SCALING STUDIES
IN
SEA WATER DISTILLATION

by

Bruce C. Jue

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INTRODUCTION

Industrial growth, population increase and rising living standards have drastically increased the world's demand for fresh water over the last few decades. Present supplies are adequate to meet the needs in many areas, but there are numerous locations where shortages already exist. As growth and development continue this problem will almost certainly become more acute and an effort is being made to evaluate possible ways of easing the situation.

Vast quantities of sea and brackish waters are readily available to many arid lands, but their high content of dissolved salts makes them unsuitable for most purposes. These waters contain about 35,000 and 5,000 parts per million of dissolved salts although the amount may vary from one location to another. Water is considered fresh if it contains less than 1,000 parts per million of dissolved salts although for municipal and domestic purposes 500 parts per million is considered the maximum allowable level. Dissolved salts can be removed by various conversion processes but the cost of such treatment is still too great for average industrial and agricultural consumption. The minimum cost today is about one dollar per thousand gallons of fresh water produced. Acceptable costs would be roughly thirty-eight cents for municipal or domestic use and twelve to fifteen cents for irrigation purposes.

Sea water is much more abundant than brackish water and emphasis has been placed on conversion of the former. The most promising methods to date are:

(1) Distillation using fuels
(2) Distillation using solar heat
(3) Ion-exchange membrane processes
(4) Separation of salts by freezing.

Research is in progress on all of these techniques but distillation using fuels appears to be the most economical. This is the oldest and most commonly used process and may be described as follows.

The crude supply is fed continuously to a tube boiler where a certain fraction is evaporated to form the final product. The remainder is removed from the system continuously to prevent gross precipitation of salts which would soon clog the system. The percentage of feed removed from the system is called the blowdown rate. The necessary heat must be transferred from the heating medium(fuel combustion gases) through the metal tube walls to the water.

One of the most serious operating problems encountered in the distillation process is the formation of scale on the heating surfaces which seriously reduces heat transfer. This scale must be removed periodically by mechanical and/or chemical treatment (descaling) to maintain operating efficiency. The costs associated with descaling and consequent loss of operating time are quite significant and in most instances raise the overall cost to a prohibitive level. Many attempts have been made to solve the problem of scale formation, usually by the addition of chemicals to the sea water feed. These have not been very successful. The basic chemistry of scale formation has also been studied and many of the reactions and conditions have been fairly well established. However, little work has been done to determine the mechanism of scale formation and this thesis represents an attempt to extend our knowledge of this aspect of the problem.

HISTORICAL

Mechanism of Scale Formation

The chemical composition of sea water is relatively constant regardless of source. The following table lists the major components as compiled by Barnes (1).

Table 1

Component	grams/kilogram water
Chloride ions	18.9799
Bromide ions	0.0646
Sulphate ions	2.6486
Bicarbonate ions	0.1397
Fluoride ions	0.0013
Calcium ions	0.4001
Magnesium ions	1.2720
Potassium ions	0.3800
Strontium ions	0.0133
Sodium ions	10.5561
Boric acid molecules	0.0260
	34.4816

When sea water is evaporated scale formed on the heating surface is not unlike boiler scale. In boilers, the most common components are calcium sulphate or calcium and magnesium silicates. Calcium and magnesium hydroxides and calcium carbonate occur less frequently. In sea water evaporators the principal components of scale are calcium sulphate, calcium carbonate and magnesium hydroxide. Hillier (2) and Langelier (3) have found that calcium sulphate deposition can be avoided if the blowdown rate is maintained above thirty-three per cent. Normal practice is to use a fifty per cent blowdown and most scale, therefore, consists of calcium carbonate and/or magnesium hydroxide. Hillier has found that calcium carbonate is predominant in scale formed below 170°F. but magnesium hydroxide is the main component above this temperature. Both occur at temperatures close to 170°F.

Several mechanisms of scale formation have been suggested. Partridge (4) proposed that boiler scale forms in three ways; (a) by the settling of suspended particles, (b) by direct crystallization of salts from supersaturated boiler water and (c) by the action of bubble evolution at an evaporating surface. Hall (5) stated that scale formation does not occur by the settling of suspended particles. Badger (6) noted the adherence of such particles to the heating surface but the effect was attributed to poor fluid circulation.

The second mechanism occurs if the feed is saturated with a compound having an inverse solubility. The heated solution becomes supersaturated and direct crystallization occurs at the region of highest temperature, i.e., on the heating surface. Scale containing calcium sulphate is believed to be formed in this manner.

The third mechanism is associated with boiling action. Bubbles of steam or carbon dioxide gas form on the heating surface and temporarily insulate the bulk of the liquid from the surface. Rapid evaporation of water into the bubble from a ring of solution around it and adjacent to the heating surface (the hottest region) causes supersaturation and the precipitation of scale in a ring-like structure.

These mechanisms are possible in sea water evaporators because both calcium carbonate and magnesium hydroxide have inverted solubility curves and boiling does occur. However, a third factor may be supersaturation caused by the shift in bicarbonate-carbonate equilibrium due to carbon dioxide evolution (2,3,7,8).

