/a^2_{H_2O} \tag{16}$$

where <u>a</u> represents thermodynamic activity.

Based on the above hydration-dehydration equilibrium, Barnes and Rimstidt (1975) have emphasized the value of diluting the hot geothermal brine with water in order to increase the activity of water and, according to Eq. (16), the solubility of silicic acid monomer. A possible effect of salt concentration on the activity coefficient, $\gamma_{H_4SiO_4}$, of the monosilicic acid has generally been overlooked. Thus, the solubility of amorphous silica according to Eqs. (15) and (16) should be given by

$$[H_4SiO_4] = K_{eq} \cdot \frac{a^2_{H_2O}}{\gamma_{H_4SiO_4}} \tag{17}$$

Data on water activity with which to estimate the contribution of the $a^2_{H_2O}$ factor to the observed salting out were not found in the

Table III

Final Monomer Concentrations at 95°C for $NaCl-CaCl_2-KCl$ Brines*

Reference	ppm SiO_2	Total Salt** Content, g/l	Concentration, as equiv./l Cl^-	Remarks
This work, Run A	388, 393	20.8	0.315	--
This work, Run H	389	22.8	0.372	Maleate buffer
This work, Run F	341	42.6	0.689	--
This work, Run E	276	90.3	1.50	--
Lenher and Merrill (1917)	450			Extrapolated from 90°C
Alexander *et al.* (1954)	355			Extrapolated from 80°C
Okamoto *et al.* (1957)	475			Extrapolated from 90°C
Elmer and Nordberg (1958)	470			--
Kitahara (1960)	375			--

*pH 5.0 - 5.3; silica solubility not expected to be sensitive to pH over a wide range below pH 9.

**Does not include electrolyte anion (usually acetate) added for buffering.

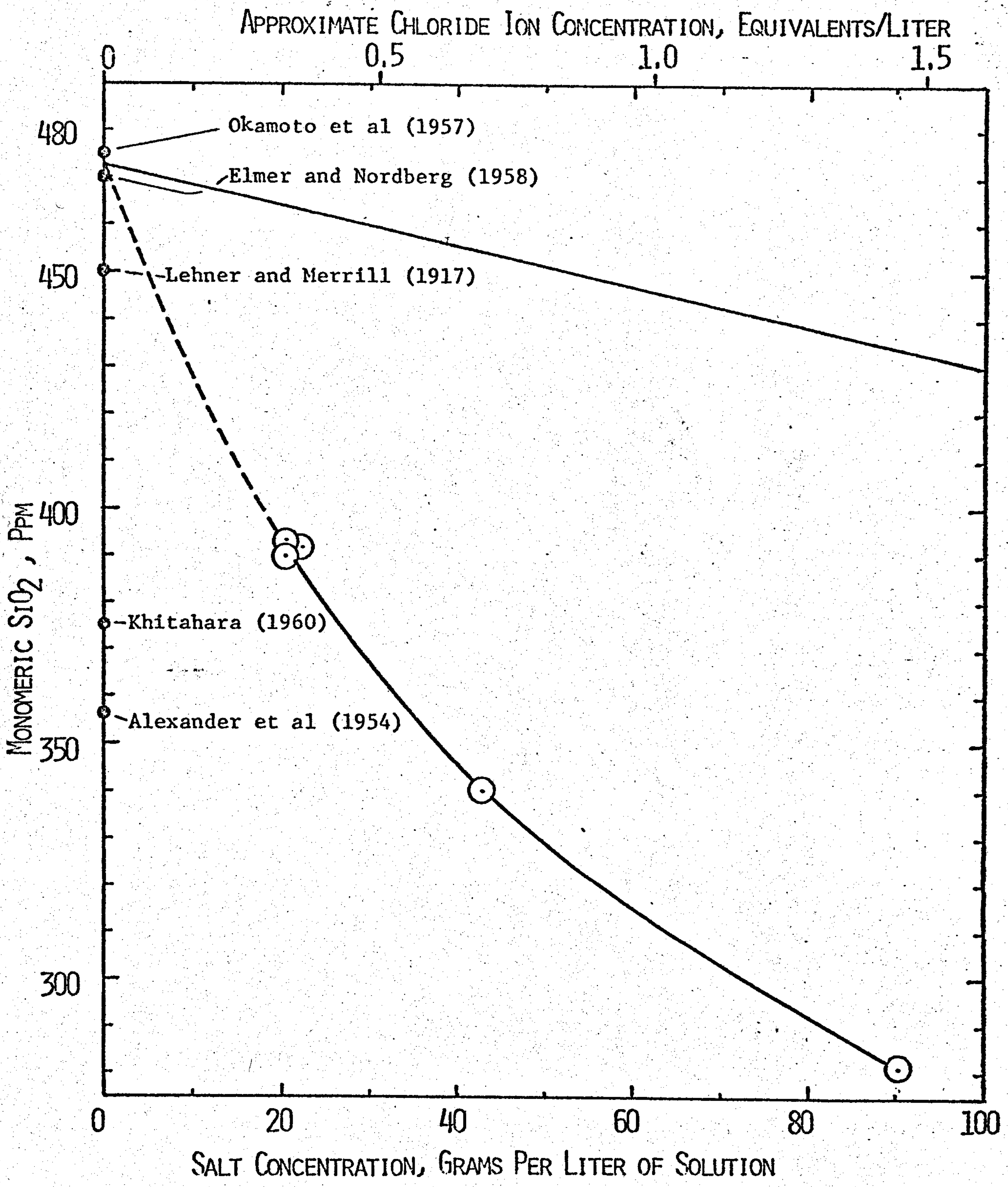

Fig. 5: The effect of salt concentration on the equilibrium solubility of amorphous silica at 95 ± 2° C. The curve shown is preliminary. The straight line represents the decrease in solubility expected from a salt effect on the activity of water at 95° C.

literature for brines having our proportions of NaCl, KCl and $CaCl_2$. Instead, values of a_{H_2O} in NaCl brines at 95°C were extracted from data by Barnes and Rimstidt (1975), Crerar (1974), and Helgeson (1969), and values of a_{H_2O} in $CaCl_2$ brines at 95°C were estimated from data given by Barnes and Rimstidt (1975). Calculated effects of the $a^2_{H_2O}$ term on the final concentration of monomer are compared with observation in Fig. 5 at the same salt concentration, as Cl^- normality. The hydration number of monosilicic acid in these brines would have to be 4 or greater, rather than 2, in order to yield the observed salting out by reduction in water activity alone. Moreover, partial hydration of the solid silica phase would be expected to diminish the effect of water activity.

An alternative explanation lies in an increase in the activity coefficient of the neutral silicic acid solute species ($\gamma_{H_4SiO_4}$ in Eq. (17)) brought about by the added salt. The literature is not definitive on this point. Thus, Hutchinson (1975) and Reed (1975) observed a salting-<u>in</u> of silica in geothermal brines from the Salton Sea area. By contrast, Kato and Kitano (1968) found a reduced solubility for amorphous silica in sea water (about 27% reduction as compared to solubility in distilled water) and an even more marked salting-<u>out</u> in 1N NaCl (about 5.4% NaCl brine).

