CALCIUM CARBONATE PRECIPITATION KINETICS

By

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Declaration

I hereby declare that this thesis is my own work and has not been submitted for a degree at any other university.

Signed by candidate

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SYNOPSIS

A modified equation from that of Nancollas and Reddy is presented to describe the rate of calcium removed from water in $CaCO_3$ precipitation. The mass of $CaCO_3$ precipitated at any moment was obtained by monitoring pH and utilizing this in the equilibrium equations for the Ca - H_2CO_3 system including ion pairing and ionic strength effects. Both batch and back mixing steady state conditions were studied. The precipitation rate constant was found to be independent of pH, and functionally related to the state of initial supersaturation in the batch tests and the state of supersaturation in the steady state tests. Both steady state and batch tests gave the same dependence of the precipitation rate constant with supersaturation.

Introduction

Calcium and magnesium ions are the predominant contributors to hardness in water. They are present in varying concentrations in all natural waters but are particularly evident in underground and surface waters derived from dolomitic areas. In water reclamation, addition of $Ca(OH)_2$ as a flocculating agent is widely used. The effluent pH is high ($>$10,5) and subsequently the pH of the water must be reduced and the residual calcium removed. The Ca^{++} ions are usually removed from solution by the precipitation of calcium carbonate.

In 1973 Loewenthal and Marais developed the modified Caldwell-Lawrence diagram. This diagram relates the pH, alkalinity, acidity and calcium concentration of a water. If a water is sipersaturated with respect to Ca^{++} the amount of $CaCO_3$ that will eventually precipitate can be estimated. However, the Caldwell-Lawrence diagram gives no indication of the time required for the estimated precipitation to take place.

To design a water-softening plant it is necessary to know the rate of $CaCO_3$ precipitation under different conditions so that the hydraulic retention time and hence the volume of the reactor can be calculated.

In water reclamation the same situation applies. However, experimental data on water reclamation plants indicate that the residual calcium concentration in effluents is higher than the solubility product for $CaCO_3$, Ksp, would appear to indicate. This observation could be due to three factors :

/ (1) The Ksp ...

(1) The Ksp value has changed.

(2) The Ksp value is the same as for the pure system but complexing of Ca^{++} with organic and phosphorous compounds occurs or,

(3) Poisoning of the crystal surface occurs. Before the removal of calcium in water reclamation can be quantified in a theoretical model, it is necessary, as a first step, to determine the rate of $CaCO_3$ removal from pure systems (where Ksp is known) to serve as a criterion against which the real life system can be compared.

Reddy and Nancollas (1971) proposed a model for the kinetics of calcium carbonate precipitation as follows : -

$$- d\,[Ca^{++}]_T\,/dt \;=\; KS_f\left([Ca^{++}]_F\,[CO_3^{=}]_F \;-\; Ksp/f_D^{\,2}\right) \qquad (1)$$

where : K = rate constant.

S_f = surface are of $CaCO_3$ crystals

$[Ca^{++}]_T$ = total concentration of calcium in solution.

$[Ca^{++}]_F$, $[CO_3^{=}]_F$ = concentration of free Ca^{++} and $CO_3^{=}$ ions respecitvely.

Ksp = solubility product for $CaCO_3$.

F_D = activity coefficient for a divalent ion.

To test the validity of Eq.(1) Reddy <u>et al</u> monitored the changes in calcium and pH in supersaturated solutions of $CaCO_3$ seeded with calcite crystals of known surface area. They determined the parameters $[Ca^{++}]_F$ and $[CO_3^{=}]_F$ from the theory of the carbonic system taking due account of all possible ion pairs. Supersaturated solutions with concentrations of Ca^{++} 15 - 45

/ and CO_3 ...

and CO_3 20 - 40 ppm as $CaCO_3$ were inocculated with calcite seed crystals at concentrations from 340 to 2 800 ppm as $CaCO_3$. After an initial surge of growth a value of K was obtained whcih was independent of the seed mass and initial Ca^{++} and $CO_3^{=}$ concentrations. They concluded that within the ranges of ionic and seed concentration Eq. (1) applied.

Wiechers (1973) critically examined the work of Reddy _et al_. He concluded that the concentration and supersaturation used by Reddy _et al_ were very low compared with the concentration which might be encountered in water treatment plants and that the model should therefore be tested at higher supersaturations. Also, the concentration and size of $CaCO_3$ crystals in solution could vary considerably under different conditions. Wiechers proposed that Eq. (1) be modified in terms of the mass, M, instead of the surface area, S_f, of $CaCO_3$ seed crystals, i.e.

$$- d\,[Ca^{++}]_T\,/dt \;=\; KM([Ca^{++}]_F\,[CO_3^{=}]_F \;-\; Ksp/f_D^{\,2}) \qquad (2)$$

This modification has the disadvantage of limiting the model, and any data obtained, to the particular size, type and brand of $CaCO_3$ seed crystals used. However by doing an investigation using one batch of seed crystal it is still possible to determine the laws relating the parameters of precipitation.

To test if Eq. (2) described the precipitation reaction at practical $CaCO_3$ concentrations, Wiechers did experiments at Ca^{++} and $CO_3^{=}$ concentrations each up to about 400 ppm measured as $CaCO_3$. He showed theoretically that by neglecting the CaOH ion pair, which is low at pH 9,5 and below, he could determine each of the parameters in Eq. (2) by measuring the pH only. In contrast Reddy et al had to measure both the pH and calcium concentration. The measurement of calcium is possible when the rate of crystallization is slow as in the case studied by Reddy et al but when the rate of precipitation is high it is difficult to do this measurement accurately.

The value of K was determined by plotting $-d[Ca^{++}]/dt$ against $M([Ca^{++}]_F [CO_3^{+}]_F - Ksp/f_D^{2})$. This plot yielded a straight line for any particular experiment, as did the results of Reddy et al. In this respect the model described the precipitation reaction.

Wiechers, Sturrock and Marais (1975) then investigated the effects of (1) seed crystal concentration, (2) temperature, (3) stirring speed and (4) concentration of $CO_3^{=}$ and Ca^{++} ions on the rate constant, K : -

(1) To determine the effect of seed crystal concentration the Ca^{++} concentration (72 ppm as $CaCO_3$), the $CO_3^{=}$ concentration (38 ppm as $CaCO_3$), temperature (25°C) and stirring speed (500 r.p.m.) were all kept constant while the seed crystal mass was varied from 100 to 1 000 ppm as $CaCO_3$. At seed crystal concentration less than 400 ppm as $CaCO_3$ an initial growth surge was observed and thereafter for each experiment the value of K became steady at a similar value to that obtained for experiments with seed crystal concentrations greater than 400 ppm as $CaCO_3$. It was therefore concluded that, provided sufficient area or growth sites are supplied by the inocculated seed mass, the value of the rate constant, K, is independent of the seed mass.

/ (2) To determine ...

(2) To determine the effect of temperature experiments were done at 10, 20, 30 and 40°C while the stirring speed (500 rpm), Ca^{++} concentration (80 ppm as $CaCO_3$) and $CO_3^=$ concentration (33 ppm as $CaCO_3$) were kept constant. The van't Hoff-Arrhenius equation was used to describe the relationship between K and temperature : -

$$K_T = K_{20}\,\theta^{(T-20)} \qquad (3)$$

$$\text{or} \quad \log K_T = \log K_{20} + (T-20)\log\theta \qquad (4)$$

where T = temperature °C.

K_T, K_{20} = K at temperature T°C and 20°C respectively.

θ = constant.

The plot of $\log K_T$ versus T°C approximated to a straight line yielding : -

$$K_T = 1{,}53*1{,}053^{(T-20)}\ (l.mol^{-1}.min^{-1})/(mg\ seed.l^{-1})$$

(3) With regard to stirring energy, it was found that provided the stirring speed was sufficient to keep the $CaCO_3$ crystals in suspension, it had no marked effect on the rate constant K.

(4) To determine the effect of Ca^{++} and $CO_3^=$ concentrations the seed mass (700 ppm as $CaCO_3$), temperature (25°C) and stirring speed (500 rpm), were kept constant while the concentration of the reagents were varied (Ca^{++} 330-70 ppm as $CaCO_3$, $CO_3^=$ 18-54 ppm as $CaCO_3$). As the concentration varied, different values of K were obtained. A plot of K versus pH showed that K was apparently related to the initial equilibrium pH. However, in any particular

/ experiment ...

experiment, as the reaction proceeded and the pH decreased, the value of K remained constant, whereas one would expect the value of K to change concurrently with the change in pH. Wiechers et al could give no satisfactory explanation for this apparently inconsistent behaviour.

In this thesis Eq. (2) is modified and in the light of this modification further experimental data are analysed in an attempt to gain insight into the kinetics of $CaCO_3$ precipitation. Also, a calculation procedure to determine the parameters in Eq. (2) is developed. This procedure requires the measurement of pH and alkalinity at the start of each test, thereafter only the pH need be measured. It takes account of all ion pairs; therefore the limitation $pH < 9{,}5$ falls away.

$CaCO_3$ crystal growth and precipitation model

Calcium carbonate crystal growth occurs in four sequential steps (Stumm and Morgan 1970) : -

1) The reaction takes place whereby the hydrated $CaCO_3$ ion pair is formed : $[Ca^{++}]_F + [CO_3^=]_F \rightleftarrows [CaCO_3^o]$
2) The hydrated $CaCO_3$ ion pair is transported to the crystal/solution interface.
3) At the crystal/solution interface the ion pair is dehydrated and adsorbed onto the crystal surface, i.e. $[CaCO_3^o] \rightleftarrows [CaCO_3]_s$ This reaction takes place in both directions. The forward reaction, whereby the $[CaCO_3^o]$ is dehydrated, is called precipitation and the reverse reaction whereby the $[CaCO_3]_s$ is hydrated is called dissolution.
4) The $CaCO_3$ adsorbed onto the crystal is incorporated into the crystal lattice - a process called ripening.

At low turbulence the rate of transportation of $CaCO_3^o$ ion pairs to the crystal face is the controlling factor in crystal growth, i.e. growth is controlled by the diffusion rate of $CaCO_3^o$ ion pairs to the crystal face - called diffusion controlled growth. At high turbulence levels $CaCO_3^o$ transportation to the crystal face is adequate and the rate of crystal growth becomes limited by the rate at which the $CaCO_3^o$ ion pairs are adsorbed and incorporated into the crystal lattice - called interface controlled growth. The experiments reported by Wiechers et al indicate that, provided the stirring speed is sufficient to keep the

/ seed crystal ...

seed crystal in suspension, variation in stirring speed (i.e. turbulence) has no effect. This suggests that the $CaCO_3$ crystal growth is interface controlled.

The rate of precipitation in any seeded solution (either supersaturated, saturated or undersaturated with respect to $CaCO_3$) is assumed proportional to the surface area of seed and the concentration of the zero ion pair, $CaCO_3^o$, in the bulk solution, thus

$$\text{Rate of precipitation} = K_pS(CaCO_3^o) \qquad (5)$$

where K_p = the rate constant for precipitation.
Note that the ion pair has zero charge so that its active and molar concentrations in solution are equal.

Dissolution is assumed to occur simultaneously with precipitation and to be proportional only to the surface area of seed, S_f

$$\text{Rate of dissolution} = K_sS_f \qquad (6)$$

where K_d = the rate constant for dissolution.

Eq. (4) implies that the rate of dissolution is independent of the saturation state, i.e. it is constant per unit surface area of the crystal irrespective of over- or undersaturation. For a solution just saturated with respect to $CaCO_3$ the rates of precipitation and dissolution are equal, thus from Eqs. (3) and (4) :

$$K_pS_f(CaCO_3^o)_s = K_dS_f$$

i.e.

$$K_d = K_p(CaCO_3^o)_s \qquad (7)$$

where the subscript, s, refers to a saturated solution.
Substituting for K_d from Eq. (7) into Eq. (6) :

$$\text{Rate of dissolution} = K_pS_f(CaCO_3^o)_s \qquad (8)$$

/ As the rate ...

As the rate of dissolution, Eq. (8), is constant per unit surface area, the rate of precipitation from a supersaturated solution is given by the difference in the rates of precipitation and dissolution :

$$\text{Net rate of precipitation} = -\delta[CaCO_3^o]/\delta t$$

$$= K_p S_f \{CaCO_3^o - (CaCO_3^o)_s\} \quad (9)$$

The negative sign arises as the equations refer to the species in the bulk solution.

Irrespective of the saturation state of the water, the ion pair $CaCO_3^o$ must be in equilibrium with the free ions Ca^{++} and $CO_3^=$ in the aqueous phase, i.e.

$$(Ca^{++})_F(CO_3^=)_F/(CaCO_3^o) = K_3 \quad (10)$$

where K_3 = thermodynamic equilibrium constant for the ion pair $CaCO_3^o$.

Taking ionic strength effects into account Eq. (10) is written in the molar form :

$$[CaCO_3^o] = f_D{}^2[Ca^{++}]_F[CO_3^=]_F/K_3 \quad (11)$$

i.e.

$$[Ca^{++}]_F[CO_3^=]_F = [CaCO_3^o]K_3/f_D{}^2 \quad (12)$$

For a saturated solution :

$$[Ca^{++}]_F[CO_3^=]_F = K_{sp}/f_D{}^2 \quad (13)$$

where K_{sp} = solubility product constant for $CaCO_3$.

Substituting Eq. (13) into Eq. (10) and simplifying :

$$[CaCO_3^o]_s = K_{sp}/K_3 \quad (14)$$

Substituting Eqs. (11) and (14) into Eq. (9) :

$$-\delta[CaCO_3]/\delta t = K_p S_f f_D^2/K_3 \ \{[Ca^{++}]_F[CO_3^=]_F - K_{sp}/f_D{}^2\} \quad (15)$$

/ and defining ...

and defining $K_p/K_3 = K$

$$-d[CaCO_3]/dt = KS_f f_D^2\{[Ca^{++}]_F[CO_3^=]_F - K_{sp}/f_D^2\} \qquad (16)$$

Eq. (16) differs from Eq. (1) proposed by Reddy and Nancollas in that an activity coefficient term is included outside the bracket on the right-hand side of Eq. (16).