Sea water is a very complex system and involves numerous equilibria. One of the most important of these is:

$$2HCO_3^- \rightleftharpoons H_2O + CO_2 + CO_3^= \qquad (1)$$

This equilibrium is affected by biological species present in sea water. Carbon dioxide released by animal metabolism is absorbed by reaction to the left. Convection and diffusion bring high carbon dioxide water into contact with plant life where the process is reversed. On the average, therefore, there is a steady condition which approaches the equilibrium for some intermediate partial pressure of carbon dioxide. Other equilibria are:

$$CO_2\ (\text{gas}) \rightleftharpoons CO_2\ (\text{dissolved}) \qquad (2)$$

$$CO_2\ (\text{dissolved}) + H_2O \rightleftharpoons H_2CO_3 \qquad (3)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (4)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad (5)$$

$$CaCO_3\ (\text{solid}) \rightleftharpoons Ca^{++} + CO_3^= \qquad (6)$$

When sea water is heated the solubility of carbon dioxide in solution is decreased. This displaces equilibrium 1 to the right and the carbonate ions produced combine with calcium ions to form solid calcium carbonate (equation 6). If the temperature is increased further, carbonate ions may react to form hydroxyl ions and more carbon dioxide gas.

$$CO_3^= + H_2O \rightleftharpoons CO_2 + 2OH^- \qquad (7)$$

Magnesium ions combine with the hydroxyl ions formed to produce magnesium hydroxide precipitate.

$$Mg^{++} + 2OH^- \rightleftharpoons Mg(OH)_2 \qquad (8)$$

Langelier used these relations to describe the change from calcium carbonate to magnesium hydroxide precipitate with temperature. Obviously, the ratio $\frac{[CO_3^=]}{[OH^-]^2}$ indicates which precipitate is favoured. However, the magnitude of this ratio is not easily measured but the ratio can be expressed as follows:

$$\frac{k'' \, [HCO_3^-] \, [H^+]}{k_w^2}$$

where k" is the second dissociation constant of carbonic acid and k_w is the dissociation constant for water. The dissociation constant for water increases rapidly with temperature and appears in the denominator of the ratio raised to the second power. Consequently, magnesium hydroxide precipitation is favoured at higher temperatures.

Hillier proposed a mechanism based on "electronic forces of attraction and cohesion". A heated surface in contact with liquid accumulates scale-forming ions by adsorption. Ionic charge provides the necessary force for ions to adhere to a surface. A number of ions from the scale compound may return to the solution but a condition is reached where some ions remain attached to a surface as scale. The rate of scale formation is proportional to the rate at which scale-forming ions collide with the heated surface. This rate is increased by heating because ionic movement is increased. If boiling also takes place there is increased concentration of scale-forming ions at the perimeter of contact of steam bubbles formed with the heated surface. Scale growth rate is increased because ionic activity in the neighbouring liquid is increased. Thus, heating, evaporation and concentration of brine all serve to increase scale formation.

Langelier noted that in sea water evaporation, scale formed on surfaces both hotter and colder than the concentrated brine. This led him to reject the theory that scale formation was due to salts which decreased in solubility with temperature rise. A mechanism based on nucleation was proposed. The brine in the evaporator contains scale-forming components in a metastable state. If the brine is heated and evaporation occurs, the metastable solubility limit of the scale components is exceeded and precipitation occurs on the heated surface. Precipitate detached from the surface induces further precipitation in the bulk of the solution. However, the latter tends to remain in suspension or to settle as a sludge; it rarely forms scale. This mechanism is used as a basis for scale control. If supersaturation is produced by evaporation and subsequent precipitation occurs on a heated surface, adherent scale forms. If, however, supersaturation is removed by contact with foreign substances (seed) a dispersion is formed which may be discharged in blowdown. Badger and Banchero (7) reported that scale is formed by this mechanism and that supersaturation of a solution can occur in the region of the heated surface with solutes which have normal solubility curves. However, with solutes having inverted solubility curves, supersaturation occurs both by concentration due to evaporation and decreased solubility of scale components with temperature rise. The degree of supersaturation necessary for nucleation is a function of many variables such as: the particular solute which is precipitated as a solid phase, the nature of the heating surface, the operating conditions and the presence of other solid substances which may induce precipitation. Once the degree of supersaturation necessary for nucleation is reached, further precipitation occurs at lower supersaturation values. Growth of the solid phase takes place and subsequent deposition occurs on that already formed since it provides surfaces for crystallization. Based on these studies, the most likely mechanism of scale formation involves a series of steps. The solution becomes supersaturated with respect to the solid phase by heating and evaporation. Then, nucleation and growth of the solid phase occur.

In an evaporator further complications arise. Sea water feed continuously mixes with a concentrated brine which is being heated and evaporated while some of the concentrated brine is removed by continuous discharge. The accumulation of scale-forming components in the brine either in suspension or solution thus depends on three rates; sea water feed, brine withdrawal and precipitation. Consequently, only part of the total bicarbonate contributes to scale formation. The remainder forms, by dissociation, carbon dioxide gas which evolves and suspended calcium carbonate precipitate which is removed by discharge.

Because of the role of bicarbonate and carbonate ions in scale formation, several rate studies of the thermal decomposition of calcium bicarbonate solutions have been made. In these studies attempts were made to identify the rate-determining or slow step in the decomposition. Meunier (9) followed the decomposition at the boiling point and found it to be "bimolecular" (second order). The rate-determining step was postulated as,

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2 \qquad (9)$$

Under other conditions which were not specified, diffusion of carbon dioxide gas was the slow step. Orlow (10) studied the decomposition at room temperature and found that in the presence of solid calcium carbonate the reaction was "bimolecular". He believed that at lower temperatures the slow reaction would be carbon dioxide evolution although this was not verified. Based on work by Meunier and Orlow, Stumper (11,12) conducted an extensive investigation of the decomposition rate. The results of his work may be summarized as follows:

(1) Decomposition of calcium bicarbonate solutions at boiling point was "bimolecular" and was dependent on the degree of boiling.

(2) If removal of carbon dioxide was accelerated by a current of air and if solid calcium carbonate was present, the decomposition at the boiling point was also "bimolecular".

(3) The presence of dissolved calcium salts accelerated the decomposition reaction. Organic compounds such as dextrin, gelatin, starch and tannin plus salts such as sodium chloride, magnesium chloride and magnesium sulphate all retarded decomposition. Sulphates were more effective than chlorides in retardation but no mechanisms were proposed. Stumper suggested that these materials affected the evolution of carbon dioxide.

(4) The decomposition was retarded by introducing carbon

dioxide gas but accelerated by introducing air. Carbon dioxide or air did not take part in the reaction but merely retarded or accelerated carbon dioxide evolution. The faster the carbon dioxide removal, the more the decomposition followed the "bimolecular" scheme. If carbon dioxide removal was retarded, decomposition tended to higher reaction orders. The latter observation was not explained.