In their review article on effect of salts on activity coefficient of nonelectrolytes, Long and McDevit (1951) present data showing salting-<u>out</u> of most nonelectrolytes in aqueous solutions. The general behavior is that the logarithm of the activity coefficient of the nonelectrolyte is proportional to the concentration of the salt, $\log\gamma = \underline{k}C$. The sign and magnitude of the proportionality constant are determined principally by the effect of the nonelectrolyte on the interaction between solvent and ionic solute. For aqueous systems, k is usually positive, resulting in a lower solubility of nonelectrolyte with increasing salt concentration, i.e., salting-out.

Systematic salting-out experiments do not appear to have been made for silicic acid in brines. The closest chemical analog of aqueous silicic acid in the Long and McDevit paper is carbon dioxide. From their plots of $\log\gamma_{CO_2(aq.)}$ vs. salt concentration (g-equiv/l, or normality), the following results are found for 25°C:

$$1.5N\ NaCl:\ \log\gamma_{CO_2(aq.)} = 0.11,\ \gamma_{CO_2(aq.)} = 1.29 \qquad (18)$$

$$1.5N\ KCl:\ \log\gamma_{CO_2(aq.)} = 0.15_5,\ \gamma_{CO_2(aq.)} = 1.43 \qquad (19)$$

An increase in the activity coefficient of aqueous monomeric silica of comparable magnitude could explain the marked decrease of final monomer concentration in the strong brines (Fig. 5).

5. Effect of pH

The pH range of natural geothermal brines is about 4-8, with brines of highest temperature and salinity generally having the lowest pH (Ellis, 1970). Most of the experiments reported here were carried out at pH 5.15 ± 0.10 (95°C) in an acetate-buffered brine. The molar ratio of acetate to acetic acid was generally maintained at 5.7. The buffering capacity of acetic acid falls off rapidly above pH 5.2, so that another buffer (with pK_a greater than that of acetic acid) should be used above this pH.

Hydroxide has a well-known catalytic effect on silica polymerization. As noted in our previous report, literature values of the reaction order with respect to hydroxide range between 0.5 and 1.0. The mechanism of the catalytic effect is believed to involve the the reaction of ionized silicic acid ($H_3SiO_4^-$ or $H_5SiO_5^-$ in the case of the monomer) with unionized silica species.

As discussed in Section III.3, added salt also causes an approximately first-order acceleration of the rate of monomer disappearance. Preliminary experiments indicate that this effect is due mainly to chloride. It is conceivable that chloride, like hydroxide, can bind to silicic acid, giving rise to a charged complex (perhaps $H_4SiO_4Cl^-$) that reacts rapidly with neutral silica species. There are many mechanistic possibilities, but in the limiting cases it is expected that the observed rate constant would depend on salt and hydroxide in either serial or parallel fashion:

$$k_{obs} = k(S)(OH^-)[(M)_o^q - (M)_{eq}^q] \qquad (20)$$

or

$$k_{obs} = [k_s(S) + k_b(OH^-)][(M)_o^q - (M)_{eq}^q] \qquad (21)$$

In the case of parallel catalysis, Eq. (21), the observed effective reaction orders with respect to salt and hydroxide should be less than one.

To obtain explicit information on the influence of pH, experiments using the acetate buffer were carried out at the lower pH of 4.20. The results are shown in Table IV and Figs. 6(a) and 6(b). Results of duplicate runs in Fig. 6(b) illustrate the degree of reproducibility that can be obtained in experiments of this nature. Because the rate of disappearance of monomer at lower pH (upper curves) is so slow, we did not

Table IV

Data Summary for 95°C Kinetic Runs: Tests for pH and Specific Buffer Effects

Run	Initial Monomer Concentration (ppm)	Apparent Supersaturation (ppm)	Total Salt Concentration (g/l)	Cl^- (m/l)	pH	Buffer	Ac^- or $Mal^=$ (m/l)	HAc or $HMal^-$ (m/l)	Half-Life of Excess Monomer (min)	First Rate Rate Constant (k_{obs}, min^{-1})
A	1034	656	20.8	0.315	5.13	Ac	0.089	0.018	60	0.0178
B	940	561	18.9	0.286	5.05	Ac	0.081	0.016	90	0.0144
C	862	482	17.3	0.262	5.10	Ac	0.074	0.015	160	0.0076
D	795	414	16.0	0.242	5.25	Ac	0.068	0.014	286	0.0045
H	1037	659	21.3	0.345	4.19	Ac	0.037	0.064	-	0.002
I	965	587	22.9	0.371	4.21	Ac	0.040	0.068	-	0.001
J	1036	658	22.8	0.372	5.24	Mal	0.012	0.010	35	0.0320
K	888	525	16.3	0.234	5.16	Mal	0.019	0.025	67	0.0187
L	877	498	19.0	0.310	4.79	Mal	0.0083	0.0097	163	0.0095
M	892	513	19.7	0.339	4.85	None	-	-	109	0.0099