Replacing S_f in Eq. (16) by M, the mass concentration of a particular brand of crystal seed :

$$-d[CaCO_3]/dt = KMf_D^2\{[Ca^{++}]_F[CO_3^=]_F - K_{sp}/f_D^2\} \qquad (17)$$

Eq. (17) can also be derived as follows :

A general equation for interface controlled growth is given by Stumm and Morgan (1970) :

$$-dC/dt = K'S_f(C - Co)^n \qquad (18)$$

where S_f = surface area of crystals in solution

C = concentration of solution

Co = concentration of solution immediately surrounding the crystals

The term (C - Co) defines the supersaturation with respect to C. Making the modification proposed by Wiechers (i.e. substituting mass of seed crystals, M, for surface area, S_f) Eq. (18) becomes :

$$-dC/dt = K'M(C - Co)^n \qquad (19)$$

Applying Eq. (19) specifically to $CaCO_3$ precipitation : -

$$-d[Ca^{++}]_T/dt = K'M\{(CaCO_3^o) - (CaCO_3)_s\}^n \qquad (20)$$

The equilibrium equation for the $CaCO_3^o$ ion pair is : -

$$f_{Ca}[Ca^{++}]\,f_{CO_3}[CO_3^=]\,/\,[CaCO_3^o] = K_{CaCO_3} = K_{13} \qquad (21)$$

which can be written

$$[CaCO_3^o] = [Ca^{++}]\,[CO_3^=]\,f_{Ca}\,f_{CO_3}\,/K_{13} \qquad (22)$$

/ At saturated ...

At saturated equilibrium :

$$[CaCO_3^o]_s = [Ca^{++}]\,[CO_3^=]\;f_{Ca}\,f_{CO_3}\,/K_{13} \qquad (23)$$

Also at saturation the solubility product equilibrium for $CaCO_3$ must be satisfied, i.e.

$$[Ca^{++}]\,[CO_3^=] = K_{sp}/\,f_{Ca}\,f_{CO_3} \qquad (24)$$

Substituting Eqs. (22), (23) and (24) in Eq. (20) :

$$-\,d[Ca^{++}]_T/dt=K'M\left\{[Ca^{++}]_F[CO_3^=]_F\;f_{Ca}\,f_{CO_3}/K_{13}-K_{sp}/K_{13}\right\}^n \qquad (25)$$

Since $K = K'/K_{13}$

$$-d[Ca^{++}]_T/dt=KM\,(f_{Ca}\,f_{CO_3}\;[Ca^{++}]_F[CO_3^=]_F\;-Ksp/\,f_{Ca}\,f_{CO_3})^n \qquad (26)$$

Eq. (26) is proposed as an improved model for $CaCO_3$ precipitation.

Apparatus

Chemical reagents

Analytical reagent grade chemicals were used throughout. Calcium carbonate crystals (Hopkins and Williams, Analar grade) were used as seed. The solutions were made up using carbon dioxide free distilled water with a conductivity less than 5μS. Stock solutions (0.01M) of sodium bicarbonate, sodium hydroxide and calcium chloride were made up and standardized before each series of tests. The $NaHCO_3$ and NaOH were standardized against hydrochloric acid (0.01N) with borax as a primary standard. The $CaCl_2$ solution was standardized by the EDTA method (see Standard Methods).

Reactor

A reactor, designed by Wiechers (1973) was used for the study of the reaction kinetics with the minimal solution - atmosphere contact to minimise CO_2 transfer with the air. The reactor (see Figs. 1, 2, 3, 4, and 5) consists of a cylindrical vessel, constructed of thin perspex, with its interior sealed from the atmosphere by an O-ring sealed lid. It has four circular openings in the lid, lined with O-rings, to allow easy air-tight insertion of three probes, i.e. glass and calamel electrodes and a thermometer. The fourth hole is very small and allows air-solution pressure equalization. Two perspex cylinders are fitted to the reactor through a joint connection for the purpose of injecting the reactants. The reactants are well mixed within a period of two to three seconds. The temperature of the reactor is controlled by means of a

/ waterbath ...

and a Haake E51 thermostat. The reactants and buffers are placed in the waterbath to attain a constant temperature before use. The reaction solution is completely insulated (electrically) from its surroundings by using perspex screws and rubber O-rings, to prevent stray electric currents from affecting measuring probes. The solution is stirred by magnetic stirrer using a Teflon coated stirring bar.

<u>pH Meter</u>

The radiometer pH meter, type PHM 26, has the following specifications which make it suitable for measuring pH changes which occur as calcium carbonate is precipitated from solution :

Read out :	1,4 pH for full-scale detection.
Smallest scale div :	0,01 pH.
Repeatability :	± 0,002 pH.
Relative accuracy :	± 0,002 pH at buffer point. ± 0,005 pH sample in the range as buffer. ± 0,007 pH typical with buffer and sample in different ranges.
Amplifier drift :	± 0,002 pH/day non-accumulative.
Temperature compensation :	0 to $100^{\circ}C$
Recorder output :	10 mV/pH.

The pH meter has a built-in device to correct for loss of electrode sensitivity. The meter has an iso pH adjustment device with which the electrical zero of the output voltage can be set at any convenient value, for recorder purposes.

The glass electrode, G202C, is made of glass which responds very rapidly to pH changes.

/ NBS - standard buffers ...

NBS - Standard buffers

NBS standard buffers, in the pH range of interest, were used to calibrate the electrode system. Borax and phosphate buffer solutions were made up as follows : The borax buffer (0,01M) is prepared by dissolving 3,81 g. borax in fresh carbon dioxide free distilled water and making it up to one litre. The phosphate buffer is prepared by dissolving the following quantities of salts in distilled water and maing it up to one litre :

$K H_2PO_4$	3,44 g.
Na_2HPO_4	3,55 g.

The phosphates must be dried in an overn at 110°C for one to two hours and left to cool in a desicator.

The pH of these NBS standard buffers as a function of temperature is described by Bates (6), and is as follows :

Temperature °C	20,0	21,0	22,0	23,0	24,0
Borax pH	9,220	9,210	9,200	9,195	9,185
Phosphate pH	6,880	6,876	6,872	6,868	6,864

The accuracy of the pH of the buffers is given as ± 0,01 pH.

Strip chart recorder

The Hewlett Packard strip chart recorder type 7100B with amplifier module type 17501A has a chart speed range which covers all the speeds necessary to study the calcium carbonate precipitation reactions. Its specifications are : -

Recorder mechanism :	Servo activated electro-burning pen drive.
Response time :	One half second for full scale.

/ Chart speeds ...

Chart speeds :	1;2 in/hour: 0,1; 0,2; 0,5; 1;2 in/minute: 0,1; 0,2; 0,5 1;2 in/second

Experimental method

The volume of the reactor was 500 ml. Two 250 ml. flasks one containing the sodium bicarbonate and sodium hydroxide solutions and the other containing the calcium chloride solution, were made up and placed in the waterbath to attain the required temperature. The pH meter and recorder were calibrated using NBS standard buffers. The carbonate solution, together with the required mass of seed, was poured into the reactor and the pH electrodes and thermometer were positioned in their respective holes in the reactor. The calcium solution was poured into the injecting cylinder. The stirrer in the reactor was switched on. When the valve of the injecting cylinder was opened (i.e. when mixing of the Ca^{++} and $CO_3^{=}$ solutions began) $CaCO_3$ ion pairs were immediately formed which resulted in an instantaneous decrease in pH (see Fig. 6) due to the removal of free $CO_3^{=}$ ions from solution. Thereafter as the reaction proceeded and $CaCO_3$ precipitated, the pH dropped, and a graph of pH versus time was recorded. As the $CaCO_3$ precipitates the acidity remains constant and the pH and alkalinity decrease. Therefore, since the initial alkalinity was known and the change of pH was recorded, the change in alkalinity (and hence the rate of $CO_3^{=}$ removal) could be calculated (see Appendix A). For each part of $CO_3^{=}$ that is removed one part of $CaCO_3$ is precipitated. Therefore if the rate of $CO_3^{=}$ removal is known, then the rate of calcium removal can be calculated.

Back mix reactors

The method of running the precipitation tests described above is unlikely to be duplicated in practical processes. In water treatment works it is more probable that back mix reactors will be used in preference to batch reactors. Therefore in order to establish whether the data obtained under batch conditions also applied to backmix reactors, a series of steady state experiments were done. The experimental apparatus was similar to that used for batch tests but modified as follows : Two CO_2 free feed tanks are connected to the reactor. The one tank contains a carbonate solution and the other a calcium solution together with $CaCO_3$ seed crystals (Hopkins and Williams Analar brand) at a concentration of 1800 ppm (see Fig. 7). The seed is kept in suspension in the feed tank by means of a magnetic stirrer. Solutions from each tank are pumped at equal ratios into the reactor and the pH of the reactor contents is monitored.

For any given hydraulic retention time, the flow is maintained until the pH attains a steady reading and remains steady for a period of two retention times. The influent feeds are then stopped and the decrease in pH with time is recorded for a period until the pH shows no significant change. The feed flows are then restarted to give a different hydraulic retention time in the reactor.

At any particular steady state, knowing only the pH, temperature, alkalinity and concentration of Ca^{++} of the influent feeds, it is possible to determine each of the parameters in Eq. (17) (exactly as was done for the batch tests described previously). Consequently the $CaCO_3$ supersaturation at steady state can be calculated. Also, when the feed flow is stopped the rate of precipitation can be calculated, the initial rate giving an

/ estimate ...

estimate of the rate at that particular steady state. By this means a value for the reaction constant, K, is determined for each steady state condition (see Table 2).

By comparing the values of K obtained for batch tests (Table 1) and those for completely mixed tests (Table 2) it can be seen that they are very similar. Therefore batch tests, which are simpler and less time-consuming to run, can be used to establish data for completely mixed conditions. The work reported here, on both batch and completely mixed reactors utilised pure solutions and pure seed masses. The absolute value of K is very sensitive to the type of seed. This was verified by using the same brand of $CaCO_3$ crystals, but from a different manufactured batch, when the K values were notably different (see Fig. 9). Therefore it is very likely that the absolute value of K will differ between laboratory and full scale works where the seed crystals are self-generated.

Specifically to separate the effects of pH and supersaturation on the rate constant K, in a proportion of tests the supersaturation was kept constant but the initial pH varied and vice versa. The initial pH of the experiments covering a range from 8,6 to 10,3 was controlled by varying the relative concentration of the hydroxide and bicarbonate solutions. The initial $CaCO_3$ supersaturation* was varied from 100 to 2500 ppm (as $CaCO_3$) by adding different concentrations of calcium and carbonate solutions.

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* "Supersaturation" refers to the parameter $(CaCO_3^o - (CaCO_3^o)_s)$ which is the apparent instantaneous supersaturation; this parameter will not equal the mass concentration of $CaCO_3$ to be precipitated because with precipitation there is a resultant decrease in pH which decreases the concentration of $CO_3^=$ in solution.

Analysis

In Eq. (26) to determine the variation in the rate constant, K, an analysis must first be carried out to establish the reaction order, n. By taking the log of Eq. (26) :

$$\log(d[Ca^{++}]_T/Mdt)=\log K+n\log(f_{Ca}f_{CO_3}[Ca^{++}]_F[CO_3^=]_F-K_{sp}/f_{Ca}f_{CO_3}) \quad (27)$$

The value of n is determined by plotting :

$$\log(d[Ca^{++}]_T/Mdt) \text{ versus } \log(f_{Ca}f_{CO_3}[Ca^{++}]_F[CO_3^=]_F-K_{sp}/f_{Ca}f_{CO_3})$$

The slope of the plot gives the value of the reaction order, n. The values of n are listed (see Table 1). The mean value of $n = 0{,}98 \pm 0{,}09$ indicates an apparent first order reaction (i.e. n=1) with respect to Ca CO_3^o supersaturation. If n equals unity, the value of K can be determined either by substituting n = 1 in Eq. (27) or by plotting Eq. (26), i.e. :

$$d[Ca^{++}]/dt \text{ versus } Mf_{Ca}f_{CO_3}\{[Ca^{++}]_F[CO_3^=]_F - K_{sp}/f_{Ca}f_{CO_3}\}$$

The slope of the plot above gives the value of K (see Fig. 9). Both methods will yield the same results. Note in Fig. 8 that the plots for seed concentrations equal to 900 ppm approximate to straight lines, i.e. in these experiments the value of K remained constant throughout the precipitation period even though the pH and $CaCO_3^o$ supersaturation were steadily decreasing. The dependence of K on initial pH and/or initial super saturation was determined by plotting K versus pH (Fig. 10) and K versus initial supersaturation (Fig. 8). From Fig. 10 it would appear that there is no decided relationship between pH and K. At any particular pH a range of K values can be obtained. This data tends to show that the conclusion of Wiechers <u>et al</u> - that the rate constant depends on initial pH - is not sustained.

/ From Fig. 13 ...