(5) Colloidal and coarsely dispersed additives influenced the precipitation reaction specifically. Colloidal additives acted as protective colloids and retarded precipitation while coarsely dispersed materials acted as nuclei and accelerated the process. The mechanism was still to be investigated.

(6) The precipitation of calcium carbonate began only after an induction period. This period increased with decreasing concentration of calcium bicarbonate and with decreasing temperature.

(7) The rate-determining step at the boiling point was as follows:

$$2HCO_3^- \rightleftharpoons CO_3^= + H_2CO_3 \qquad (10)$$

The rate of evolution of carbon dioxide was rapid at boiling and, therefore, was not rate-determining.

(8) In the neighbourhood of the boiling point the rate of decomposition increased sharply but was dependent on foreign substances present in solution.

(9) Fine calcium carbonate powder added to the boiling solution which was agitated by a current of air removed the induction period. Other fine particles exerted this effect, the induction period decreasing with increasing fineness of material. However, zinc compounds were found to prolong the induction period. It was felt that selective adsorption of these materials on the seeds of the precipitate formed a protective cover and retarded growth of the solid phase.

(10) At lower temperatures and in the absence of activating agents, the decomposition was believed to be intermediate between "monomolecular" (first order) and "bimolecular". This was not verified experimentally.

Van Hook (13) found that the decomposition rate depended on the rate of both carbon dioxide and water loss. The controlling factor in the loss of the two materials was their diffusion rates. At 34°C., in the presence of solid calcium carbonate, decomposition was found to be first order. The effect of excess calcium carbonate appeared to depend on the amount of added surface.

More recently, Howland and Simmonds (14) studied the decomposition rate of calcium bicarbonate solution at temperatures of 75 - 90°C. The following conclusions were reached.

(1) Rate of formation of calcium carbonate increased with increasing temperature and initial calcium concentration.

(2) The rate was unaffected by the presence of glass surfaces but considerably enhanced by various finely divided materials, particularly calcium carbonate.

(3) Rate of decomposition was dependent on the area of calcium carbonate added, the effect increasing with temperature rise.

Based on experimental results the following rate expression was derived:

$$-{}^{dC}/dt = 1.99 \times 10^{-8} (C_1 - C_E)^{2.5} (C - C_E) \qquad (11)$$

where C is the concentration at time t

C_1 is the initial concentration

and C_E is the equilibrium concentration.

The decomposition appears to be dependent on supersaturation which is related to the solubility of calcium carbonate. Garrels and Dreyer (15) summarized the effects of pH, amount of total carbon dioxide in solution, added salts, temperature and pressure on the solubility of calcium carbonate as follows:

(1) an increase in temperature decreased the solubility of calcium carbonate,

(2) an increase in pressure increased the solubility of the carbonate,

(3) a decrease in pH increased the solubility of calcium carbonate appreciably, and

(4) addition of soluble salts increased the solubility of the carbonate although this effect also depended on the amount of dissolved carbon dioxide.

Despite the work of Meunier, Orlow, Stumper and Howland and Simmonds further study of the thermal decomposition of calcium bicarbonate solutions is desirable, especially at temperatures below the boiling point. The mechanism of the reaction is not clearly defined and explanations are lacking for many of the effects reported by earlier workers.

Control of Scale Formation

Much time and effort have been devoted to the control of scaling in sea water evaporators. Most of the work was done in pilot plants and the results were expressed in terms of extended periods of operation before descaling became necessary. However, the criteria for descaling were not usually specified and appear to be quite arbitrary.

To control or eliminate scale formation four general methods have been proposed:

(1) acid treatment of feed water to promote increased solubility of the scale-forming components,

(2) feed water treatment to modify the physical nature of the precipitate,

(3) alternative sources for crystallization nuclei

(4) changes in evaporation equipment or technique.

The first method involves the addition of acid or acidic compounds to the sea water feed. Based on pilot plant studies Hillier found that both magnesium hydroxide and calcium carbonate precipitates were completely eliminated by treatment with strong acid. However, handling difficulties and the danger of extensive corrosion restricted its use. Ethylene bis-imino diacetic acid and sodium salts of dinaphthyl methane disulphonic acid produced a weaker scale which could be removed by cracking. However, such scale was considered more objectionable than inorganic scale due to increased resistance to heat flow.

Neville-Jones (16) tested numerous compounds including ferric chloride, ferric sulphate, aluminium chloride, potassium acid sulphate, sodium acid sulphate, commercial citric acid, 100 and 30 per cent hydrochloric acid. He found that aluminium chloride formed undesirable aluminium hydroxide sludge while sodium acid sulphate caused excessive foaming.

In agreement with Hillier, Neville-Jones reported greatest success with ferric chloride. Ferric hydroxide precipitate was formed instead of calcium carbonate or magnesium hydroxide and the iron precipitate was easily removed as a suspension in the discharge operation. However, this compound is corrosive and deliquescent and careful control was necessary to prevent excessive foaming in the evaporator. Direct handling of ferric chloride was avoided by using iron anodes to produce ferrous chloride which was subsequently oxidized to ferric chloride. Additions were controlled by varying the electrolytic current.

Spaulding and Lindsten (17) and Williams (18) also employed continuous or intermittent additions of acid. Williams reported that a pH of 6 was sufficient to prevent scale formation. Badger advocated the use of sulphuric acid and believed that no difficulties in handling would be experienced. He felt that such treatment would be economical but did not consider the added cost due to corrosion.

Langelier used citric acid as a buffer to promote increased solubility of scale components. Intermittent additions of the acid with frequent descaling prevented the build up of appreciable scale on the heating surface. Although Langelier believed this method was practical, particularly for military installations of limited capacity, Badger felt that the cost of citric acid was still too great for general scale control. Campobasso and Latham (19) using compression distillation employed sodium acid sulphate or muriatic acid to extend the operating period before mechanical cleaning was necessary. After three hundred hours of operation, a solution containing two pounds of sodium acid sulphate per gallon of sea water was circulated for one and one-half hours. Elliott (20) also employed the above compounds as surface cleaning agents every six hundred to one thousand hours in super-tanker distillers.