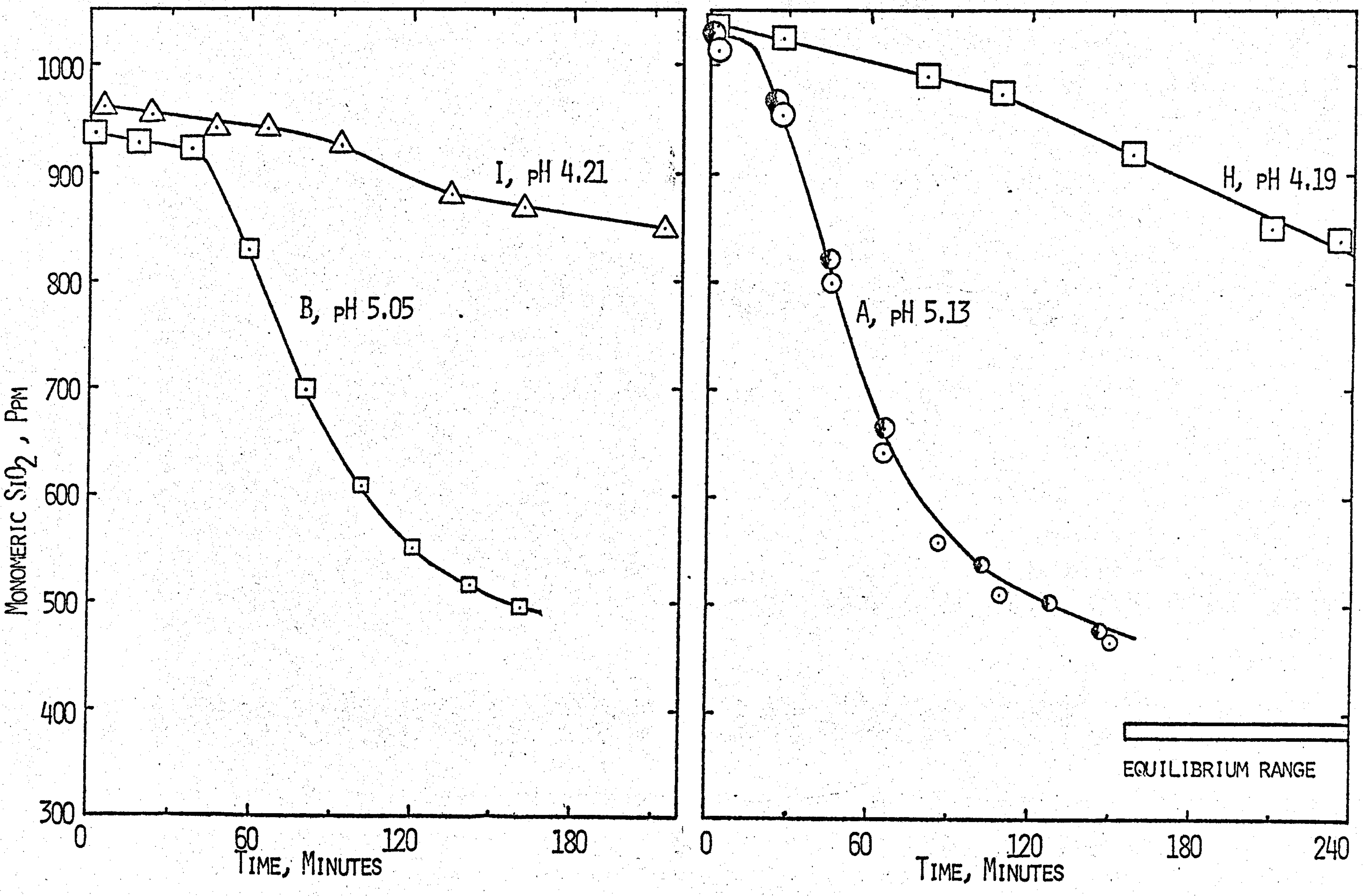

Fig. 6: The effect of pH (acetate buffering) on monomer disappearance, at two initial SiO_2 concentrations.

obtain accurate estimates of the rate constant. However, the rate constant is roughly a factor of ten greater at pH 5.1 than at pH 4.2 for runs in which the salt concentration and monomer supersaturation are the same. The ratio of hydroxide ion activities, calculated from the known ratios* of acetate to acetic acid, is 9.8 ± 0.8, so the apparent order of reaction with respect to hydroxide is close to 1.0. This result would appear to rule out parallel catalysis, Eq. (21), although further studies are clearly needed.

Baumann (1959) used maleic acid as a buffer in his studies of silica polymerization. Our own preliminary tests indicated its suitability: like acetate (but unlike citrate or phthalate), it does not precipitate Ca^{++}, and its effective pK_a under the experimental conditions is about 0.8 unit greater than the pK_a for acetate. Maleate buffer should, therefore, be effective at 95°C up to pH 6.0.

To investigate a possible specific buffering agent effect, kinetic runs were carried out near pH 5 using the maleate buffer. The results are shown in Table IV and Figs. 7 and 8. Based on a comparison of first-order rate constants in acetate- and maleate-buffered brine, corrected to the same supersaturation, salt concentration, and (approximately) pH, the rate constant for monomer disappearance is 1.7 ± 0.7 times greater in the maleate-buffered solution. This difference in rates, if real, is apparently greater than can be explained by a pH shift between the two

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*The hydroxide activity ratio, calculated (less accurately) from the observed pH values, is 8.9 ± 2.0.

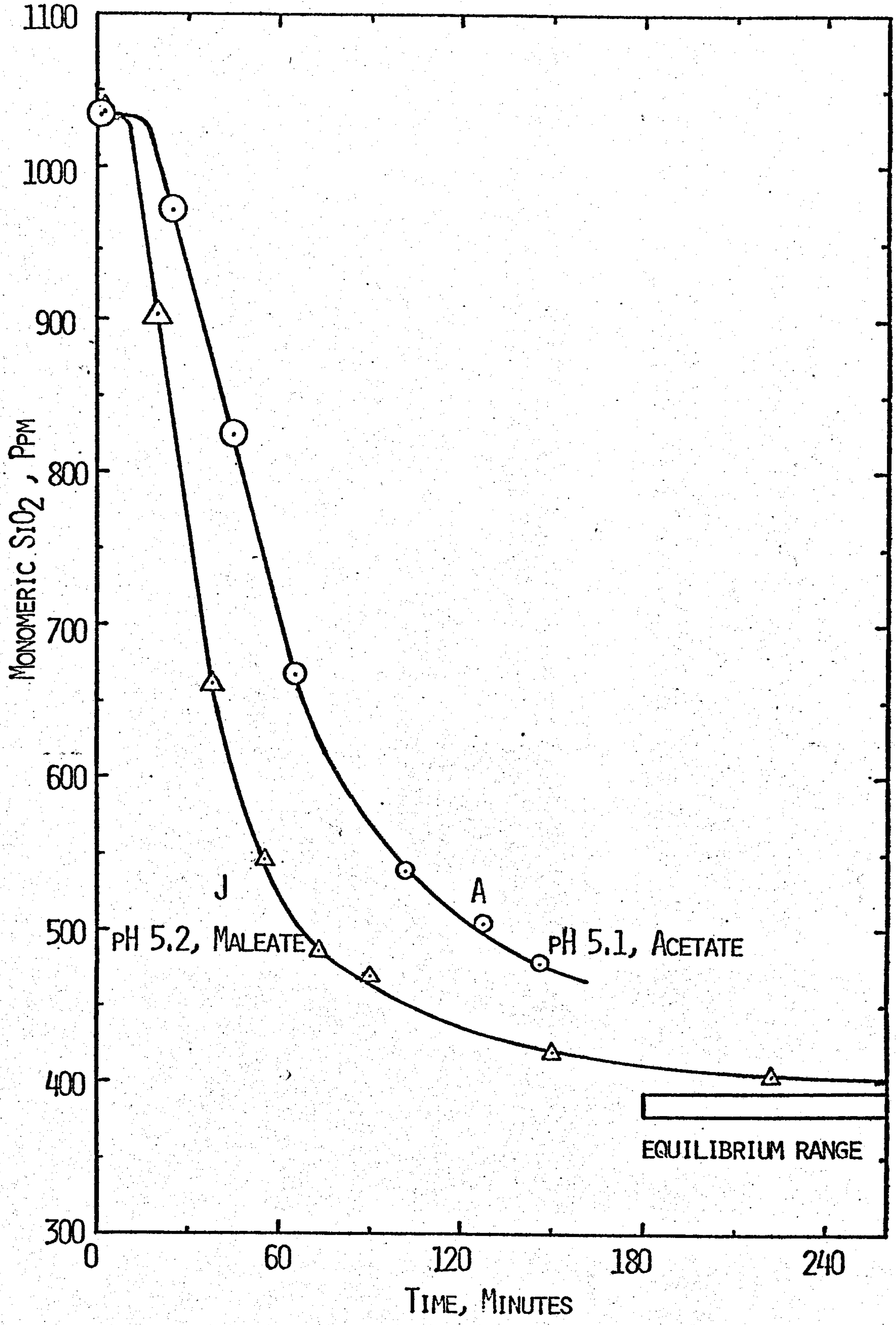

Fig. 7: The effect on monomer disappearance of acetate versus maleate buffering, with relatively high initial SiO_2 concentration.