From Fig. 8 there appears to be a decided relationship between K and the initial $CaCO_3$ supersaturation. A functional relationship between K and the initial $CaCO_3^o$ supersaturation was identified from various plots assuming different basic relationships. A basic relationship of the kind expressed by Eq. (28) was found to give excellent correlation :

$$K = Ko + (Km - Ko)\ (1 - e^{c'S}) \qquad (28)$$

where K = rate constant (ppm Ca^{++} precipitated as $CaCO_3$). $(min)^{-1}$ (ppm $CaCO_3$ seed. ppm $CaCO_3$ supersaturation as $CaCO_3)^{-1}$

= (min. ppm as $CaCO_3)^{-1}$

Km = maximum value of K

Ko = value of K at zero supersaturation

c' = constant

S = initial $CaCO_3$ supersaturation (ppm as $CaCO_3$)

The functional relationship was established as follows. A value of Km was assumed and for each experimental K value the function (Km - K) was found and plotted against initial supersaturation on semi-log paper (Fig. 11). By trial and error a value of Km was found that gives a straight line plot ($Km=3{,}25.10^{-5}$). The difference between Km and the K values given by the intersection of the straight line plot with the abscissa provides an estimate of the rate constant at zero supersaturation ($Ko = (3{,}25-2{,}65).10^{-5} = 0{,}60.10^{-5}$), (see Fig. 11). The slope of the plot gives an estimate of $C' = 0{,}00162$. Substituting numerical values, Eq. (15) becomes :

$$K.10^5 = 0{,}60 + \left[2{,}65(1-e^{-0{,}00162S})\right] \text{ (min. ppm. as } CaCO_3)^{-1} \qquad (29)$$

The fact that K is a function of the initial supersaturation (Eq. 29) leads to a contradiction:

/ From Eq. (26) ...

From Eq. (26)

$d[Ca^{++}]_T/dt$ = KM (supersaturation)

and at the initial state this must be :

$d[Ca^{++}]_T/dt$ = KM(initial supersaturation)

But K = function (initial supersaturation)

Substituting for K at the initial state :

$d[Ca^{++}]_T/dt$ = function (initial supersaturation)M(initial supersaturation)

From this contradiction it would appear that the precipitation model is wrongly formulated, i.e. that the equation of Reddy and Nancollas and the one proposed in this thesis do not adequately explain the precipitation phenomena.

A number of practical consequences are exposed in this investigation. In back mix reactors in water softening plants where the $CaCO_3$ supersaturation is low, the rate of precipitation is very slow. This means that either there must be a long hydraulic retention time or else the mass of crystals in the reactor must be large to speed up the precipitation. Also the rate of precipitation will be slow in pipes in water supply systems where the supersaturation is usually very low.

Summary and Conclusion

1. The equation proposed by Nancollas and Reddy, to describe $CaCO_3$ precipitation rate, was modified to :

   $$d[Ca^{++}]_T/dt=KM(f_{Ca}f_{CO_3}\{[Ca^{++}]_F[CO_3^{=}]_F-K_{sp}/f_{Ca}f_{CO_3}\})$$

2. It was established that batch tests give similar values for K to the back mix reactions.

3. The reaction approximates to a first order reaction with $n = 0{,}98 \pm 0{,}09$

4. The rate constant, K, appears to be independent of pH.

5. In both batch and steady state tests the value of K is very sensitive to the type of seed mass.

6. For batch and back mix reactions K varies with initial $CaCO_3$ supersaturation according to the expression :

   $$K.10^5 = 0{,}60 + [2{,}65\ (1-e^{-0{,}00162S})]\ (\text{min. ppm. as } CaCO_3)^{-1}$$

   The fact that K is a function of initial supersaturation leads to a contradiction since, at the initial state, both the rate and K are functions of the initial $CaCO_3$ supersaturation. Therefore it would appear that the formulation of Reddy and Nancollas is not sustained.

   From this investigation the following practical conclusions can be drawn :

   a) In back mix reactors in water softening plants the supersaturation is usually very low and hence the rate of precipitation is slow. In order to speed up the precipitation a large seed mass is required.

   b) Precipitation will be slow in water supply systems where the supersaturation is usually very low.

TABLE 1.

Expt. No.	Initial pH	Initial $CaCO_3^{\circ}$ Supersaturation ppm as $CaCO_3$	Seed mass mg/ℓ	Reaction Order n	Reaction Constant $K(min)^{-1}.(ppm\ as\ CaCO_3)^{-1}$
1	8,60	135	900	0,89	1,16
2	8,72	166	900	0,72	1,09
3	9,34	241	900	0,72	1,41
4	8,90	245	900	0,79	1,36
5	9,20	279	900	0,97	1,43
6	9,61	287	900	1,06	1,71
7	8,88	301	900	1,00	1,85
8	9,55	308	900	0,89	1,75
9	9,00	320	900	0,90	1,65
10	9,95	463	900	0,98	2,16
11	9,20	482	900	0,93	2,20
12	9,18	529	900	0,96	2,10
13	9,56	616	900	1,01	2,30
14	8,83	630	900	0,90	2,10
15	9,37	656	900	0,98	2,40
16	9,50	740	900	0,95	2,40
17	9,48	754	900	1,06	2,60
18	9,05	786	900	0,94	2,26
19	9,62	952	900	1,04	2,63
20	9,60	995	900	1,02	2,65
21	9,61	1000	900	1,02	2,80
22	9,73	1200	900	1,02	2,91
23	9,83	1210	900	0,99	3,00
24	9,77	1304	900	1,04	2,85
25	9,59	1623	900	1,00	3,00
26	10,00	2061	900	1,06	3,07
27	10,13	2190	900	1,18	2,90
28	9,68	2443	900	0,97	2,75
29	10,30	2500	900	1,12	2,75
30	10,28	2227	1500	1,08	2,72
31	10,00	1290	1500	1,05	2,75
32	9,80	1250	1500	1,06	2,90
33	9,77	905	1500	1,01	2,56
34	9,64	888	1500	0,97	2,65
35	9,35	627	1500	0,99	2,10
36	9,65	954	300	1,06	2,75
37	9,36	697	300	1,00	2,57
38*	9,78	840	900	0,95	1,02

* Batch B of seed crystals

TABLE 2.

Expt. No.	Steady State Supersaturation ppm as $CaCO_3$	Seed Mass mg/ℓ	Reaction constant K $(\text{min})^{-1}.(\text{ppm as } CaCO_3)^{-1}$
1	1220	900	2,58
	533	915	2,30
	434	919	2,30
	353	923	2,00
	242	927	1,70
	199	929	1,15
2	542	914	2,30
	224	927	1,70
	175	930	1,15
3	829*	900	1,05
	639*	912	0,96
	450*	918	0,84
	316*	922	1,00
	247*	925	0,90

* Batch B of seed crystals

LIST OF SYMBOLS

C = concentration of solution (mass.unit vol^{-1})

S_f = surface area of crystals in solution

S = initial $CaCO_3$ supersaturation (ppm as $CaCO_3$)

C_o = concentration of solution immediately surrounding crystals (mass.unit vol^{-1})

$[\ ]_T$ = total concentration of solution (ppm as $CaCO_3$)

$[\ ]_F$ = concentration of free solution (ppm as $CaCO_3$)

K_{sp} = solubility product for Calcite

f_D = activity coefficient for divalent ion

f_{ca} = activity coefficient for Calcium ions

F_{co_3} = activity coefficient for Carbonate ions

t = time (min)

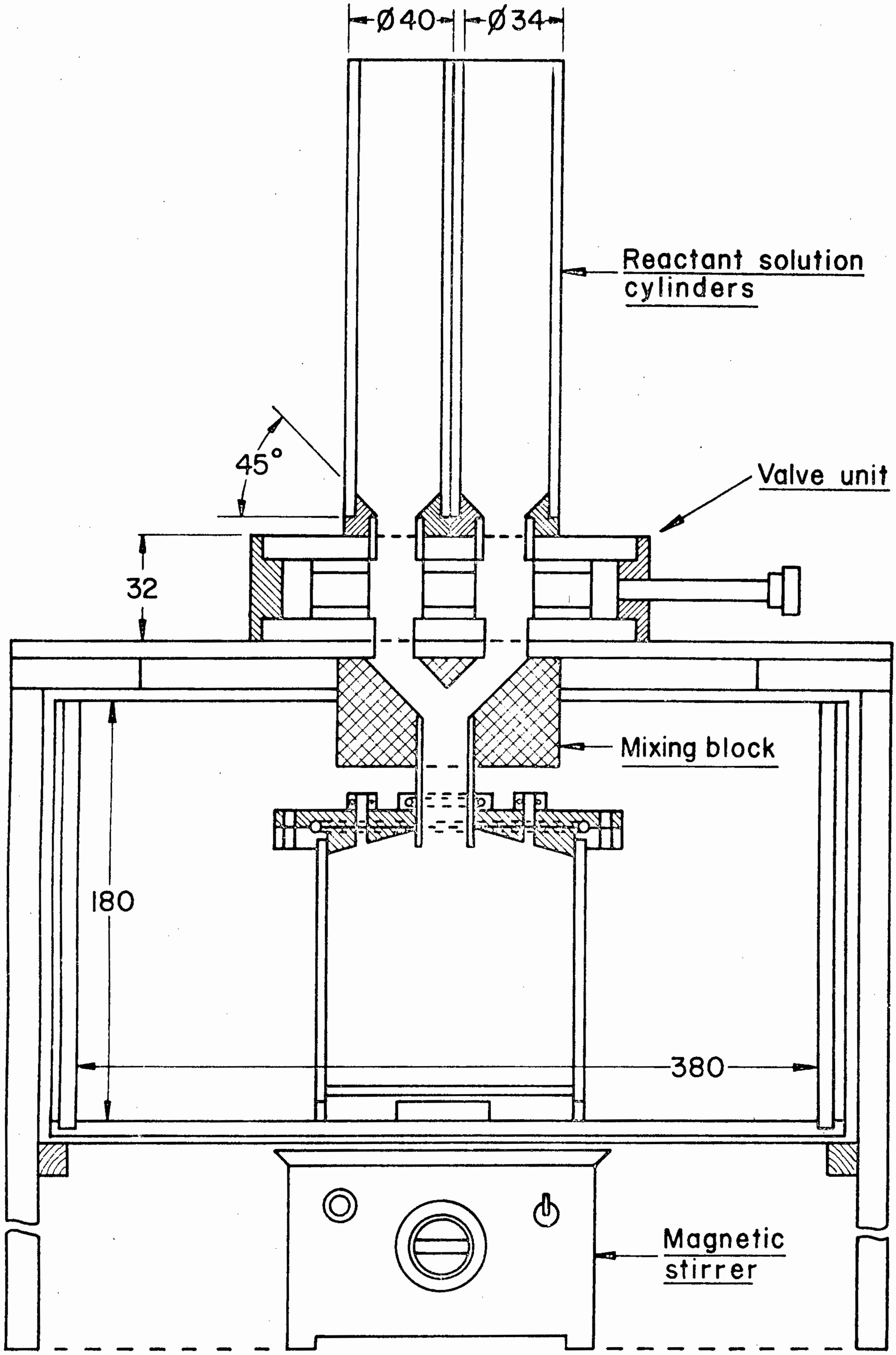
M = Mass concentration of seed crystals (ppm as $CaCO_3$)

K = rate constant (ppm Ca precipitated as $CaCO_3$).$(min)^{-1}$.(ppm $CaCO_3$ seed.ppm $CaCO_3$ supersaturation as $CaCO_3)^{-1}$

= (min.ppm as $CaCO_3)^{-1}$

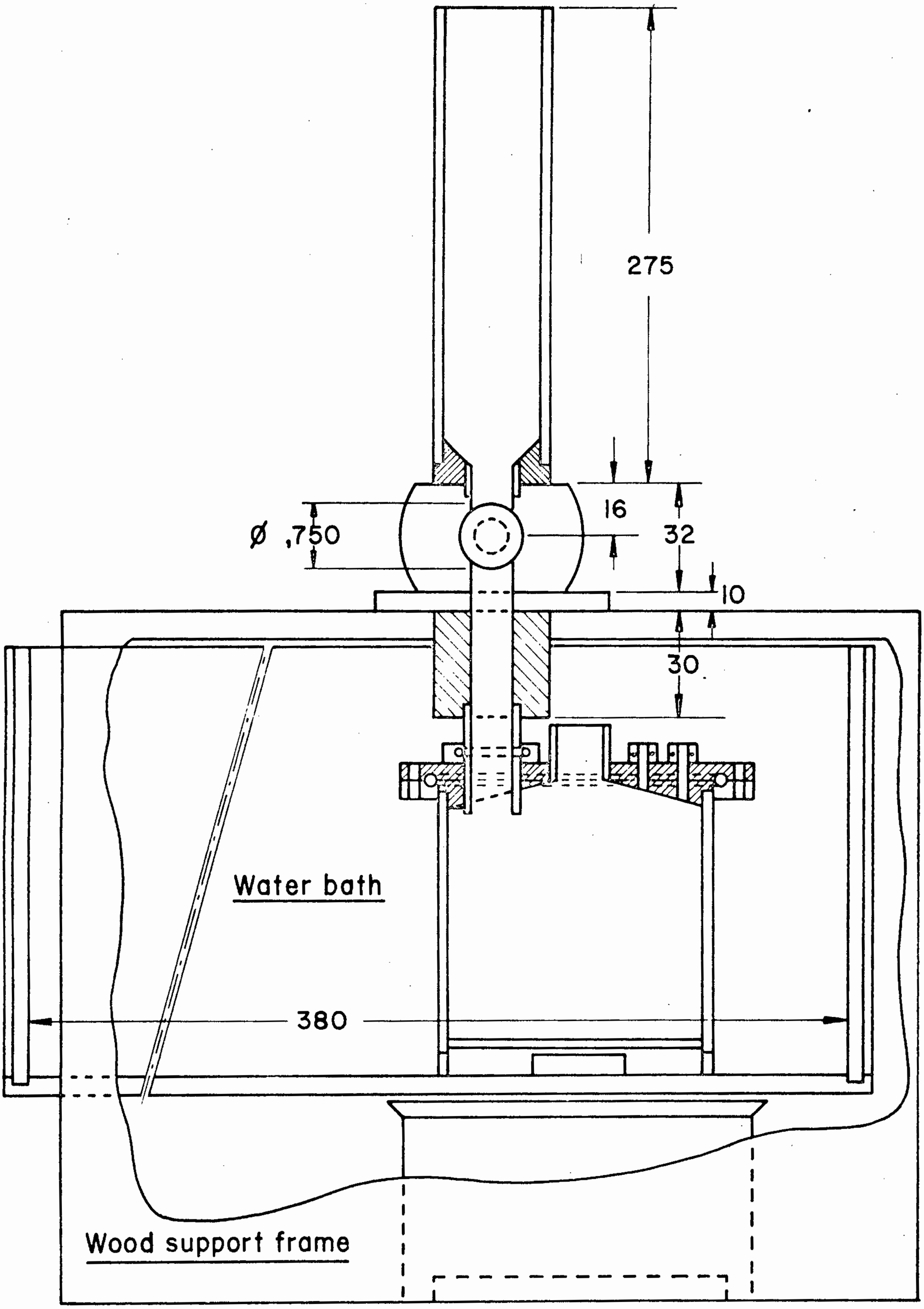
K_m = maximum value of K

K_o = value of K at zero $CaCO_3$ supersaturation



NOT TO SCALE

Fig. 1 Front elevation of water bath, supporting frame and reactor vessel.