The second general method of scale control involves the addition of compounds which may alter the physical form of the deposit. Scale formation is not prevented but a softer less adherent form is obtained. Hillier used sodium phosphate, tannins and mixtures of the two compounds. He found that the mixtures reduced deposition of calcium carbonate but formation of magnesium hydroxide was promoted. Neville-Jones employed surface active materials to restrict crystal growth and layer formation and to facilitate discharge of the deposit as a fine suspension. Increased operating periods were reported using the sodium salt of dinaphthyl methane disulphonic acid. The scale was softer and less adherent but in some cases was thick and layered. With copper heating coils the bond between scale and copper consisted of a magnesium-copper complex. Magnesium hydroxide adhesion was prevented by the addition of a chelating agent which complexed with copper and inhibited magnesium-copper bond formation. Ethylenediaminetetracetic acid (EDTA) chelating agent was used with cold shocking to extend the output of the evaporator for longer periods. Cold shocking refers to the mechanical distortion of the heating surface to break the scale formed. Roche (21) employed EDTA and polyphosphates of sodium to reduce deposits of calcium carbonate on heated surfaces. However, Badger indicated that EDTA was too expensive for sea water treatment. Leicester (22) used a dinaphthyl methane disulphonic compound as a dispersing agent and an ethylene bis-imino diacetic compound as a sequestering agent. In vapour compression distillation with reduced pressure, low brine density and a mixture of the two compounds, the total weight of scale was reduced. The dispersing agent conditioned the solids so that they remained in suspension. These solids were then removed by the brine discharge. The deposit formed on the heating surface was friable and cracked during operation. Successful treatment was obtained by addition of 0.003 per cent by weight of the mixture based on the incoming sea water.

Karl et al. (23) worked with synthetic sea water in an experimental evaporator using powdered alfalfa and a fifty per cent blowdown. As little as 0.035 per cent alfalfa was sufficient to prevent scale formation. The mechanism by which scale formation was prevented was not explained but the effective component of alfalfa was believed to be a protein or polypeptide. Badger believed these components restricted the growth of precipitates and reduced the adherence of scale deposits. Further study (24) indicated that corn, peas, buckwheat and oats were also capable of eliminating scale formation.

Phosphates were proposed for the prevention of scale formation although they were used mainly to prevent calcium carbonate precipitation. Reitemeir and Buehrer (25) using a solution containing 200 p.p.m. calcium bicarbonate and 500 p.p.m. ammonia prevented precipitation of calcium carbonate with dissolved amorphous sodium hexametaphosphate. The crystalline form was ineffective under similar conditions. Pyrophosphates and orthophosphates were effective but to a lesser degree. The concentration of hexametaphosphate required to prevent precipitation increased with ammonia and calcium bicarbonate concentration. The conceived mechanism of inhibition involved a restricted growth of calcium carbonate precipitate due to adsorption of metaphosphate on the crystal faces. Hatch and Rice (26) found that the addition of 2 p.p.m. of hexametaphosphate inhibited scale formation from solutions containing 300 p.p.m. initial calcium carbonate concentration, up to roughly 80°C. They believed precipitation was prevented because the phosphate was absorbed on metal surfaces and on any nuclei which may have formed. The absorbed phosphate layer hindered further deposition on these surfaces. This is the mechanism of inhibition currently accepted. Badger, however, believed such treatment could not be used in sea water conversion because of the high cost. It was suggested that phosphates might be used with an acid treatment to raise the pH and reduce severity of corrosion.

Badger and Banchero believed that additions to modify the physical nature of the scale were less promising than either acid additions or methods providing alternative sources for crystallization nuclei. Langelier believed that additions used to modify the nature of the scale actually catalyzed a nucleation step and part of their action was perhaps due to adsorption effects.

The third method of scale control involves the use of solids to promote precipitation of the scale-forming components away from heating surfaces. Langelier employed beach sand as a contact medium in a unit external to the evaporator. The evaporator brine was circulated through this medium so that precipitation was induced in the unit instead of in the evaporator. Intervals between descaling were appreciably extended. Spaulding and Lindsten increased operating periods with this technique although success was quite sensitive to total alkalinity of the supply water. Loebel (27) also employed "contact stabilization" and noted that the most successful operation was obtained when the effluent from the stabilizer contained finely divided solids. It should be pointed out that such external units would not be acceptable where space is limited, e.g. aboard ship. Also, Badger and Banchero found that careful control of the supersaturation values had to be maintained since precipitation occurred in the unit external to the evaporator. They proposed the use of a fine suspension of scale-forming components. The suspension was placed in the evaporator to act as seed crystals and to promote deposition in the body of the solution. The seeds were recycled by separation from the brine discharge and by addition to the evaporator feed. However, further study is necessary for successful operation. This method was also attempted by Langelier and Spaulding and Lindsten. Circulation in the still was not sufficiently vigorous to keep the seeds in suspension. Neville-Jones tried magnesium oxide, silica and a mixture of magnesium hydroxide and sand as contact materials. The solids were continuously injected with the sea water feed. The most promising results were obtained with silica plus EDTA chelating agent but high silica losses were experienced.

Langelier suggested that by-products of electrochemical processes might be more convenient and economical than straight chemical additions to the sea water feed. Pourbaix and co-workers (28,29) used an impressed current corrosion cell to control scale formation.

The cell, containing iron electrodes, was placed in the feedwater line. Colloidal ferric hydroxide formed by oxidation of ferrous ions produced at the anode appeared to act as a nucleating agent for the crystallization of calcium carbonate. A non-scaling form of carbonate was precipitated in the feedwater. Success, based on extended operating periods, depended on the avoidance of passivity of the iron anodes.