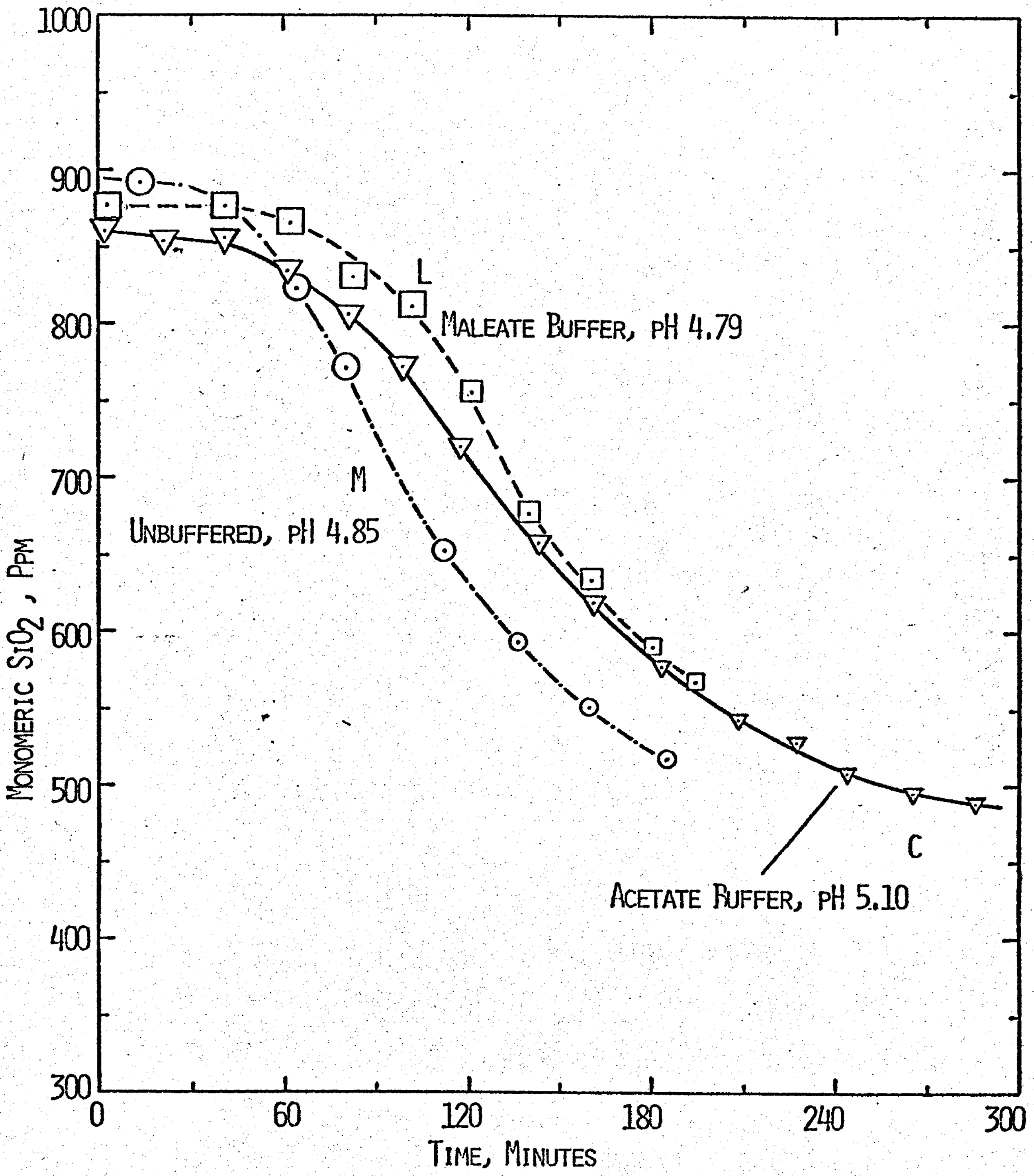

Fig 8: The effect of different buffers on the disappearance of monomer at 95 ± 2° C.

buffers, although it is possible that inaccuracies in pH measurement at 95°C are at fault. To test this possibility, a pH electrode specially designed for high temperature measurement will be employed in confirmatory experiments.

In addition to the foregoing, attempts were made to carry out kinetic runs in unbuffered brines. Such runs are experimentally difficult since the pH tends to drift randomly. In Run M (see Fig. 8), however, the pH stabilized at 4.85 ± 0.05. The rate constant in this run is within 10% of the interpolated rate constant for a run carried out in an acetate buffer at pH 5.15 at the same supersaturation and salt concentration, although the hydroxide concentration in Run M is a factor of 2 smaller. It appears, therefore, that the acetate buffer inhibits the rate of monomer disappearance. Maleate buffer appears to have a smaller inhibiting effect, but it must be noted that the acetate concentration is considerably larger than the maleate concentration (see Table IV). Since these comparisons are based on a small number of kinetic runs, and since pH measurements at 95°C are not as accurate as at room temperature, these conclusions must be regarded as tentative.

In natural geothermal brines, the buffering action is presumably due to the effects of CO_2, HCO_3^-, $CaCO_3$, and silicic acid. To use this buffering system in the laboratory -- and hence eliminate the effects of "foreign" buffering species -- it is necessary to use a pressure vessel so as to maintain a CO_2 atmosphere. A series of experiments was therefore carried out in the autoclave, and the pH was regulated by controlling the ratio of CO_2 to HCO_3^-. Use of the autoclave also allows investigation of polymerization and precipitation kinetics at higher temperatures. The results of these experiments are reported in the next section.

IV. EFFECT OF TEMPERATURE ON MONOMER DISAPPEARANCE

1. Water Bath Experiments

Since the equilibrium solubility of amorphous silica increases with temperature, the temperature effect on rate of monomer disappearance at a given initial silica concentration includes a change in supersaturation and a change in the rate constant. In order to determine the effect of temperature on the rate constant alone, polymerization rates should be compared at the same silica supersaturation.

Figure 9 compares the rates of monomer disappearance at 78°C and at 95°C for experiments with similar initial supersaturations. The 78°C brine was somewhat more supersaturated (580 vs. 550 ppm supersaturation) and also slightly higher in pH (5.19 vs. 5.05). Either of these factors alone would lead to a higher rate of monomer disappearance for the 78°C experiment. Based on the known effect of pH, the maximum rate of monomer disappearance in the 78°C experiment would be expected to be about 38% faster than in the 95°C experiment. Similarly, the difference in the supersaturation should lead to a ∿17% higher maximum rate for the 78°C experiment.

Since the rate constants are comparable in these two experiments (Fig. 9), an increase in rate with increasing temperature is indicated. Roughly, the rate enhancement factor is 1.6 for a 17°C rise in temperature. Accordingly, the activation energy for monomer disappearance in the post-induction period appears to be less than that for a typical chemical