NOT TO SCALE

Fig. 2 Side elevation of water bath, supporting frame and reactor vessel.

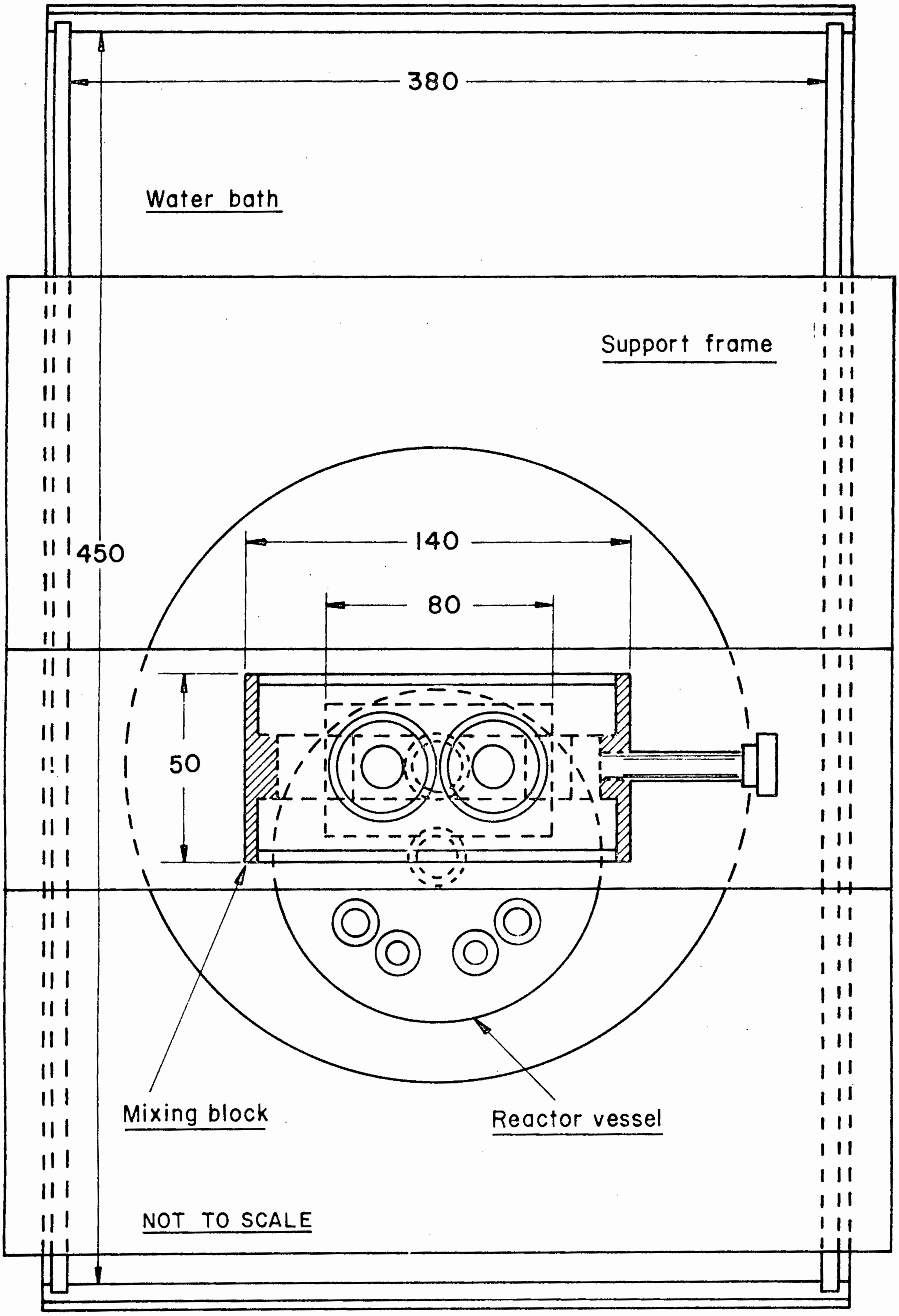


Fig. 3 Plan of water bath, supporting frame and reactor vessel.

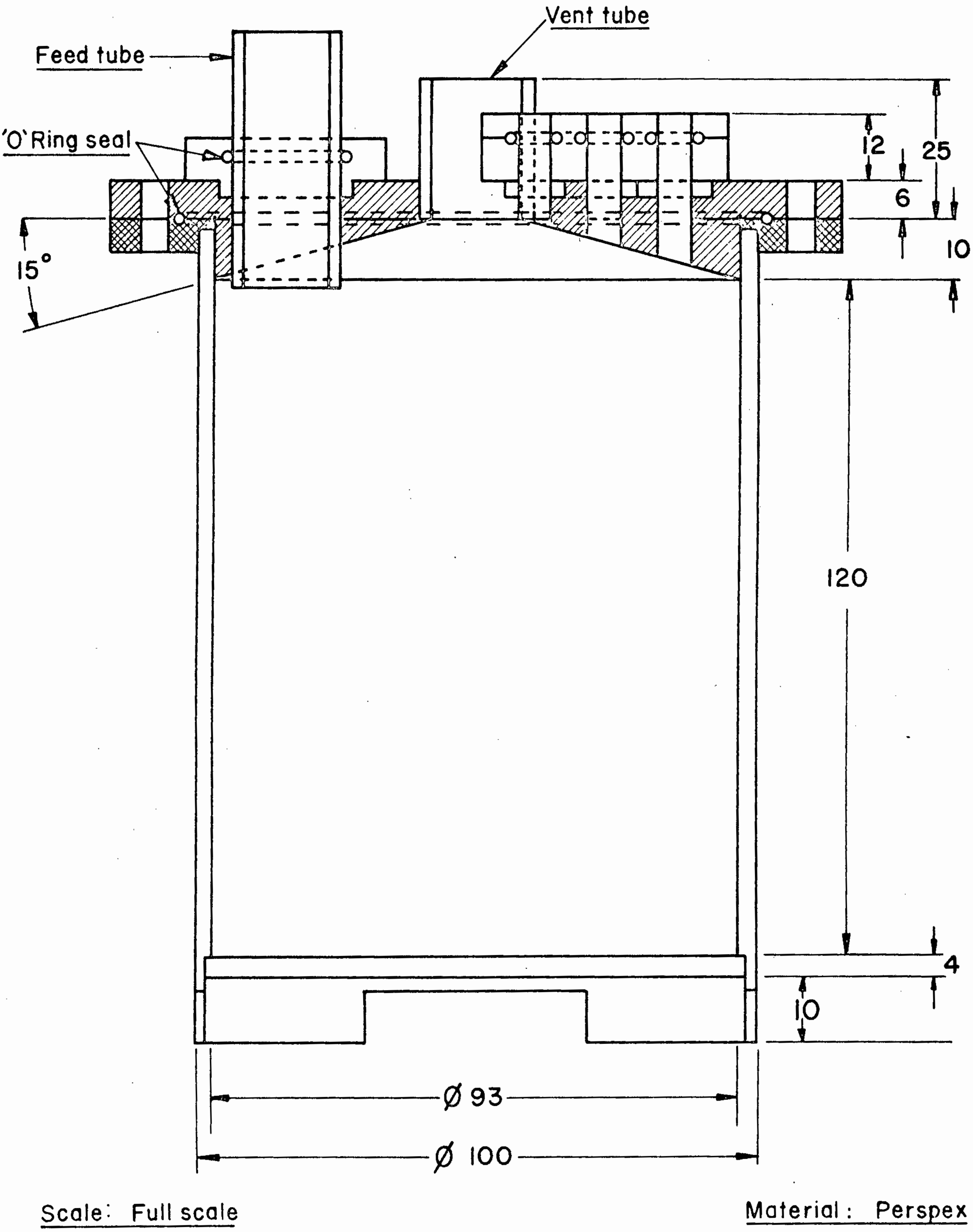


Fig. 4 Elevation of reactor vessel.

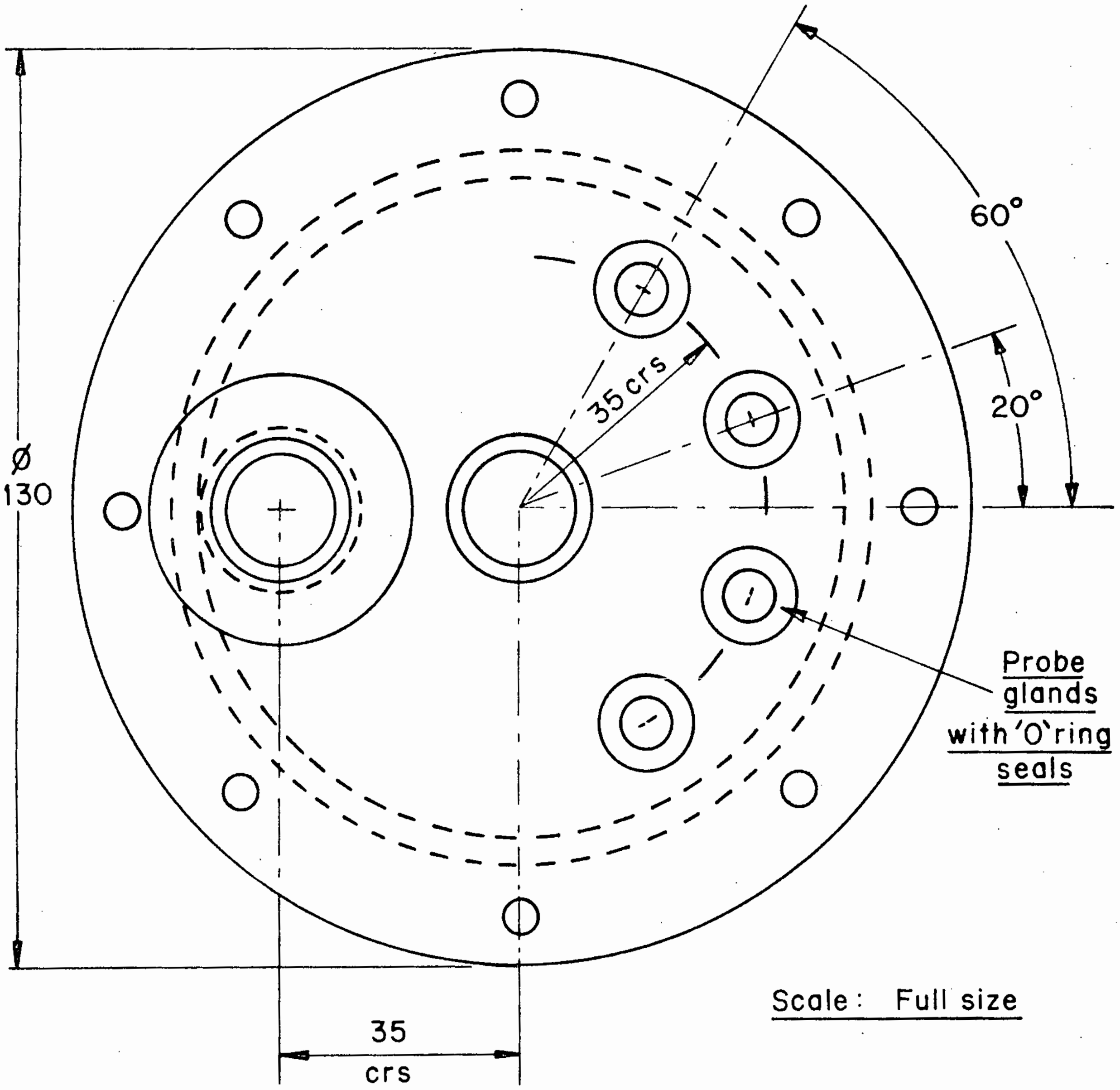


Fig. 5 Plan of reactor vessel.