Langelier believed that sonic and electromagnetic forces could reduce scale formation. No mechanisms were proposed except that these forces might stabilize supersaturated solutions. Many fraudulent devices based on electrical treatment for the prevention of scale formation were proposed. Eliassen and Uhlig (30) and Welder and Partridge (31) reported these methods could not be evaluated because of insufficient quantitative data. The latter also found that electrochemical treatments which introduced corrosion products into the system had no effect on the precipitation of calcium sulphate. Traces of zinc inhibited only calcium carbonate precipitation. The effect of corrosion products on magnesium hydroxide precipitation was not studied. Francis (32) and Garber (33) concluded that electrical devices in feed lines to thermocompression evaporators neither prevented scaling nor improved efficiency. Badger and Banchero thus felt this method had little probability of success in preventing scale formation.

The fourth method of scale control involves changes in evaporation equipment or technique. Hillier reported that the rate and character of scale formed depended to a large extent, on operating conditions and evaporator design.

Scale deposition was affected by the condition of the heated surface. Eibling and Allen (34) tested neoprene, titanium and a steel tube coated with teflon in a laboratory evaporator using synthetic sea water. They concluded that scale formation was not appreciably hindered by water-repellent surfaces. Also, these coatings had lower thermal conductivities than the metal and therefore reduced heat transfer. Krappe (35) showed that the metal used in water heaters did not markedly affect scale deposition. Kirschbaum and Wachendorf (36) studied several materials under forced and natural circulation of feed using hard city water in a laboratory vertical tube evaporator. Glass and enamelled steel, plain steel and copper tubes were tested. Smooth surfaces were found to offer greater resistance to scale formation than rough surfaces. The effect was not attributed to a decrease in the amount of scale deposited but to lower adherence of deposited scale on smooth surfaces. Leister (37) studied the effect of ground glass, rough and unglazed porcelain surfaces on scale formation. He noted that scale adherence on these materials was just as great as on metal plates. Corners and edges enhanced scale deposition. From the above studies Badger and Banchero felt that polished metal surfaces were useful in decreasing scale formation.

By changing some of the operating conditions scale formation was minimized. Bliss (38), Kirschbaum and Wachendorf found that forced circulation of brine reduced scale formation. Badger and Banchero also studied the effect of forced circulation and reported that complete elimination of scale by this technique was unlikely. However, further study on rates of scale formation from sea water in forced circulation systems was considered desirable.

Some workers (19,22,39,40) found less scale at lower operating temperatures although Hillier reported the opposite. Lower operating temperatures were believed advantageous in decreasing the rate of scale formation (40) because:

(1) the scale-forming components were more soluble at lower temperatures,

(2) the rate of carbon dioxide evolution was slower thereby retarding the formation of calcium carbonate and/or magnesium hydroxide,

(3) a higher degree of supersaturation was obtained with calcium carbonate than magnesium hydroxide, the former being the principal component of scale at lower temperatures.

However, for a given output, operation at lower evaporation temperatures required larger units. The overall result was an appreciable increase in the total cost of the process.

Evaporation techniques which would minimize scale deposition were devised. In one method, flash evaporation, sea water is heated to the desired maximum temperature and allowed to drop in pressure in a series of stages. Part of the liquid is vapourized in each pressure reduction step. Heat for vapourization is supplied by cooling the unvapourized liquid. Little scale was experienced since no heating surfaces are present in sections where boiling occurs. However, scale did form in the heaters for the incoming feed water. The amount of scale was decreased by limiting the maximum temperature of the water before entering the first stage, but low distillate product per unit of feed resulted.

Other methods were proposed to minimize scale formation. These included increased blowdown rates, continuous removal of scale by mechanical means and lower residence times of the brine in the evaporator. Badger found the first two proposals uneconomic. The third proposal, although not studied, was believed to be economically possible. During heating and evaporation supersaturation of the brine with scale-forming compounds increases. The pH also rises due to carbon dioxide evolution. Both conditions favour precipitation of scale-forming materials but since these conditions take time to build up, shorter residence times were thought advantageous in reducing scale formation. Further study was felt necessary. Badger proposed that if carbon dioxide removal were not so slow, an economical method of eliminating scale formation would be possible. By heating and aeration, all of the carbonate and bicarbonate ions could be removed from sea water as carbon dioxide gas. Magnesium hydroxide precipitate formed could then be removed and the remaining liquid fed to an evaporator. The costs would be for heating and aeration only since no chemicals are added.

In spite of voluminous literature on the problem of scale control an adequate solution to the problem has not been found. Results of investigations are seldom in strong agreement and sometimes appear to be contradictory. This may be due to lack of control of important variables which remain unrecognized because the basic chemistry of the process is not clearly understood. Few rate studies have been attempted on calcium carbonate precipitation although this compound is the principal component of scale formed in low temperature distillation. For these reasons, a study of calcium carbonate precipitation has been made.

PROCEDURES

Attempts to grow scale in a reasonable period of time under laboratory conditions were unsuccessful. Evaporation using a simple flow system with synthetic sea water required a minimum of 300 hours to develop appreciable scale. Growth was strongly influenced by minor fluctuations in operating conditions and measurement was difficult. A modification to promote scale formation on a thin removable copper sheet was equally unsuccessful due to inadequate control of flow rates and cracking and spalling of the product. Such an investigation would require an elaborate control system. A complete laboratory distillation unit would probably be adequate but a fundamental approach to the problem was considered more suitable at this stage.

Scale obtained in the above experiments was identified by x-ray diffraction. At operating temperatures of 70 - 75°C. it was predominantly aragonite, a form of calcium carbonate. This product is presumably formed by decomposition of bicarbonate ions as carbon dioxide is evolved during evaporation. The mechanism, however, is still uncertain although several investigations of this reaction have been reported.

It was therefore decided to study the precipitation of calcium carbonate from calcium bicarbonate solutions.