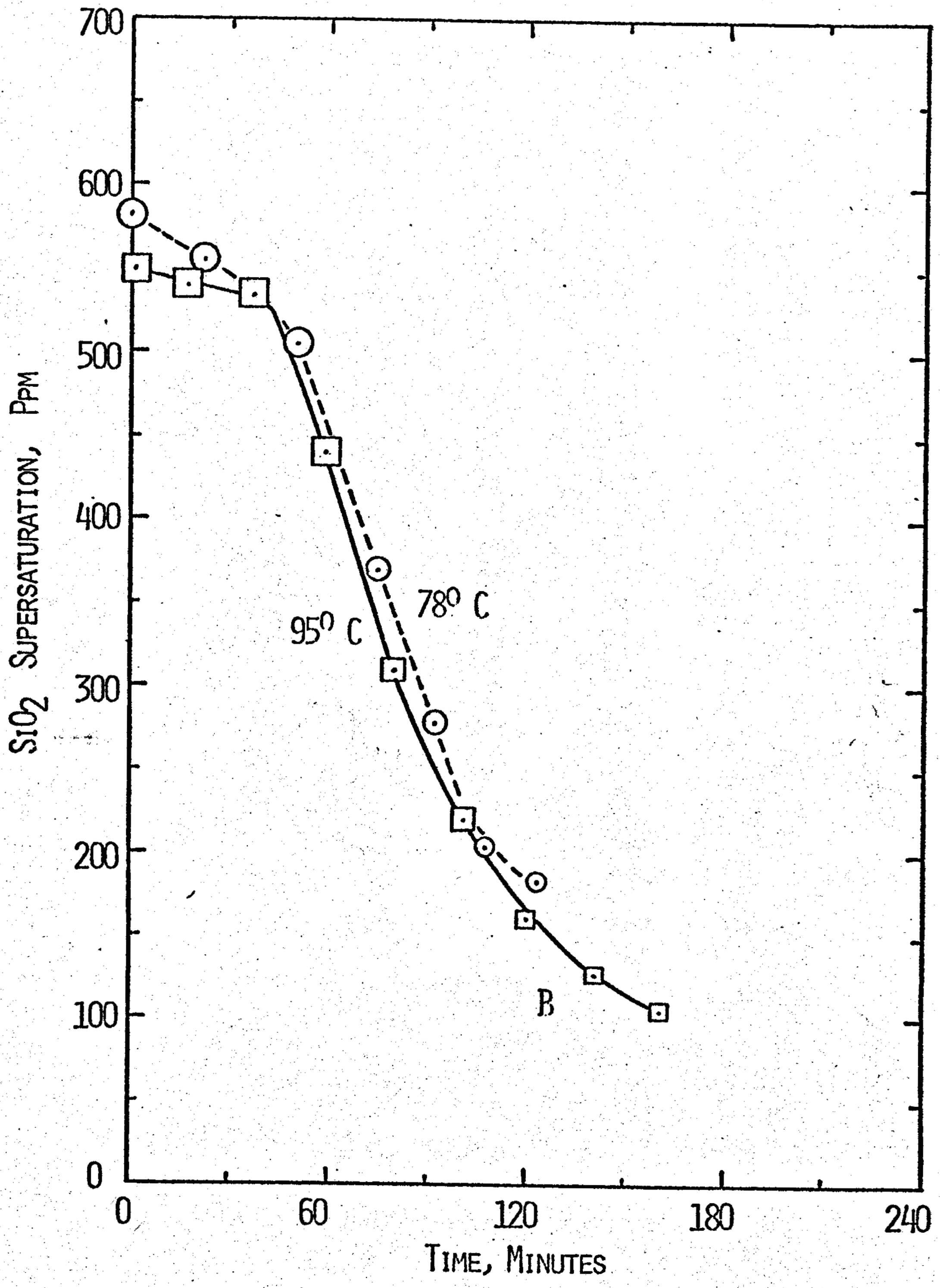

Fig. 9: The effect of temperature on monomer disappearance. Note that the vertical axis portrays supersaturation. The circles show a test at 78° C and pH 5.19. The squares show a test at 95° C and pH 5.05.

reaction. Qualitatively, an activation energy of about 7 kcal/mole is obtained for our results. This result is comparable to the value of about 10 kcal/mole obtainable from the experimental findings of Kitahara (1960).

2. Autoclave Experiments

In the previous report, it was noted that in attempts to prepare a simulated brine by dissolving amorphous silica in the autoclave at a relatively high temperature (≥200°C), a ring of hard scale formed at the liquid-vapor interface. Chemical analysis of a sample of this scale showed it to be comprised of anhydrous silicon dioxide ($103 \pm 3\%$ SiO_2), and its x-ray diffraction pattern was that of α-quartz. The formation of quartz may explain our inability to prepare solutions that were slightly undersaturated with respect to amorphous silica (e.g., 800 ppm SiO_2) at and above 200°C, in that the solubility of quartz at 200°C is less than 300 ppm. It was surprising to find relatively rapid formation of quartz at these temperatures: scale rings formed within a few hours at and below 250°C. Since others may be studying, or preparing to study silica scaling from simulated geothermal brines in pressure apparatus, a further brief account of experimental difficulties encountered in the present work may be helpful.

The design of the autoclave heating jacket is conducive to somewhat uneven heating of the autoclave walls. Consequently, it was thought that quartz formation might have been initiated at local hot spots. However, heating the autoclave uniformly in an oven at 220°C did not prevent formation of a scale ring. These largely negative observations may yet have some value if a correlation can be made with the case of a hot brine undergoing flashing.

A scale ring could also have been produced by the evaporation of a film of solution when the liquid level was lowered during sampling. Use of a Teflon liner should retard scale formation if this were the case and if the Teflon surface retained its hydrophobicity. Unfortunately, the Teflon liner tended to disintegrate at 250°C. At 200°C, the liner was relatively stable, and scale formation was greatly reduced. However, we were not able to dissolve more than 700 ppm SiO_2 at this temperature, out of 800 ppm SiO_2 or greater originally introduced into the brine.

We also attempted to eliminate incidental scale formation by use of an internal stainless steel liner, which was covered by a drip shield so that condensate would, in theory, run down the liner walls and redissolve any scale. The space between the autoclave wall and the liner was filled with solution, so that heat would be transferred evenly to the solution in the liner. This method successfully prevented scale formation, and SiO_2 concentrations as high as 1100 ppm were achieved. However, evaporation of water from the solution in the liner and condensation in the outer solution, or vice versa, made it impossible to prepare a brine with a targetted concentration of SiO_2 and salt; further, concentration changed erratically as water evaporated from one part of the system and condensed into the other. These difficulties seriously impaired the quantitative value of the data obtained. Thus, we are not yet in a position to report rate data for temperatures higher than 95°C.

We are presently of the opinion that it is probably not feasible to prepare accurately simulated brines in the autoclave, with a predetermined concentration of silica, unless the liquid-vapor interface is eliminated. (Equilibration of the three constituent solutions -- Section II.1 -- in an autoclave prior to mixing at the desired temperature is a possible, though very difficult alternate approach.) Accordingly, the autoclave is being fitted with an internal bellows to raise the pressure on the solution above the equilibrium vapor pressure of water. In that way, the vapor space will be eliminated enabling the preparation of simulated brines that are just undersaturated with respect to amorphous silica at 200°-250°C and, hence, supersaturated at the lower temperatures of interest.

V. SILICA PRECIPITATION AND SCALE FORMATION

One of the most important questions in this study is whether silica scaling involves deposition of monomer, deposition of larger aggregates, or both. We have tried several experimental approaches to this question. First, we have followed the rate of disappearance of total dispersed silica, so as to obtain a measure of the rate of deposition. Second, we have carried out experiments in which the total surface area of the system was considerably increased by the addition of pyrex or quartz wool. Third, we have used filtration to bracket the sizes of the polymeric silica species.