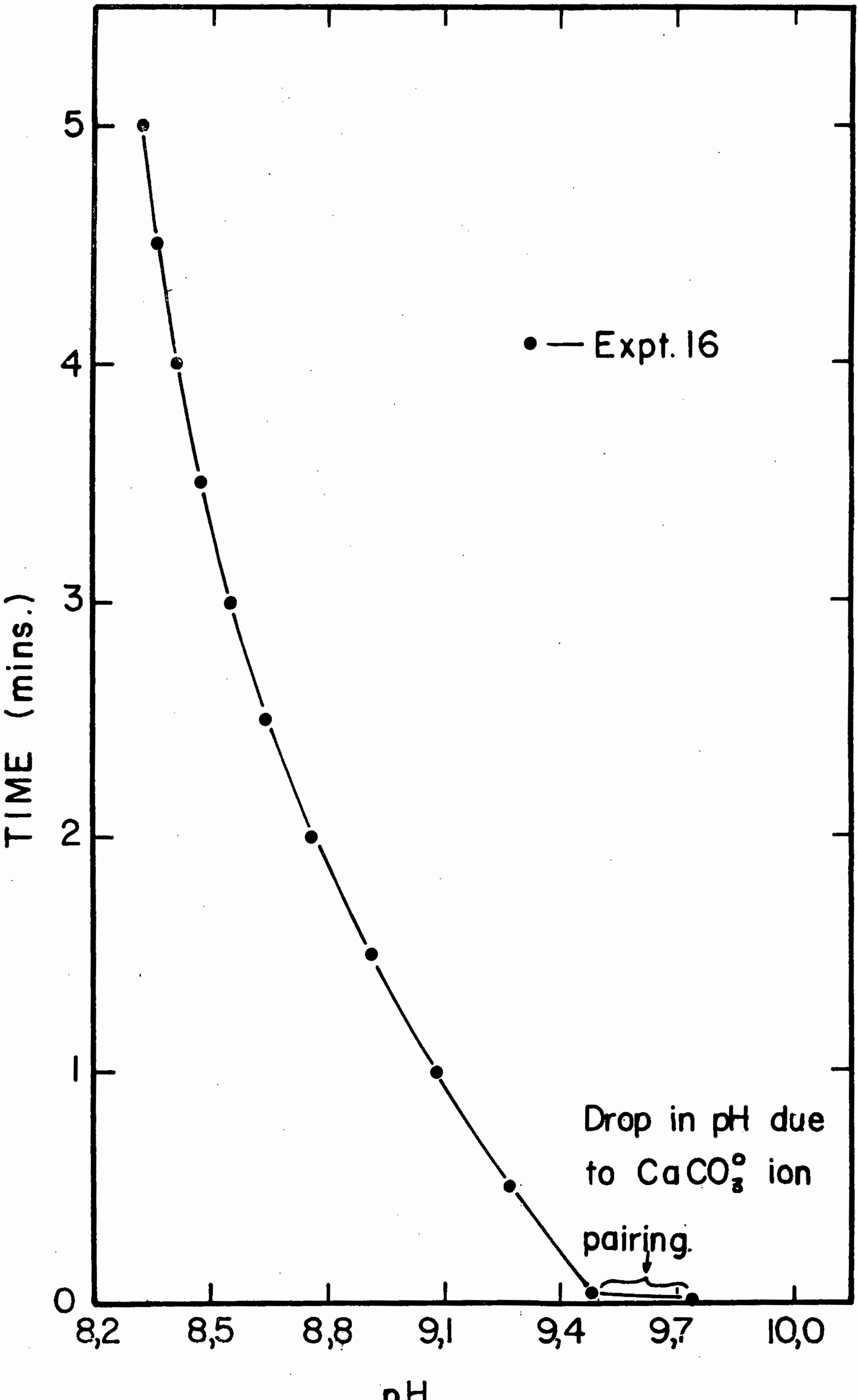


Fig. 6 Relationship between time and pH. The pH drops instantaneously at start of reaction due to pairing of Ca^{++} and $CO_3^=$ ions and thereafter decreases steadily as $CO_3^=$ is removed from solution.

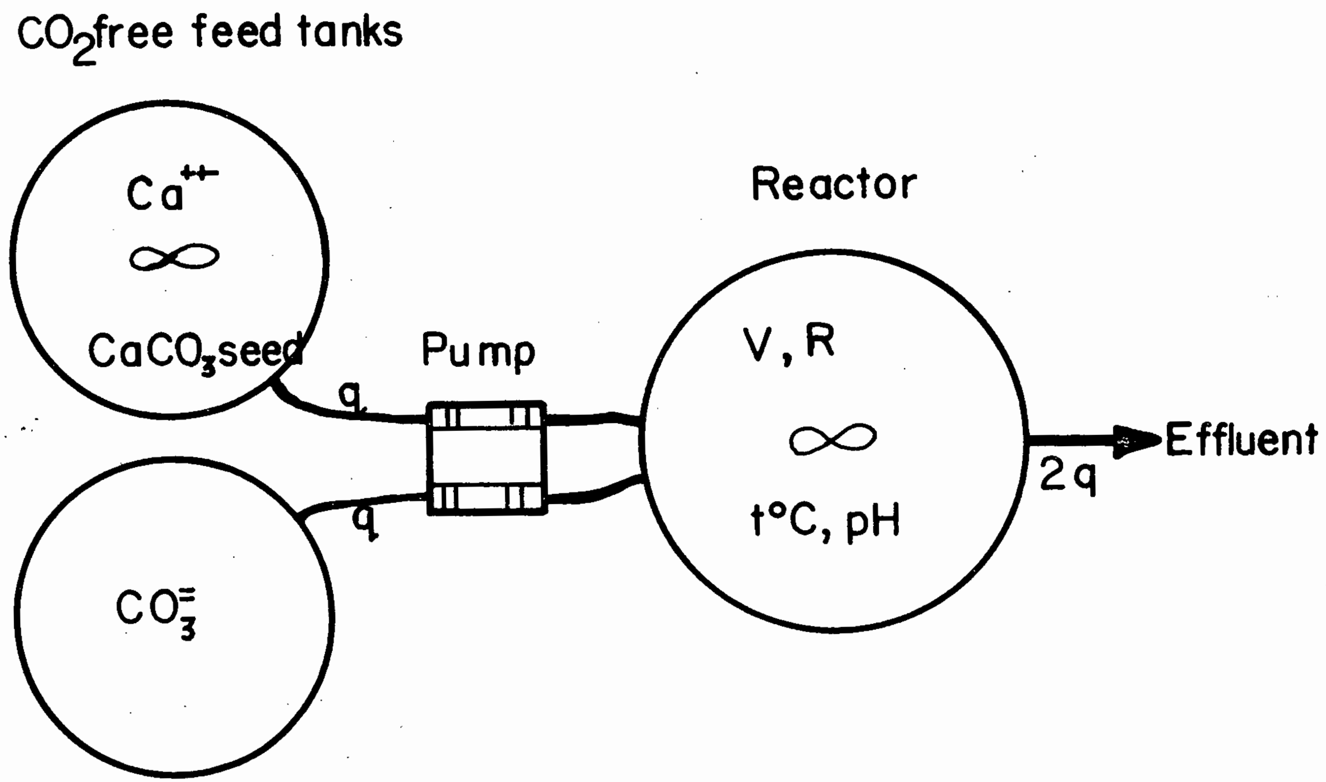


Fig. 7 Schematic diagram of apparatus for steady state tests.

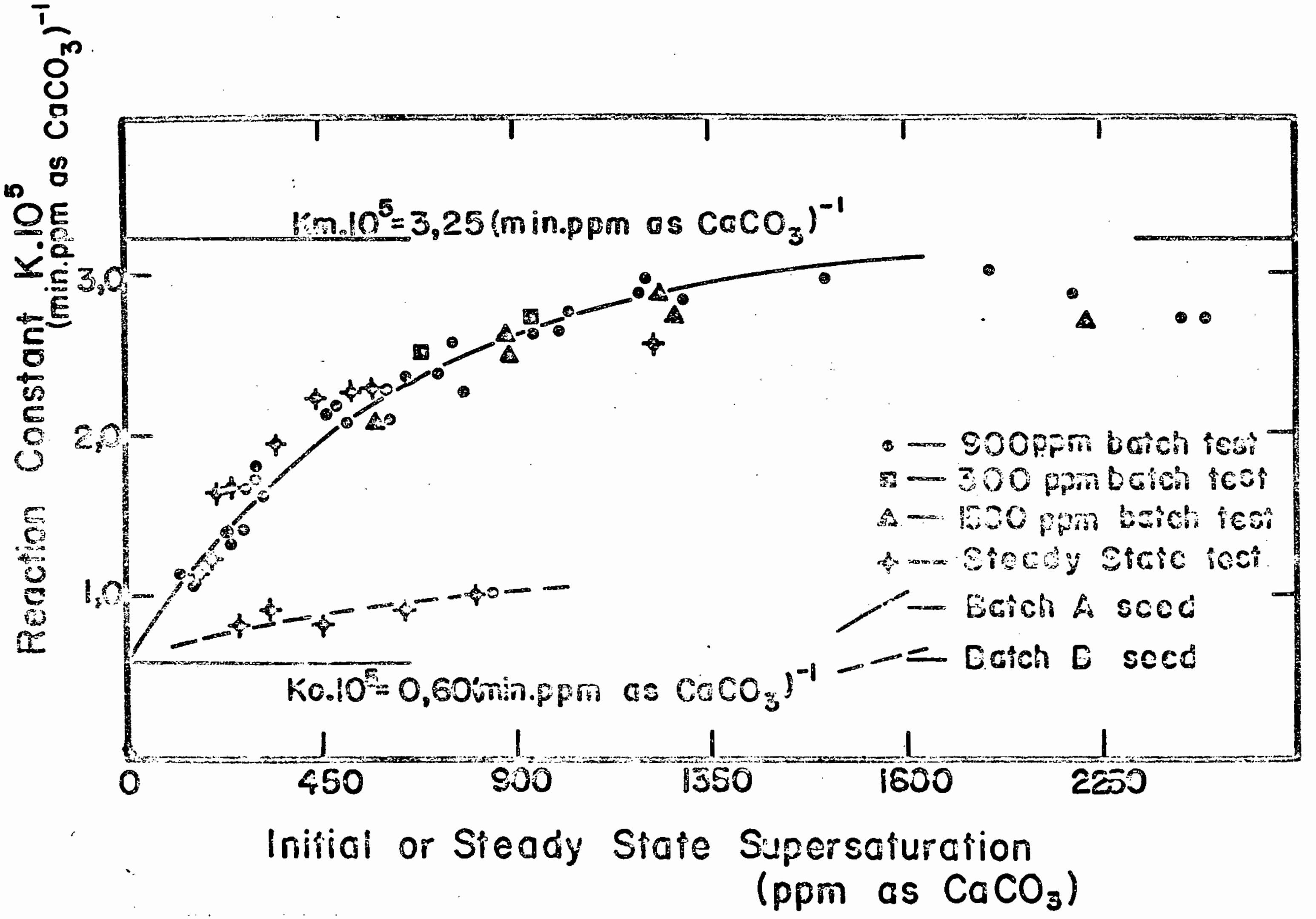


Fig. 8 Relationship between rate constant, K, and initial CaCO$_3$° supersaturation.

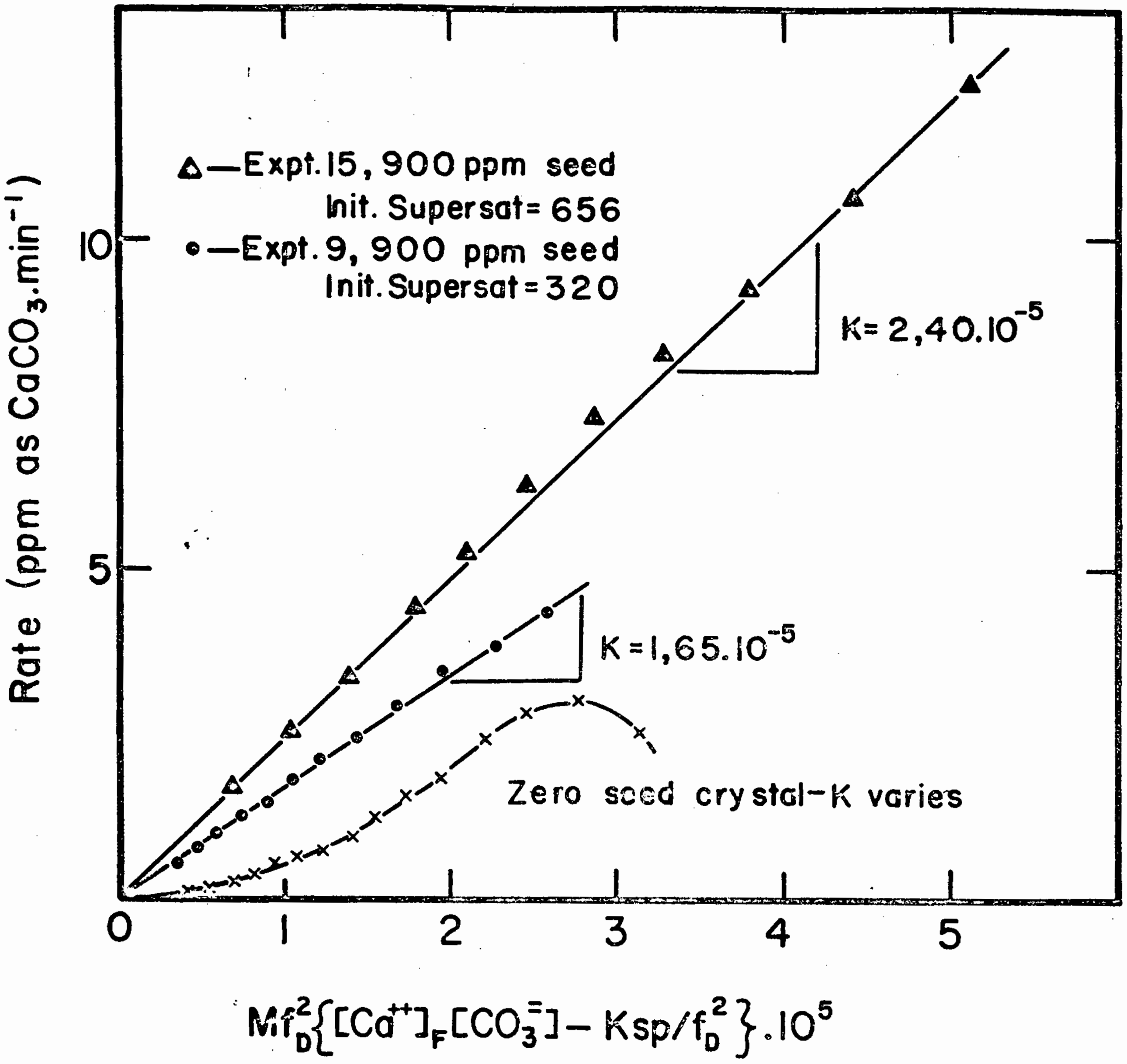


Fig.9. Relationship between the rate of Ca^{++} precipitation and the function $Mf_D^2\{[Ca^{++}]_F[CO_3^=]_F - K_{sp}/f_D^2\}.10^5$.