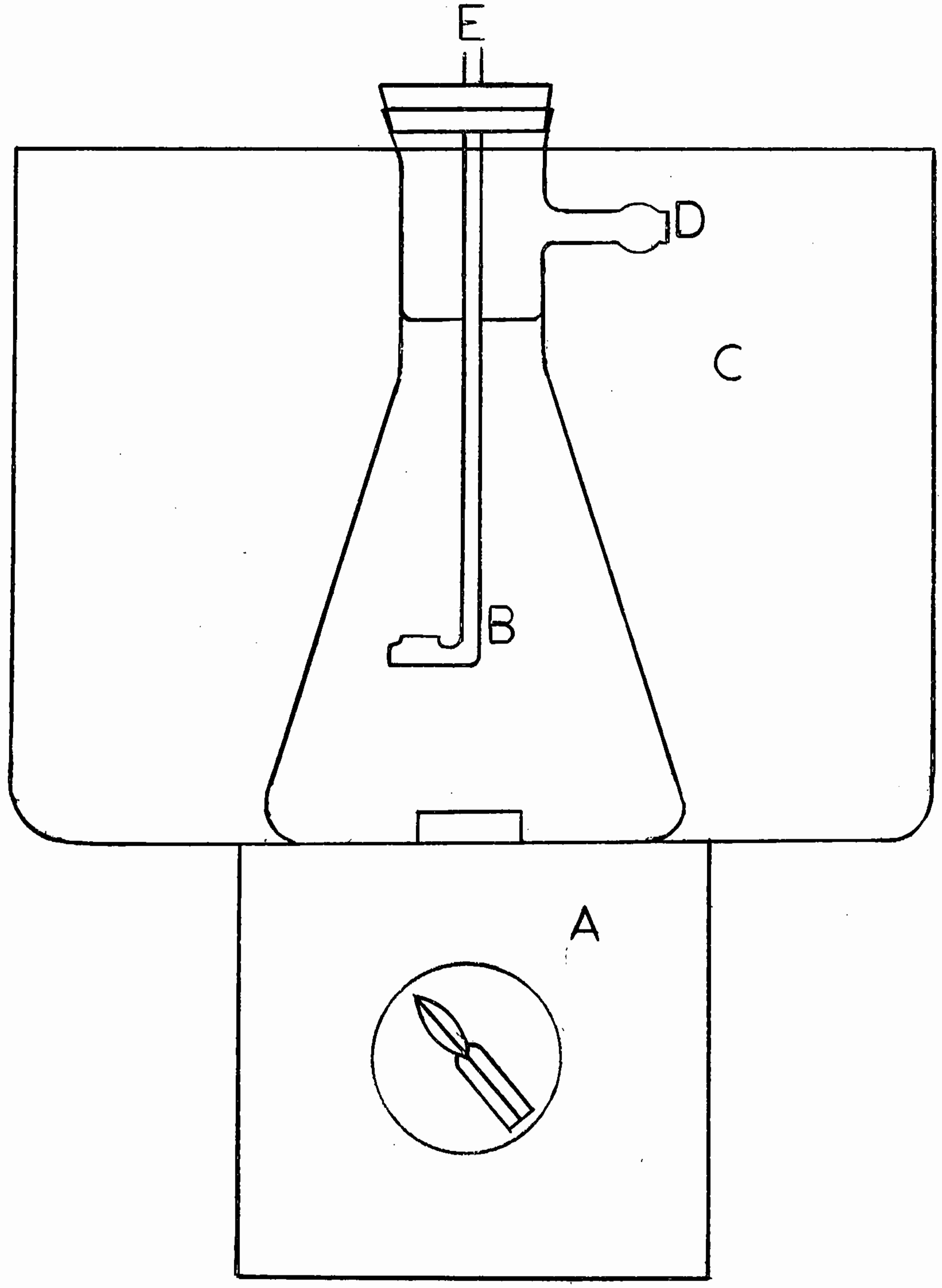
Preparation of Solution

Calcium carbonate, conforming to A.C.S. standards, and calcium-free distilled water were used to prepare a calcium bicarbonate solution of about 925 parts calcium carbonate per million parts of solution. Sufficient carbonate and distilled water were placed in a two litre suction flask immersed in crushed ice. A rubber stopper fitted with a sintered glass bubbler was wired in place (Fig. 1). The suction outlet was connected to a glass tube immersed in a mercury column to give a pressure of about 1.25 atmospheres. The solution was agitated by a magnetic stirrer and carbon dioxide gas was introduced. Dissolution was practically complete in 2 to 3 days. The solution was then filtered through No. 42 Whatman filter paper to remove undissolved solids and again placed under pressure until required. No observable precipitation occurred during this operation. Additional salts, when used, were added to the filtered stock solution and allowed to dissolve under pressure.

Figure 1.

Dissolution Apparatus

A - magnetic stirrer
B - gas bubbler
C - crushed ice bath
D - to mercury column
E - carbon dioxide inlet


E
D
C
B
A

Decomposition

Eighteen 100 ml. aliquots of bicarbonate stock solution were placed in 125 ml. Erlenmeyer flasks. The flasks, supported by aluminium rods, were immersed in a constant temperature oil bath which was agitated by a propeller driven by a 1/12 h.p. motor. Rubber stoppers fitted with fine capillaries served to reduce concentration of the solution by evaporation. At the end of each period 3 samples were removed and filtered immediately through No. 42 Whatman filter paper. Suitable aliquots were pipetted from each and analyzed for calcium (page 36).

Large differences were found between samples removed at the same time and replacement of fine capillaries by straight tubing or by rubber balloons failed to improve results.

The effect of agitation was determined by comparing samples agitated every 5 minutes by hand with rigidly fixed samples. Differences were significant but a symmetrical rearrangement of the flasks failed to improve reproducibility.

The evolution of gas from a liquid solution is strongly affected by surface conditions (41) and considerable improvement was obtained by using a single one litre thin walled Erlenmeyer reaction flask. The following procedure was finally adopted. The reaction flask was covered by a rubber stopper with a hole just large enough for the sampling pipette. When the reaction temperature was reached 3 samples of suitable volume for accurate analysis were withdrawn. Each was immediately filtered through No. 42 Whatman filter paper and suitable aliquots were taken for calcium determination. The sampling procedure was repeated every hour for periods up to 12 hours.