In the 2% brines at pH 5, the total dispersed silica remained sensibly constant (i.e., within experimental error) for several hours, by which time the concentration of monomer had dropped to within 100 ppm of the equilibrium value (Fig. 10). This behavior implies either that large particles are not formed continuously from the outset, or that their aggregation is slow. In the polymerization runs carried out in the more saline brines (42.6 and 90.3 g/l salt), a pronounced decrease in total dispersed silica was observed because, within the time of observation, the reaction had gone much further toward completion. However, as shown in Figs. 11 and 12, the rate of this decrease was relatively slow until the concentration of monomer had almost reached its final value. A rapid decrease in total dispersed silica then took place. In diagnostic experiments with pyrex or soft-glass wool present, the rate

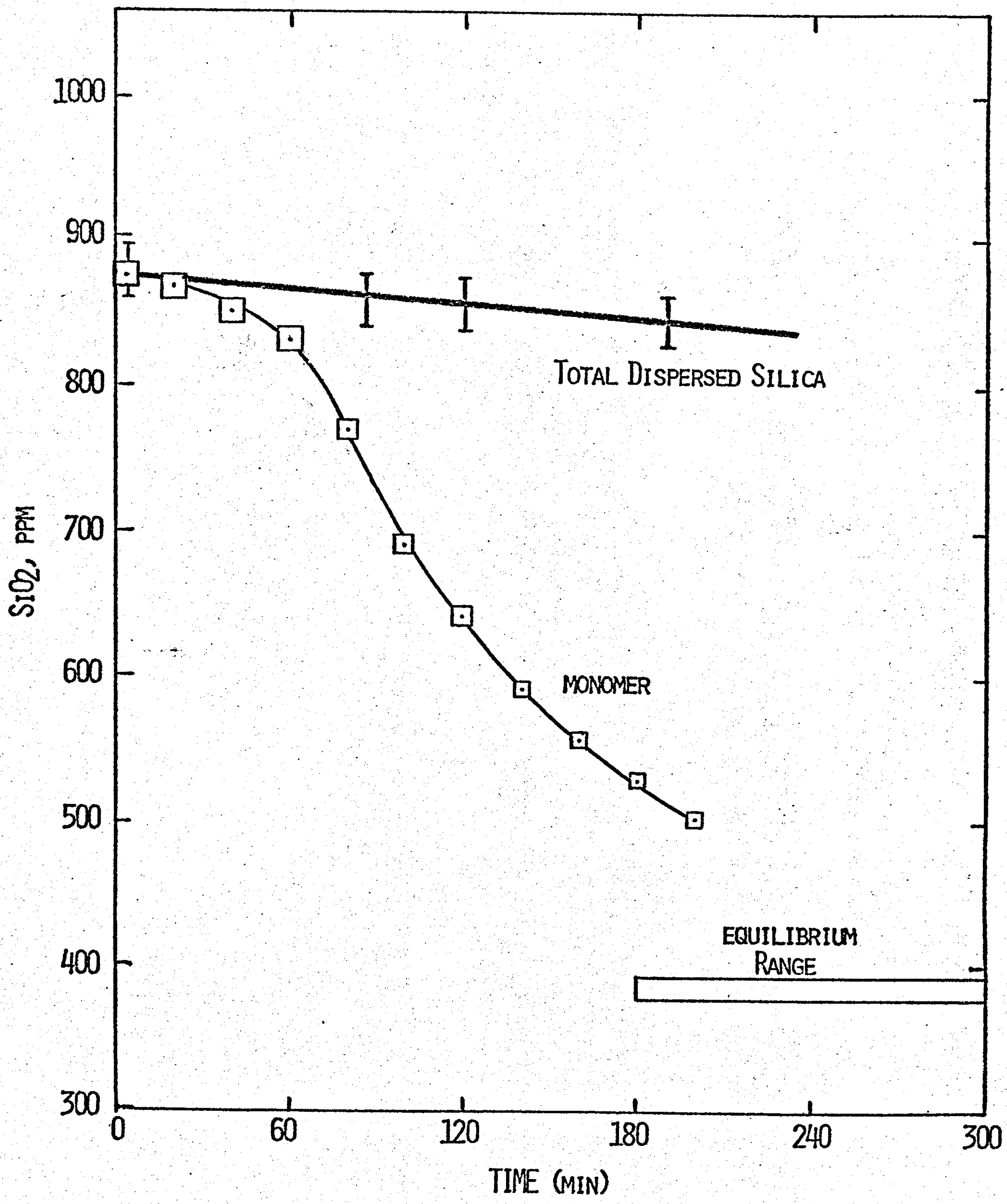

Fig. 10: The polymerization and deposition of silica from a 2% simulated geothermal brine at 95° C and pH 5.1.

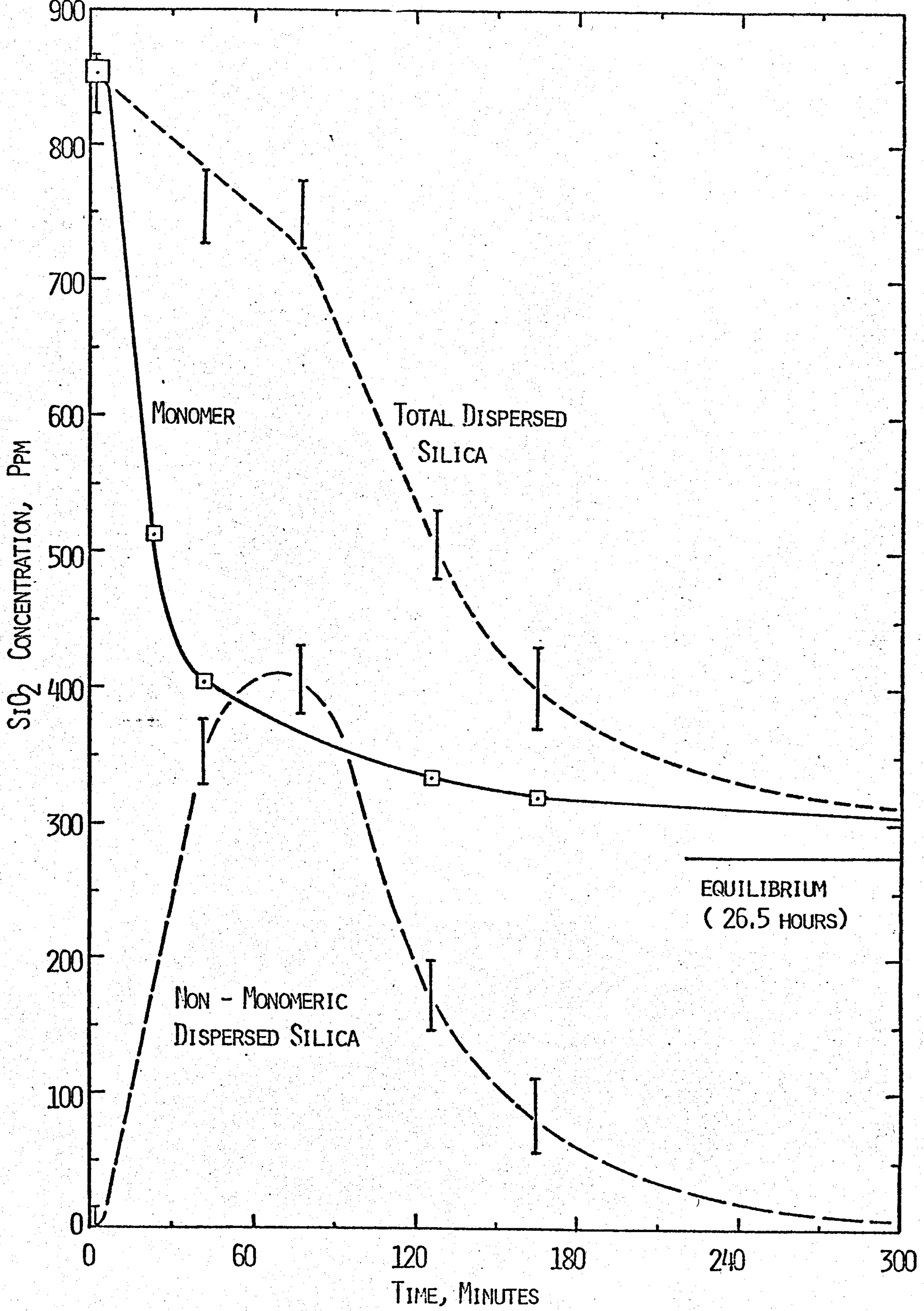

Fig. 11: The polymerization and deposition of silica in Run E, with 90.3 g/l total salt, at 95 ± 2° C and pH 5.28 ± .10 .