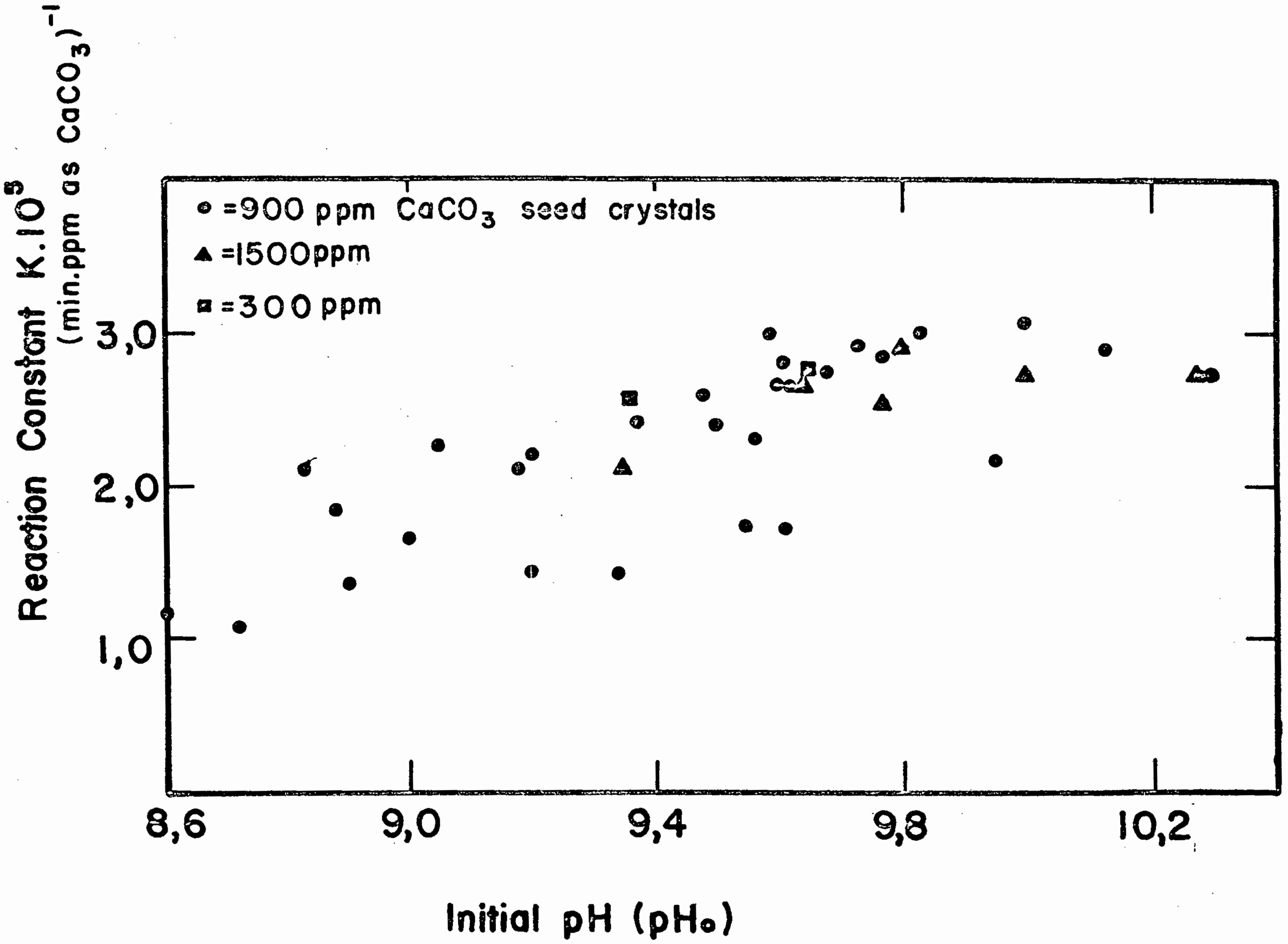


Fig. 10 No apparent relationship between rate constant, K, and initial pH.

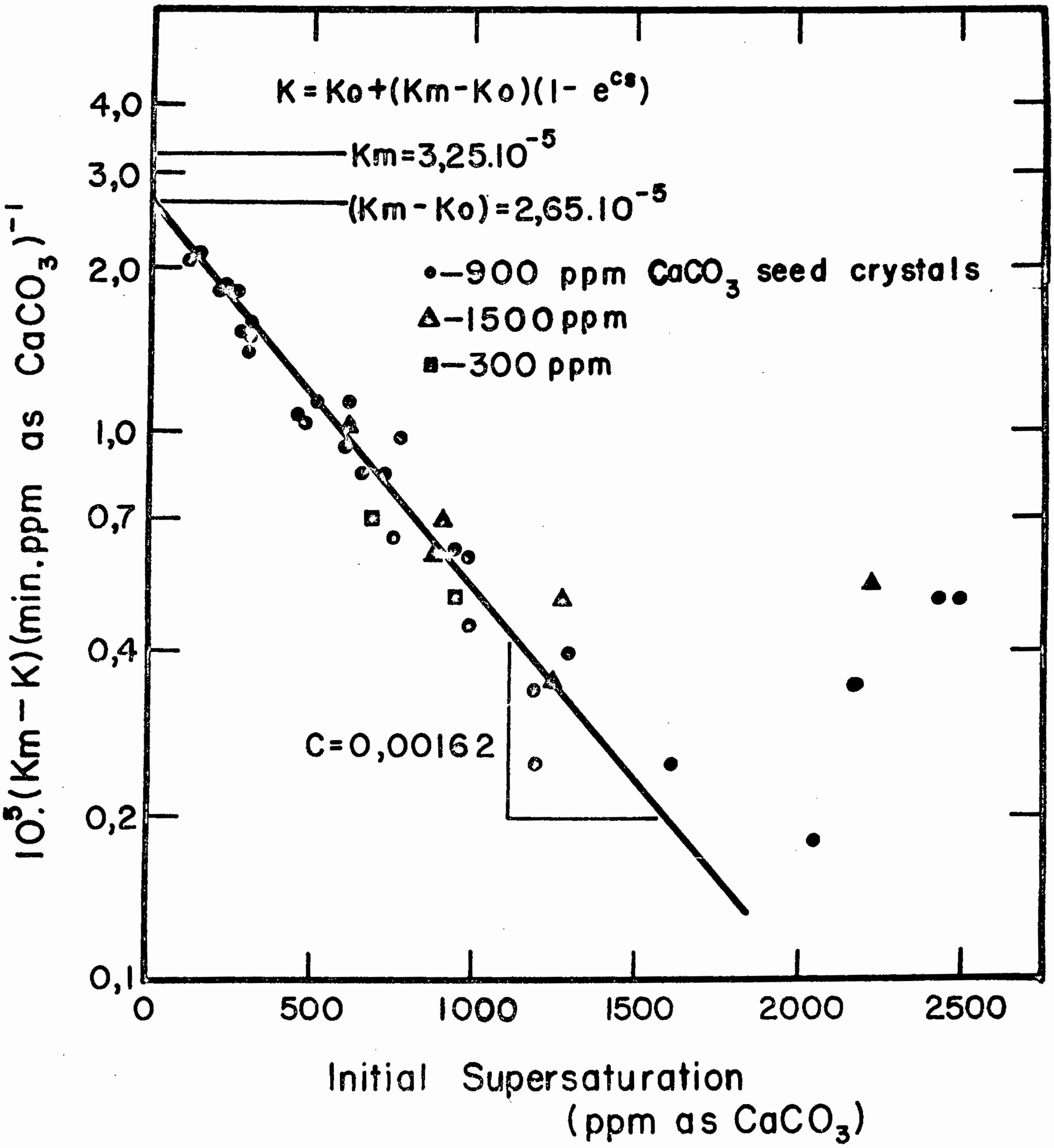


Fig.11 Method of plotting the relationship $K = K_o + (K_m - K_o)(1 - e^{cs})$ on a semi-log scale.

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Appendix A

The procedure for calculating the parameters that influence Eq. (26) is described below. The method utilizes the relationship between Alkalinity, Acidity and pH (Loewenthal and Marais, 1973). The method is not restricted to any pH range.

The pH in a water containing only carbonic species and associated cations is governed by equilibria reactions between the carbonic species (H_2CO_3, HCO_3^-, and $CO_3^=$) and water species (H^+ and OH^-). These equilibria are :

$$(HCO_3^-)_F(H^+)/(H_2CO_3^*) = K_1 \qquad (A1)$$

$$(CO_3^=)_F(H^+)/(HCO_3^-)_F = K_2 \qquad (A2)$$

$$(OH^-)_F(H^+) = K_w \qquad (A3)$$

where ( ) indicate active concentrations

K_1, K_2 and K_w = thermodynamic equilibrium constants

Subscript 'F' refers to free ion species

If Ca^{++} and Na^+ are in the water ion pairing will occur between these cations and the anions $CO_3^=$, HCO_3^- and OH^-. Equilibria equations for these ion pairing reactions are :

$$(Ca^{++})_F(CO_3^=)_F/(CaCO_3^o) = K_{CaCO_3} \qquad (A4)$$

$$(Ca^{++})_F(HCO_3^-)_F/(CaHCO_3{}^+) = K_{CaHCO_3} \qquad (A5)$$

$$(Ca^{++})_F(OH^-)_F(CaOH^+) = K_{CaOH} \qquad (A6)$$

$$(Na^+)_F(CO_3^=)_F/(NaCO_3^-) = K_{NaCO_3} \qquad (A7)$$

$$(Na^+)_F(HCO_3^-)_F/(NaHCO_3^o) = K_{NaHCO_3} \qquad (A8)$$

$$(Na^+)_F(OH^-)_F/(NaOH^o) = K_{NaOH} \qquad (A9)$$

/ For equilibriaum

For equilibrium, Eqs. (A1 to A9) must be simultaneously satisfied. The following mass balance expression must also be satisfied :

$$[Na^+]_T = [Na^+]_F + [NaHCO_3^-] + [NaOH^o] \qquad (A10)$$

$$[Ca^{++}]_T = [Ca^{++}]_F + [CaHCO_3^+] + [CaCO_3^o] + [CaOH^+] \qquad (A11)$$

$$\text{Alkalinity} = 2[CO_3^=]_T + [HCO_3^-]_T + [OH^-]_T - [H^+] \qquad (A12)$$

$$\text{Acidity} = 2[H_2CO_3^*] + [HCO_3^-]_T + [H^+] - [OH^-]_T \qquad (A13)$$

$$[HCO_3^-]_T = [HCO_3^-]_F + [CaHCO_3^+] + [NaHCO_3^o] \qquad (A14)$$

$$[CO_3^=]_T = [CO_3^=]_F + [CaCO_3^o] + [NaCO_3^-] \qquad (A15)$$

$$[OH^-]_T = [OH^-]_F + [CaOH^+] + [NaOH^o] \qquad (A16)$$

where $[\ ]$ indicates molar concentrations, and subscript T indicates the sum of free and ion paired species.

In the sixteen Eqs. (A1) to (A16) there are eighteen unknown parameters (i.e. $H_2CO_3^*$, HCO_3^-, $CO_3^=$, OH^-, H^+, Ca^{++}, $CaHCO_3^+$, $CO_{3T}^=$, Ca_T^{++}, $CaOH^+$, $CaCO_3^o$, Na^+, $NaHCO_3^o$, $NaCO_3^-$, $NaOH^o$, OH_T^-, Alkalinity and Acidity). To determine each of the parameters at least two must be measured.

In the method of solution described below, to initiate the solution theoretically only the initial pH and initial alkalinity need be measured and thereafter as $CaCO_3$ precipitation proceeds only pH needs to be measured for an additional condition applies i.e. the Acidity remains constant during precipitation and equals the initial value.

/Initially ...

Initially Alkalinity and Acidity were determined as follows : Solutions of $NaHCO_3$ and NaOH were standardized against a strong acid of known concentration. The standardized solutions of $NaHCO_3$ and NaOH were then used as the source of Alkalinity and Acidity for a particular test, thus

$$\text{Initial Alkalinity} = [NaHCO_3]_{added} + [NaOH]_{added}$$

$$\text{Initial Acidity} = [NaHCO_3]_{added} - [NaOH]_{added}$$

Initial pH was measured using a glass electrode. However, CO_2 exchange between the solution and atmosphere may occur during the experimental preparation. Such CO_2 exchange would alter the initial Acidity (estimated from the known masses of standard solutions used); the Alkalinity would not be affected. Thus, the best estimate of initial Acidity is calculated from the initial measured Alkalinity and the observed initial pH using Eqs. (A1) to (A16). Usually the Acidity based on the measured pH was about 2 ppm as $CaCO_3$ greater than the observed Acidity. A theoretical check was carried out for each experiment as follows : Using the initial Alkalinity and Acidity values (based on the masses of standard solutions used) a theoretical value of initial pH was calculated using Eqs. (A1) to (A16) and compared with the initial observed pH.

<u>Determination of initial Acidity from known Alkalinity and pH</u>

1. Calculate an initial approximate value for ionic strength, μ, from the mass concentrations of NaOH, $NaHCO_3$ and $CaCl_2$ used in an experiment.
2. Using the extended Debye Hueckel equation calculate the activity coefficients for each of the charged species

/ from the value of ...

from the value of μ above. (The ionic radius for monovalent hydrated ion pairs was assumed equal to that for HCO_3^-).

3. Calculate activity coefficients for neutral species from the relationship $-\log_{10} f_N = k_s . \mu$ (Garrels and Christ, 1965,) where f_N = activity coefficient for neutral species

   k_s = salting out coefficient for neutral species in water.

4. Calculate thermodynamic equilibrium constants, at the experimental temperature from the enthalpy and entropy for the reaction using the equation proposed by Helgesson (1969).