A control flask with tap water and mercury thermometer was used for temperature measurement to avoid possible effects associated with the thermometer surface. Control and reaction flasks, at the same temperature, were placed symmetrically in the oil bath at the same time. It was assumed that temperatures in the two flasks would remain essentially the same. This general procedure gave reasonably reproducible results and was used throughout the rest of the work.

Analyses

The standard method for calcium determination by oxalate precipitation, dissolution and titration with potassium permanganate is time consuming and subject to errors in the presence of magnesium. Consequently, a shorter more accurate method involving a complexing agent, the disodium salt of ethylenediaminetetracetic acid (EDTA), was adopted using Calcon indicator as recommended by Hildebrand and Reilley (42).

EDTA solution was prepared by dissolving sufficient powder in distilled water to give a 0.01M solution. This was standardized against a known concentration of calcium carbonate dissolved in dilute hydrochloric acid.

For calcium determination in the absence of magnesium, 10 to 25 ml. aliquots were placed in 125 ml. beakers and diluted to about 100 ml. with distilled water. The solution was made slightly acid to prevent precipitation of calcium carbonate and boiled to remove excess carbon dioxide. The solution was cooled to room temperature and neutralized with 5 per cent sodium hydroxide solution using litmus paper as indicator. About 5 ml. of diethylamine buffer and 5 to 6 drops of Calcon indicator solution were added. Standardized EDTA solution was added until the blue-green end point was obtained as recommended by Lewis and Melnick (43). The end point was determined by splitting the solution and reaching the end point in one-half of the solution. The solutions were then mixed, split and the procedure repeated until no visual difference was noted. Comparison of colours was facilitated by using Nessler tubes.

In the presence of magnesium a more distinct end point was obtained by diluting the aliquots to about 500 ml. Corresponding increases in buffer and indicator were added and the solution was magnetically stirred. The first sign of a pure blue colour was used as the end point as recommended by Lewis and Melnick.

All samples were analyzed in triplicate and the mean value was recorded. Any value differing by more than 5 per cent from the mean of the other two was rejected. For comparison, concentrations of solutions with time were expressed as percentages of the initial concentration. The latter concentration usually differed from the concentration of bicarbonate stock solution by 30 - 75 p.p.m. probably as a result of some precipitation during the warm up period.

Precipitation of Calcium Carbonate.

A solution of about 900 parts of calcium carbonate per million parts of solution was prepared by mixing appropriate solutions of sodium carbonate and calcium chloride at 74°C. Samples were immediately withdrawn and analyzed in the prescribed manner. The course of the precipitation was followed by taking hourly samples until precipitation was complete.

RESULTS

All decomposition data are tabulated in the appendix and plotted in Figures 2 to 5 which show calcium (percentage of initial value) as a function of time. The reaction generally may be described in terms of three characteristic periods:

(1) an induction period of variable length during which only a small percentage of the reaction occurs,

(2) a linear period in which the rate of reaction is roughly constant for a given set of experimental conditions,

(3) a final period during which the rate decreases and the reaction approaches completion with approximately first order kinetics (Fig. 6).

Effect of Temperature

The induction period is significantly altered by a change in reaction temperature (Fig. 2). It decreased from about 5 hours at 61°C. to 1 hour at 74°C. and ceased to be noticeable at 85°C. The amount of reaction during induction is roughly the same at the two lower temperatures: about 5 per cent.

Figure 2.

Effect of Temperature and Agitation

○ agitated at 74°C.

● 74°C.

△ 61°C.

□ 85°C.