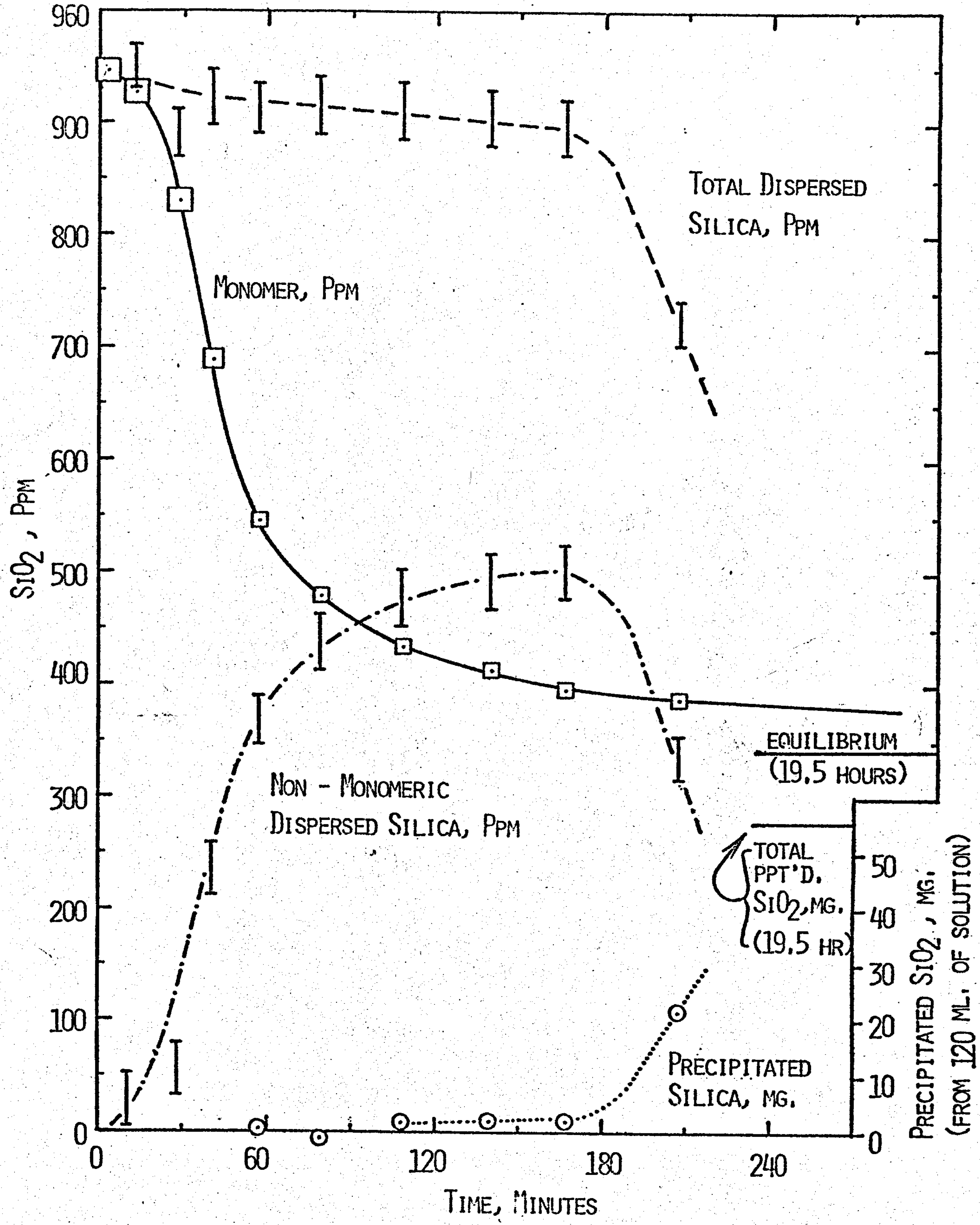

Fig. 12: The polymerization and deposition of silica in Run F, with 42.6 g/l total salt, at 95 ± 2° C and pH 5.08 ± 0.10 .

of disappearance of total dispersed silica was again negligibly small, and no gain in the mass of the wool was observed. When the concentration of total dispersed silica was followed for several hours more, the mass of the wool increased, concurrently with a decrease in total dispersed silica. Experiments designed to disclose whether the observed SiO_2 decreases were due to filtration by the wool or to scaling directly from aqueous species indicated that filtration of suspended silica flocs was responsible for the decrease. Experiments with pyrex wool are consistent with a picture in which the decrease of total dispersed silica is principally by agglomeration and settling rather than by direct adhesion of monomer or polymer.

The time lapse prior to precipitation can be explained by assuming that the polymeric particles that formed at an early stage of the reaction grow by addition of monomer or by agglomeration; the particles eventually reach a size at which they are massive enough or adherent enough to flocculate, settle or deposit. To determine the magnitude of particle sizes at which precipitation occurred, a series of filtration experiments has been initiated. As shown in Fig. 13, by the mid-stage of the reaction, a 0.1 micron millipore filter removed over 80% of the non-monomeric silica from dispersion. At a later stage of the reaction, the average particle size was such that a much larger pore size filter (0.8 micron) removed about 34% of the silica in suspension. These experiments, while not yet refined to the point where the rate of growth of particles can be estimated, clearly indicate that the polymeric parti-