5. Adjust equilibrium constants for ionic strength effects to give K'.

6. Calculate $[H^+]$ from the measured pH and the approximate value for the activity coefficient, f_H, determined in setp (2), i.e. $[H^+] = (10.^{-pH})/f_{H.}$

7. Calculate an approximate initial value for $[HCO_3^-]_F$ from measured Alkalinity and pH assuming no ion pairing, i.e. $[HCO_3^-]_F = (Alk - K_W' /[H^+] + [H^+])/(1 + 2K_2'/ [H^+])$

8. Calculate values for $[H_2CO_3^*]$, $[CO_3^=]_F$ and $[OH^-]_F$ from equilibrium equations, Eqs. (A1) to (A3), and the assumed values for $[H^+]$ and $[HCO_3^-]$, i.e. $[H_2CO_3^*] = [H^+].[HCO_3^-]_F/K_1'$ and $[CO_3^=] = K_2'.[HCO_3^-]_F/[H^+]$

9. Calculate ion paired species $[NaCO_3^-]$, $[NaHCO_3^o]$, $[NaOH^o]$, $[CaCO_3^o]$, $[CaHCO_3^+]$ and $[CaOH^+]$ from equilibrium equations, Eqs. (A4) to (A9). (In the first iteration the species concentrations $[Ca^{++}]_F$ and $[Na^+]_F$ are assumed equal to the

/ total ...

total analytical concentrations of these species $[Ca^{++}]_T$ and $[Na^{+}]_T$).

In all subsequent iterations the values for $[Ca^{++}]_F$ and $[Na^{+}]_F$ used are those calculated from the previous iteration, i.e. those values calculated in step 10.

10. Calculate adjusted values for $[Na^{+}]_F$ and $[Ca^{++}]_F$ e.g.

$$[Na^{+}]_F = [Na^{+}]_T - [NaOH^{o}] - [NaHCO^{o}_3] - [NaCO_3^{-}]$$

11. (i) Calculate values for Alkalinity and Acidity from the values for individual species determined above using Eqs. (A12) and (A13), i.e.

$$\text{Alk. (calculated)} = 2([CO_3^{=}]_F + [NaCO_3^{-}] + [CaCO_3^{o}]) + ([HCO_3^{-}]_F + [NaHCO_3^{o}] + [NaCO_3^{-}]) + ([OH^{-}]_F + [CaOH^{+}] + [NaOH^{o}]) - [H^{+}]$$

$$\text{Acidity (calculated)} = 2[H_2CO_3^{*}] + ([HCO_3^{-}]_F + [NaHCO_3^{o}] + [CaHCO_3^{+}]) + [H^{+}] - ([OH^{-}]_F + [CaOH^{+}] + [NaOH^{o}])$$

(ii) Calculate an adjusted value for ionic strength, μ , from the individual species concentrations determined in steps 8 and 9.

(iii) Recalculate the activity coefficients, and adjust the equilibrium constants accordingly.

(iv) Recalculate $[H^{+}]$ from the measured pH and adjusted activity coefficient f_H.

12. Steps 7. to 11. are then reiterated until the calculated value for Alkalinity remains constant.

/ 13. Compare ...

13. Compare the calculated value for Alkalinity, Alk. (calculated) with the known initial Alkalinity.

14. Steps 8. to 13. are repeated with an adjusted value for $[HCO_3^-]_F$ until the calculated value for Alkalinity agrees with the true Alkalinity to within 10^{-10} moles/l When this condition is satisfied Acidity is given by acidity value calculated in step 11. (i). This calculated value usually will be ± 4.10^{-5} moles/l greater than the Acidity value based on mass of chemicals used in solution and is due to CO_2 contamination. The calculated value is now assumed constant for the remaining calculations in the particular experiment.

Determination of Alkalinity from known pH and Acidity

During a precipitation experiment pH is monitored with time. Alkalinity values corresponding to the observed pH values are determined using a similar method to that set out above, except that the parameter Alkalinity is now replaced by a known Acidity value in steps 7, 13 and 14. These calculated Alkalinity values can be used to give a plot of Alkalinity with time for a particular experiment. From this plot the change in Alkalinity with time can be estimated which equals the rate of $CaCO_3$ precipitation.