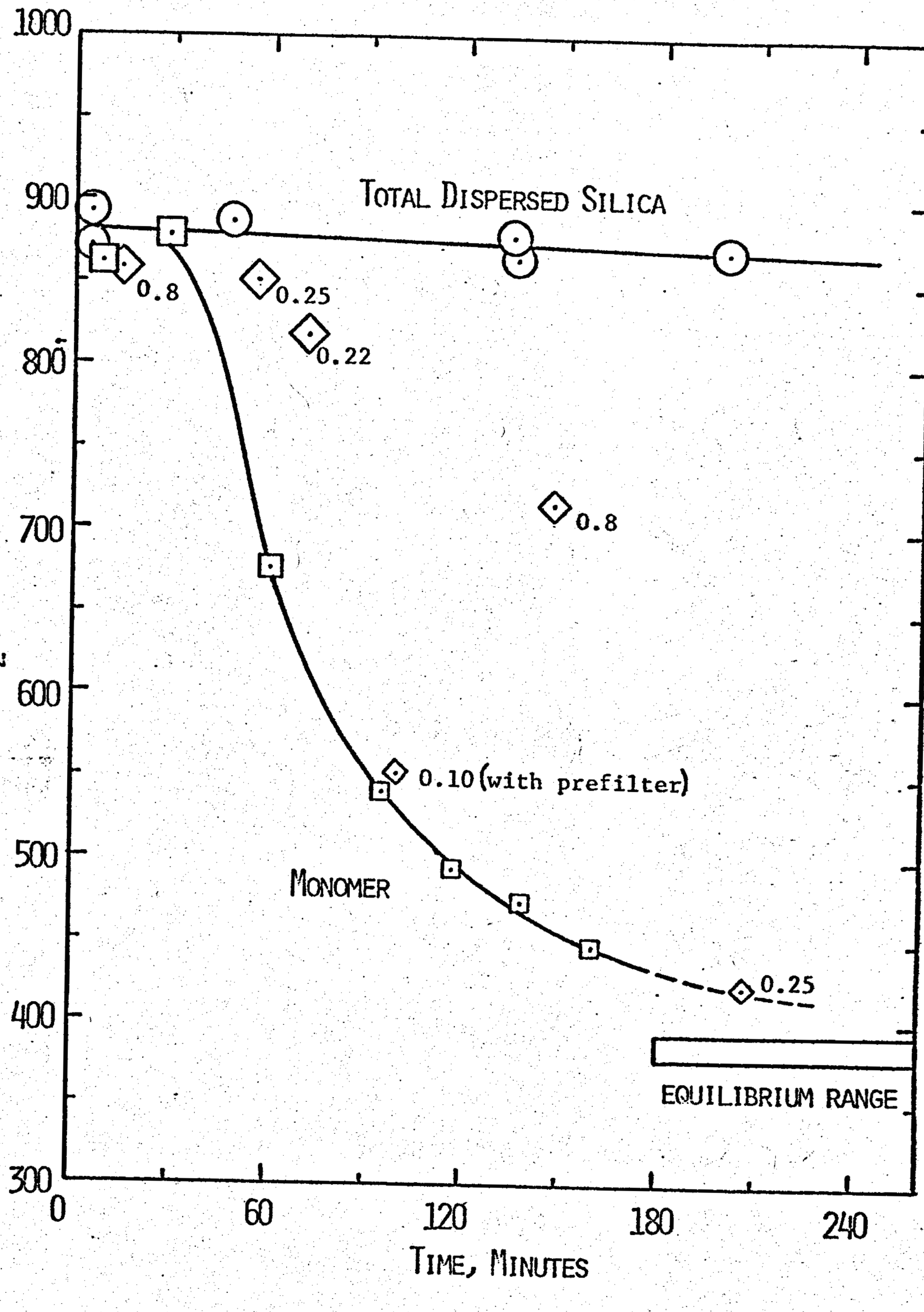

Fig. 13: Monomer, total dispersed silica, and dispersed silica passing through selected filters, for a run with pyrex wool present. Test conditions: 95 ± 2°C and pH 5.26 ± 0.10. Filter pore sizes, in microns, are indicated in the figure.

cles are extremely large, at the upper end of the range of the sizes usually termed colloidal. A 0.1 micron diameter silica particle contains about 10 million monomeric units; still larger particles should settle rapidly.

It is clear from these experiments that the term "polymerization" may be a misnomer. There is no evidence for the continued existence of units small enough to be termed polymeric, although it is possible that they exist at very low concentrations and play a role in the disappearance of monomer. Most probably, monomer adds primarily onto a relatively small number of large colloidal particles, which are formed rapidly in the earliest stages of reaction.

In this discussion, we have considered the extent of scaling to be represented by the decrease in total silica measured after a short time has been allowed for settling. The form of the precipitate is gelatinous and is probably similar to the "soft scale" found in the field (Marsh, 1975). However, our operating definition regards as scale, particles which would settle regardless of their tendency to adhere. This definition may not be suitable for the flow of brine through a pipe in a geothermal system. However, it is a useful measure of maximum scale formation under minimum flow conditions.

The type of scale formed in these experiments may not be directly related to the more prevalent "hard scale" found in the field. We have begun investigations into the conditions under which hard scale can form. From preliminary studies, it appears that formation of hard scale is favored by higher pH and by the presence of a cooled surface. Garrett Research and Development Co. (1975) similarly obtained coherent scales on cooled probes at a pH generally near 7 and with brine constituents in comparable proportions to those in our experiments.

Characterization of Scales

We have analyzed eight scale samples from our 95°C experiments. These include soft and hard scales and silica floc filtered from the brine at the termination of runs. Energy dispersive analysis by scanning electron microscopy was employed to give semiquantitative elemental analysis. All scale samples were found to be principally amorphous* silica. Traces of Na, K, and Ca were detected from energy spectra, but peaks were invariably also located for Cl in these cases, so that the presence of these cations is thought to reflect traces of residual salts from the brine. Correspondingly, the presence of any Na, K, or Ca-silicates is thought to be minor.

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*The only exception is the scale ring from the autoclave that was found to contain α-quartz.

VI. CURRENT RESEARCH PLANS

There are many areas within the scope of the program that are deserving of further attention. We currently plan to put effort into solving all of the following problems, with the anticipation, if successful, of acquiring a good understanding of the phenomenon of silica scaling. We should then be in a position to recommend changes in procedures or other means for reducing the amount or effect of silica scaling in actual operations. By way of approaching this goal, we intend to:

- Obtain more detailed information on the particle size distribution of dispersed silica during disappearance of silicic acid monomer.
- Further identify the factors determining whether excess silica is rejected from geothermal brine as particulates or as soft or hard scale. Included in this portion of the study will be specific substrate effects, thermal contrast, filtration of the growing silica particles, and incorporation of brine constituents.
- Characterize the silica scales and precipitates, produced in the laboratory, with respect to morphology, crystal structure, mechanical properties and detailed chemical composition; make comparison with silica scales and deposits from selected field sites.
- Establish which of the major brine constituents, if any, is responsible for the observed acceleration of monomer disappearance with increasing salt concentration. Additionally, investigate the influence of selected minor constituents of geothermal brines suspected of having the capability to influence the course of excess silica rejection. Included in this category are fluoride, aluminum, iron, and magnesium.
- Round out the study of pH and temperature effects on the

kinetics and course of monomer disappearance, especially in the direction of higher temperature and pH. In conjunction with this work, make an effort to overcome experimental difficulties incurred by use of an autoclave, and conduct experiments with the exclusion of the vapor phase. Further, acquire suitable techniques for utilizing CO_2-buffering, thereby removing reliance upon artificial buffer agents.

- Obtain better definition of the quantitative effects of salt and silica concentrations on the kinetics and course of silica rejection from supersaturated brine. In this connection, establish more firmly the variation of final monomer concentration with salt concentration - if possible, at two or more brine compositions and temperatures of interest.
- Extend and refine the analytical model of monomer disappearance, including delineation of events occurring during the incubation period. As a minimum goal, produce a rational framework for quantitative expression of the rate of relief of supersaturation.
- Develop a comprehensive rate expression exhibiting the functional dependence of the rate of approach of the mono-silicic acid concentration to its final value on all concentrations and brine properties known to be of significance.

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