Appendix B

Listing of Computer Programmes PRECIP. MAIN with sub-routines IONP and SG 13 used for doing the calculations described in Appendix A.

```
*PRECIP.MAIN
C*********************************************************************
C     PROGRAM PRECIP
C*********************************************************************
C     THIS PROGRAM CALCULATES THE  DISTRIBUTION OF IONIC SPECIES,
C     THE RATE OF REMOVAL OF CA++ FROM SOLUTION (DCA++/DT)/M
C     AND THE FUNCTION CAF*CO3F*(CA*CO3-KSP/CAF*CO3F)
C*********************************************************************
C
C     DATA SET
C
C     FIRST DATA CARD: IDENT IS THE EXPERIMENTAL NUMBER
C
C     SECOND DATA CARD: NAHCO3,NAOH,CACL2,MGCL2 ARE THE CONCENTRATIONS
C                       IN MOLES/L OF THE REACTANTS
C
C     THIRD DATA CARD: T IS THE TEMPERATURE IN DEGREES CELCIUS
C
C     FOURTH DATA CARD: SEED IS THE CACO3 SEED CRYSTAL CONC.
C                          IN PPM AS CACO3
C
C     FIFTH DATA CARD: NUM IS THE NUMBER OF PH VALUES READ
C                      DT IS THE TIME DIFFERENCE BETWEEN PH READINGS
C
C     THE NEXT DATA CARDS ARE THE EXPERIMENTAL PH VALUES
C           FOLLOWED BY THE ENTROPY(DSR) AND ENTHALPY(DHR) DATA FOR
C                               THE REACTIONS
C*********************************************************************
      REAL K1,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,K12,K13,KW,KMG,KS
      REAL NAHCO3,NAOH,MGCL2
      DOUBLE PRECISION TALK,TSO4,FSO4,HCO3,FRACT,SACID,OH,
     1H,COH,CO3C,HCOC,CO3
      COMMON TSO4,FSO4,TALK,HCO3,FMG,OH,H,TMG,TCA,TNA,CO3,K1,K2,K3,K4,
     1K5,K6,K7,K8,K9,K10,K11,K12,K13,KW,KMG,KS,FCA,FNA,TCL,U,SACID,
     2H2CO3,COH,CO3C,HCOC
      DIMENSION PKK(30),DSR(30),DHR(30),PH(1000),PK(30),SFUNC(1000),
     1TCAS(1000),SSEED(1000)
      DIMENSION PHS(1000)
      DIMENSION X(1000),Y(1000),Z(1000),TIM(1000)
      DIMENSION TFUNC(1000)
      LZ=1
  515 CONTINUE
      READ(8,91) IDENT
   91 FORMAT(I3)
      WRITE(5,92) IDENT
   92 FORMAT(1H1,'EXPERIMENT NO.',I3,///)
      READ(8,3) NAHCO3,NAOH,CACL2,MGCL2
    3 FORMAT(4E10.4)
      WRITE(5,4) NAHCO3,NAOH,CACL2,MGCL2
    4 FORMAT(1H,'NAHCO3=',E10.4,4X,'NAOH=',E10.4,4X,'CACL2=',E10.4,4X,
     1'MGCL2=',E10.4,'MOLES/L',///)
      READ(8,5) T
    5 FORMAT(F10.4)
      WRITE(5,6) T
    6 FORMAT(1H,'TEMPERATURE=',F10.4,'DEGREES CELSIUS',///)
      READ(8,7) SEED
    7 FORMAT(F10.4)
```

```
      WRITE(5,8) SEED
    8 FORMAT(1H,'CACO3 SEED CRYSTAL CONC.=',F10.4,'PPM AS CACO3',///)
      READ(8,1011) NUM ,DT
 1011 FORMAT(I3,F10.4)
      READ(8,123)(PH(I),I=1,NUM)
  123 FORMAT (10F5.3)
      DO 11 I=1,16
      READ(8,12) DSR(I),DHR(I)
   12 FORMAT(2F10.3)
   11 CONTINUE
      TIM(1)=0.0
      DO  113 I=2,NUM
      TIM(I)=TIM(I-1)+DT
  113 CONTINUE
      PHI=PH(1)
      WRITE(5,102)PHI
  102 FORMAT(1H,'EXPERIMENTAL INITIAL PH=',F6.4,///)
      DO 111 I=1,NUM
      X(I)=TIM(I)
      Y(I)=PH(I)
  111 CONTINUE
      NDIM=NUM
      CALL SG13(X,Y,Z,NDIM,IER)
      LDIM=NDIM-1
      DO 112 I=2,LDIM
      PHS(I)=Z(I)
  112 CONTINUE
      DALK=NAHCO3+NAOH
      DACID=NAHCO3-NAOH
      TNA=NAHCO3+NAOH
      TMG=MGCL2
      TCL=2.*(CACL2+MGCL2)
      TCA=CACL2
      U=2.*(TCA+TMG)+0.5*(TNA+TCL)
C     CONVERT CONC. IN MOLES/L TO PPM AS CACO3
C*****************************************************************
      DALK=DALK*5.*(10.**4.)
      DACID=DACID*5.*(10.**4.)
      TNA=TNA*5.*(10.**4.)
      TMG=TMG*(10.**5.)
      TCL=TCL*5.*(10.**4.)
      TCA=TCA*(10.**5.)
      TTCA=TCA
      WRITE(5,10) DALK,TNA,TMG,TCL,TTCA
   10 FORMAT(1H,'TOT ALK=',F10.4,3X,'TNA=',F10.4,3X,'TMG=',F10.4,3X,
     1'TCL=',F10.4,3X,'TCA=',F10.4,'PPM AS CACO3',///)
C     CALCULATE LOG DISS. CONSTANTS USING THERMODYNAMIC DATA
C     AND HELGESONS EQUATION
C*****************************************************************
      R=1.987
      TA=273.15+T
      TR=298.15
      DO 13 I=1,16
      YY=(EXP(-12.741+0.01875*TA))-0.000784+(TA-TR)/219.
      XX=TR-(219./1.00322)*(1.-EXP(YY))
      PKK(I)=(DSR(I)*XX)/(2.303*R*TA)-DHR(I)/(2.303*R*TA)
   13 PK(I)=-PKK(I)
```

```
      PKK(1)=8.153-0.02195*TA-2382.3/TA
      PKK(2)=5.388-0.02199*TA-2730.7/TA
      PK(1)=-PKK(1)
      PK(2)=-PKK(2)
      PK(2)=10.3718
      WRITE(5,14) PK(1),PK(2),PK(3),PK(4),PK(5),PK(6),PK(7),PK(8)
 14   FORMAT(1H,'PKH2CO3=',F6.4,2X,'PKHCO3=',F7.4,2X,'PKSO4='F6.4,2X,
     1'PKNASO4=',F6.4,2X,'PKMGSO4=',F6.4,2X,'PKNAHCO3=',F6.4,2X,
     2'PKNACO3=',F6.4,2X,'PKMGHCO3=',F6.4,/)
      WRITE(5,15) PK(9),PK(10),PK(11),PK(12),PK(13),PK(14),PK(15),PK(16)
 15   FORMAT(1H,'PKMGCO3=',F6.4,2X,'PKCAHCO3=',F6.4,2X,'PKMGOH=',F6.4,2X
     1,'PKCAOH=',F6.4,2X,'PKCACO3=',F6.4,2X,
     2'PKW=',F7.4,2X,'PKS=',F6.4,2X,'PKMGOH2=',F10.4,///)
      PK1=PK(1)
      PK2=PK(2)
      PK3=PK(3)
      PK4=PK(4)
      PK5=PK(5)
      PK6=PK(6)
      PK7=PK(7)
      PK8=PK(8)
      PK9=PK(9)
      PK10=PK(10)
      PK11=PK(11)
      PK12=PK(12)
      PK13=PK(13)
      PKW=PK(14)
      PKS=PK(15)
      PKMG=PK(16)
      LX=0
      LION=1
      NN=1
      NUMM=NUM-2
      DO 1010 I=1,LDIM
 44   U1=U**0.5
C     CONVERT BACK TO MOLES/L
C*************************************************************
      IF (LION-1)42,42,43
 43   K1=K1*HF*ANF/(2.5*ANM*10.**4.)
      K2=K2*HF*CO3F/(ANF*10.**5.)
      K3=K3*CAF*SO4F/(ANM*10.**5.)
      K4=K4*SO4F/(10.**5.)
      K5=K5*GMF*SO4F/(ANM*10.**5.)
      K6=K6*ANF*2./(ANM*5.*10.**4.)
      K7=K7*CO3F/(10.**5.)
      K8=K8*GMF/(10.**5.)
      K9=K9*GMF*CO3F/(ANM*10.**5.)
      K10=K10*CAF*(10.**5.)
      K11=K11*OHF*GMF/(10.**5.)
      K12=K12*OHF*CAF/(10.**5.)
      K13=K13*CAF*CO3F/(10.**5.)
      KW=KW*OHF*HF/(2.5*10.**9.)
      KS=KS*CAF*CO3F/(10.**10.)
      KMG=KMG*GMF*(OHF**2.)/(2.5*10.**14.)
C     CALCULATE ACTIVITY COEFFS. FOR INDIVIDUAL SPECIES
C*************************************************************
 42   AMGF=-0.509*4.*(U1/(1.+0.328*8.*U1))
```

```
      ACAF=-0.509*4.*(U1/(1.+0.328*6.*U1))
      ASOF=-0.509*4.*(U1/(1.+0.328*4.*U1))
      ANAF=-0.509*(U1/(1.+0.328*4.*U1))
      AHF=-0.509*(U1/(1.+0.328*9.*U1))
      ACOF=-0.509*4.*(U1/(1.+0.328*5.*U1))
      AOHF=-0.509*(U1/(1.+0.328*3.*U1))
      GMF=10.**AMGF
      CAF=10.**ACAF
      SO4F=10.**ASOF
      ANF=10.**ANAF
      HF=10.**AHF
      CO3F=10.**ACOF
      OHF=10.**AOHF
C           CALCULATE ACTIVITY COEFF. FOR NEUTRAL SPECIES (ANM)
C     SALTING OUT COEFF.=SK=0.75
C     LOG(ANM)=SK*U
C*********************************************************************
      ANM=0.75*U
      ANM=10.**ANM
C     ADJUST K VALUES TO INCORPORATE ACTIVITY COEFFS.
C*********************************************************************
      K1=(10.**(-1.*PK1))*ANM/(HF*ANF)
      K2=(10.**(-1.*PK2))*ANF/(HF*CO3F)
      K3=(10.**(-1.*PK3))*ANM/(CAF*SO4F)
      K4=(10.**(-1.*PK4))/(SO4F)
      K5=(10.**(-1.*PK5))*ANM/(GMF*SO4F)
      K6=(10.**(-1.*PK6))*ANM/(ANF**2.)
      K7=(10.**(-1.*PK7))/(CO3F)
      K8=(10.**(-1.*PK8))/GMF
      K9=(10.**(-1.*PK9))*ANM/(GMF*CO3F)
      K10=(10.**(-1.*PK10))/CAF
      K11=(10.**(-1.*PK11))/(OHF*GMF)
      K12=(10.**(-1.*PK12))/(OHF*CAF)
      K13=(10.**(-1.*PK13))*ANM/(CAF*CO3F)
      KW=(10.**(-1.*PKW))/(OHF*HF)
      KS=(10.**(-1.*PKS))/(CAF*CO3F)
      KMG=(10.**(-1.*PKMG))/(GMF*(OHF**2.))
C     ADJUST K VALUES TO EXPRESS CONC. OF SPECIES IN PPM AS CACO3
C*********************************************************************
      K1=K1*2.5*(10.**4.)
      K2=K2*(10.**5.)
      K3=K3*(10.**5.)
      K4=K4*(10.**5.)
      K5=K5*(10.**5.)
      K6=K6*5.*(10.**4.)
      K7=K7*(10.**5.)
      K8=K8*(10.**5.)
      K9=K9*(10.**5.)
      K10=K10*(10.**5.)
      K11=K11*(10.**5.)
      K12=K12*(10.**5.)
      K13=K13*(10.**5.)
      KW=KW*2.5*(10.**9.)
      KS=KS*(10.**10.)
      KMG=KMG*2.5*(10.**14.)
      IF(NN-1)300,300,490
300   IF(LION-4)201,201,210
```

```
C     CALCULATE EXACT IONIC STRENGTH
C**********************************************************************
201   H=1./(10.**PHI)/HF
      H=H*5.*(10.**4.)
      OH=KW/H
      KK=1
      HCO3=(DALK-OH+H)/(K2/H+1)
202   CO3=(HCO3*K2/H)
      H2CO3=(HCO3*H)/K1
      CALL IONP
      IF (TALK-DALK)204,209,203
203   HCO3=HCO3*0.9
      GO TO 202
204   FRACT=0.1*HCO3
206   HCO3=HCO3+FRACT
      CO3=HCO3*K2/H
      H2CO3=(HCO3*H)/K1
      CALL IONP
      IF(TALK-DALK)206,209,207
207   KK=KK+1
      IF(4-KK)209,209,208
208   HCO3=HCO3-FRACT
      FRACT=0.1*FRACT
      GO TO 206
209   LION=LION+1
      GO TO 44
C     CALCULATE INITIAL PH
C**********************************************************************
210   LX=LX+1
      A=DALK
      OH=0.95*A
      LM=0
      H=KW/OH
      CO3=(A-OH+H)/(1.+H/K2)
      GO TO 270
265   CO3=(A-OH*COH+H)/(CO3C+H*HCOC/K2)
270   HCO3=H*CO3/K2
      H2CO3=H*HCO3/K1
      KKK=1
      CALL IONP
      LM=LM+1
      IF(LM-3)265,265,925
925   IF(SACID-DACID)930,930,940
930   OH=0.1*OH
      LM=0
      H=KW/OH
      CO3=(A-OH*COH+H)/(CO3C+H*HCOC/K2)
      IF(CO3)930,930,935
935   GO TO 270
940   FRACT=OH
941   OH=OH+FRACT
      LM=0
945   H=KW/OH
      CO3=(A-OH*COH+H)/(CO3C+H*HCOC/K2)
      IF(CO3)947,947,948
947   OH=OH-FRACT
      FRACT=0.9*FRACT
```

```
      GO TO 941
948   HCO3=H*CO3/K2
      H2CO3=H*HCO3/K1
      FCA=KS/CO3
      CALL IONP
      LM=LM+1
      IF(LM-3)945,945,950
950   IF(SACID-DACID)955,990,941
955   KKK=KKK+1
      IF(5-KKK)990,980,980
980   OH=OH-FRACT
      FRACT=0.1*FRACT
      GO TO 941
990   IF(LX-2)44,991,991
991   HI=H/(5.*10.**4.)
      CPHI=-1.*ALOG10(HI*HF)
      WRITE(5,970) CPHI
970   FORMAT(1H,'CALCULATED INITIAL PH=',F6.4,///)
C     CALCULATE PH AND CORRESPONDING SPECIES CONCENTRATION VALUES
C*******************************************************************************
      ACID=SACID
      PHN=PHS(I)
      TIMN=TIM(I)
      NN=2
      ALKD=0.0
      ALK2=DALK
      GO TO 600
490   KKK=1
      PHN=PHS(I)
      TIMN=TIM(I)
      H=1./(10.**PHN)/HF
      H=H*5.*10.**4.
      OH=KW/H
      HCO3=(ACID-H+OH)/(1.+H/K1)
499   CO3=(HCO3*K2)/H
      H2CO3=(H*HCO3)/K1
      CALL IONP
      IF(SACID-ACID)510,550,500
500   HCO3=0.9*HCO3
      GO TO 499
510   FRACT=0.1*HCO3
520   HCO3=HCO3+FRACT
      CO3=HCO3*K2/H
      H2CO3=(HCO3*H)/K1
      CALL IONP
      IF (SACID-ACID)520,550,530
530   KKK=KKK+1
      IF(5-KKK)550,550,540
540   HCO3=HCO3-FRACT
      FRACT=0.1*FRACT
      GO TO 520
550   LION=LION+1
      IF(LION-9)560,560,599
560   GO TO 44
599   ALK1=TALK
      ALKD=ALK2-ALK1
      ALK2=ALK1
```

```
      TCA=TCA-ALKD
      TCAS(I)=TCA
      DCA=TTCA-TCA
       SSEED(I)=SEED+DCA
      FUNC=CAF*CO3F*(FCA*CO3-KS)
      SFUNC(I)=FUNC
      FUNCA=SSEED(I)*FUNC
      TFUNC(I)=FUNCA
  600 WRITE(5,610) TIMN,PHN,FCA,CO3,TCA,DCA,CO3F,CAF,ALKD
  610 FORMAT(9E10.4)
      NN=2
      LION=2
 1010 CONTINUE
      DO 586 I=3,NUMM
  730 RATE=(TCAS(I-2)-8*TCAS(I-1)+8*TCAS(I+1)-TCAS(I+2))/(12*DT)
      WRITE(5,743)PHS(I),RATE,SFUNC(I),SSEED(I),TFUNC(I)
  743 FORMAT(4F10.4,E10.4)
  586 CONTINUE
  200 CONTINUE
       IF(LZ-10)800,800,820
  800 LZ=LZ+1
      GO TO 515
  820 CONTINUE
      STOP
      END
```

```
C*PRECIP.IONP
      SUBROUTINE IONP
      REAL K1,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,K12,K13,KW ,KS
      DOUBLE PRECISION TALK,TSO4,FSO4,HCO3,FRACT,SACID,OH,
     1H,COH,CO3C,HCOC,CO3
      COMMON TSO4,FSO4,TALK,HCO3,FMG,OH,H,TMG,TCA,TNA,CO3,K1,K2,K3,K4,
     1K5,K6,K7,K8,K9,K10,K11,K12,K13,KW,KMG,KS,FCA,FNA,TCL,U,SACID,
     2H2CO3,COH,CO3C,HCOC
      LN=1
      FSO4=TSO4
   20 FMG=TMG/(1.+HCO3/K8+CO3/K9+FSO4/K5+OH/K11)
      FNA=TNA/(1.+FSO4/K4+HCO3/K6+CO3/K7)
      FCA=TCA/(1.+HCO3/K10+FSO4/K3+OH/K12+CO3/K13)
      Y=TSO4-FSO4*(1.+FNA/K4+FCA/K3+FMG/K5)
      IF(Y)30,100,40
   30 FSO4=0.9*FSO4
      GO TO 20
   40 FRACT=0.1*FSO4
   60 FSO4=FSO4+FRACT
      FMG=TMG/(1.+HCO3/K8+CO3/K9+FSO4/K5+OH/K11)
      FNA=TNA/(1.+FSO4/K4+HCO3/K6+CO3/K7)
      FCA=TCA/(1.+HCO3/K10+FSO4/K3+OH/K12+CO3/K13)
      Y=TSO4-FSO4*(1.+FNA/K4+FCA/K3+FMG/K5)
      IF(Y)70,100,60
   70 IF(5-LN)100,100,80
   80 LN=LN+1
      FSO4=FSO4-FRACT
      FRACT=0.1*FRACT
      GO TO 60
  100 CONTINUE
      TALK=CO3*(1.+2.*FNA/K7+FMG/K9)+HCO3*(1.+FNA/K6+FCA/K10+FMG/K8)+
     1OH*(1.+FCA/K12+FMG/K11)-H+CO3*FCA/K13
      SACID=H2CO3+HCO3*(1.+FNA/K6+FCA/K10+FMG/K8)+H-OH*(1.+FCA/K12+FMG/
     1K11)
      CO3C=1.+2.*FNA/K7+FMG/K9+FCA/K13
      HCOC=1.+FNA/K6+FCA/K10+FMG/K8
      COH=1.+FCA/K12+FMG/K11
      FNASO=(FNA*FSO4)/(K4*5.*10.**4.)
      FMGHC=(FMG*HCO3)/(K8*5.*10.**4.)
      FCAHC=(FCA*HCO3)/(K10*5.*10.**4.)
      FNACO=(FNA*CO3)/(K7*5.*10.**4.)
      FHCO3=HCO3/(5.*10.**4.)
      FCO3=CO3/(10.**5.)
      FFSO4=FSO4/(10.**5.)
      FFCL=TCL/(5.*10.**4.)
      FFNA=FNA/(5.*10.**4.)
      FFMG=FMG/(10.**5.)
      FFCA=FCA/(10.**5.)
      U=2.*(FFSO4+FFCA+FFMG+FCO3)+0.5*(FFNA+FFCL+FNASO+FMGHC+FCAHC
     1+FNACO+FHCO3)
      RETURN
      END
```

```
*PRECIP.SG13
C        SUBROUTINE SG13
C
C      PURPOSE
C           VECTORS OF ARGUMENT VALUES AND CORRESPONDING FUNCTION
C           VALUES.
C
C        USAGE
C           CALL SG13(X,Y,Z,NDIM,IER)
C
C        DESCRIPTION OF PARAMETERS
C           X      -  GIVEN VECTOR OF ARGUMENT VALUES (DIMENSION NDIM)
C           Y      -  GIVEN VECTOR OF FUNCTION VALUES CORRESPONDING TO X
C                     (DIMENSION NDIM)
C           Z      -  RESULTING VECTOR OF SMOOTHED FUNCTION VALUES
C                     (DIMENSION NDIM)
C           NDIM   -  DIMENSION OF VECTORS X,Y,AND Z
C           IER    -  RESULTING ERROR PARAMETER
C                     IER = -1   - NDIM IS LESS THAN 3
C                     IER =  0   - NO ERROR
C
C        REMARKS
C           (1)    IF IER=-1 THERE HAS BEEN NO COMPUTATION.
C           (2)    Z CAN HAVE THE SAME STORAGE ALLOCATION AS X OR Y.  IF
C                  X OR Y IS DISTINCT FROM Z, THEN IT IS NOT DESTROYED.
C
C        SUBROUTINES AND SUBPROGRAMS REQUIRED
C           NONE
C
C        METHOD
C           EXCEPT AT THE ENDPOINTS X(1) AND X(NDIM), EACH SMOOTHED
C           VALUE Z(I) IS OBTAINED BY EVALUATING AT X(I) THE LEAST-
C           SQUARES POLYNOMIAL OF DEGREE 1 RELEVANT TO THE 3 SUCCESSIVE
C           POINTS (X(I+K),Y(I+K)) K = -1,0,1.(SEE HILDEBRAND, F.B.,
C           INTRODUCTION TO NUMERICAL ANALYSIS, MC GRAW-HILL, NEW YORK/
C           TORONTO/LONDON, 1956, PP.258-311.)
C
C     ..................................................................
C
      SUBROUTINE SG13(X,Y,Z,NDIM,IER)
C
C
      DIMENSION X(1),Y(1),Z(1)
C
C        TEST OF DIMENSION
      IF(NDIM-3)7,1,1
C
C        START LOOP
    1 DO 6 I=3,NDIM
      XM=.3333333*(X(I-2)+X(I-1)+X(I))
      YM=.3333333*(Y(I-2)+Y(I-1)+Y(I))
      T1=X(I-2)-XM
      T2=X(I-1)-XM
      T3=X(I)-XM
      XM=T1*T1+T2*T2+T3*T3
      IF(XM)3,3,2
    2 XM=(T1*(Y(I-2)-YM)+T2*(Y(I-1)-YM)+T3*(Y(I)-YM))/XM
```

```
C
C        CHECK FIRST POINT
    3 IF(I-3)4,4,5
    4 H=XM*T1+YM
    5 Z(I-2)=H
    6 H=XM*T2+YM
C        END OF LOOP
C
C        UPDATE LAST TWO COMPONENTS
      Z(NDIM-1)=H
      Z(NDIM)=XM*T3+YM
      IER=0
      RETURN
C
C        ERROR EXIT IN CASE NDIM IS LESS THAN 3
    7 IER=-1
      RETURN
      END
```

T PRINTS