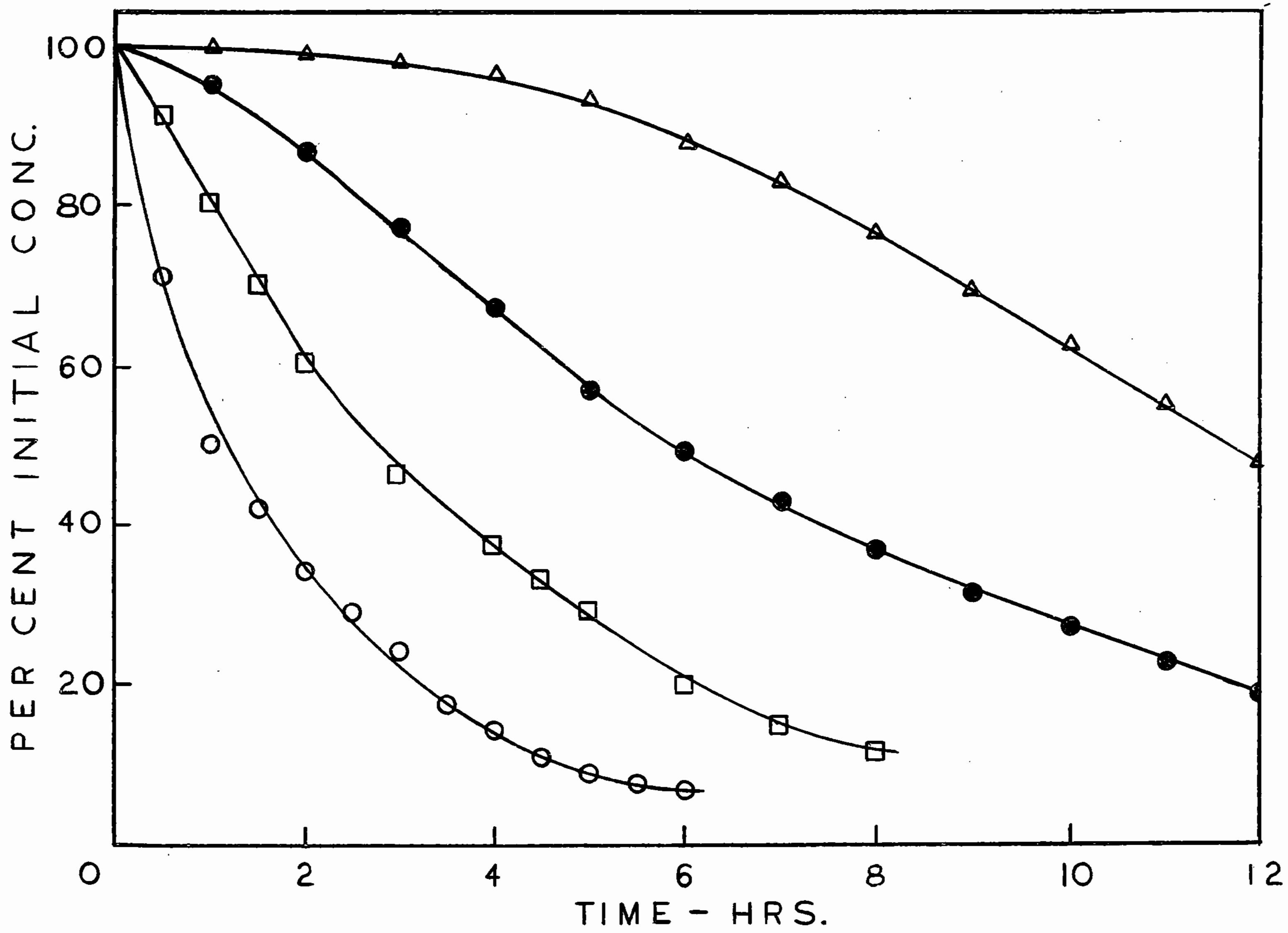
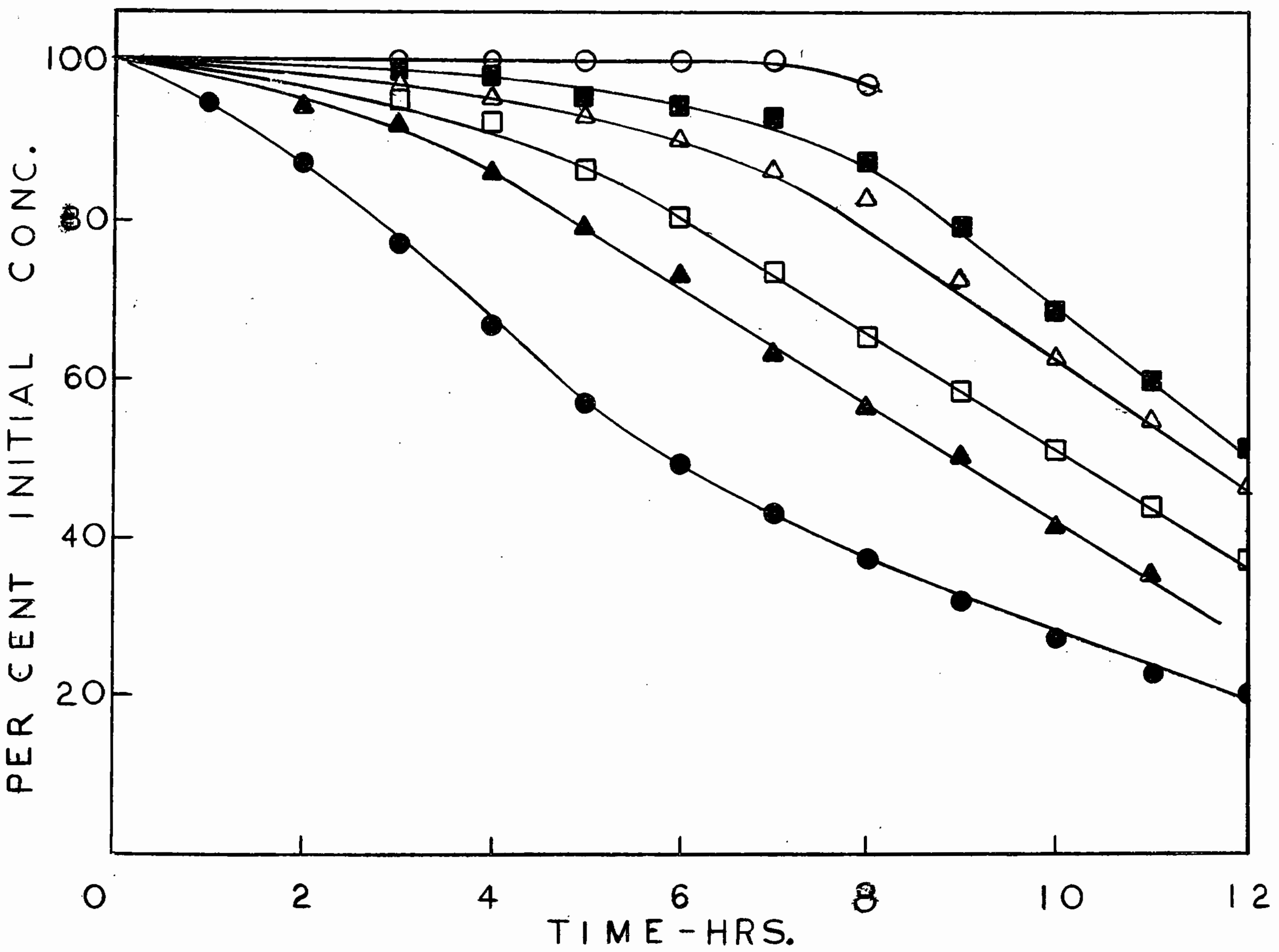

PER CENT INITIAL CONC.
100
80
60
40
20
0
2
4
6
8
10
12
TIME - HRS.

Figure 3.

Effect of Added Materials

●	no addition
▲	5 g. sodium chloride/l.
□	10 g. sodium chloride/l.
△	15 g. sodium chloride/l.
■	23.476 g. sodium chloride/l.
○	150 g. sodium chloride/l.



100
80
60
40
20
PER CENT INITIAL CONC.
0
2
4
6
8
10
12
TIME-HRS.

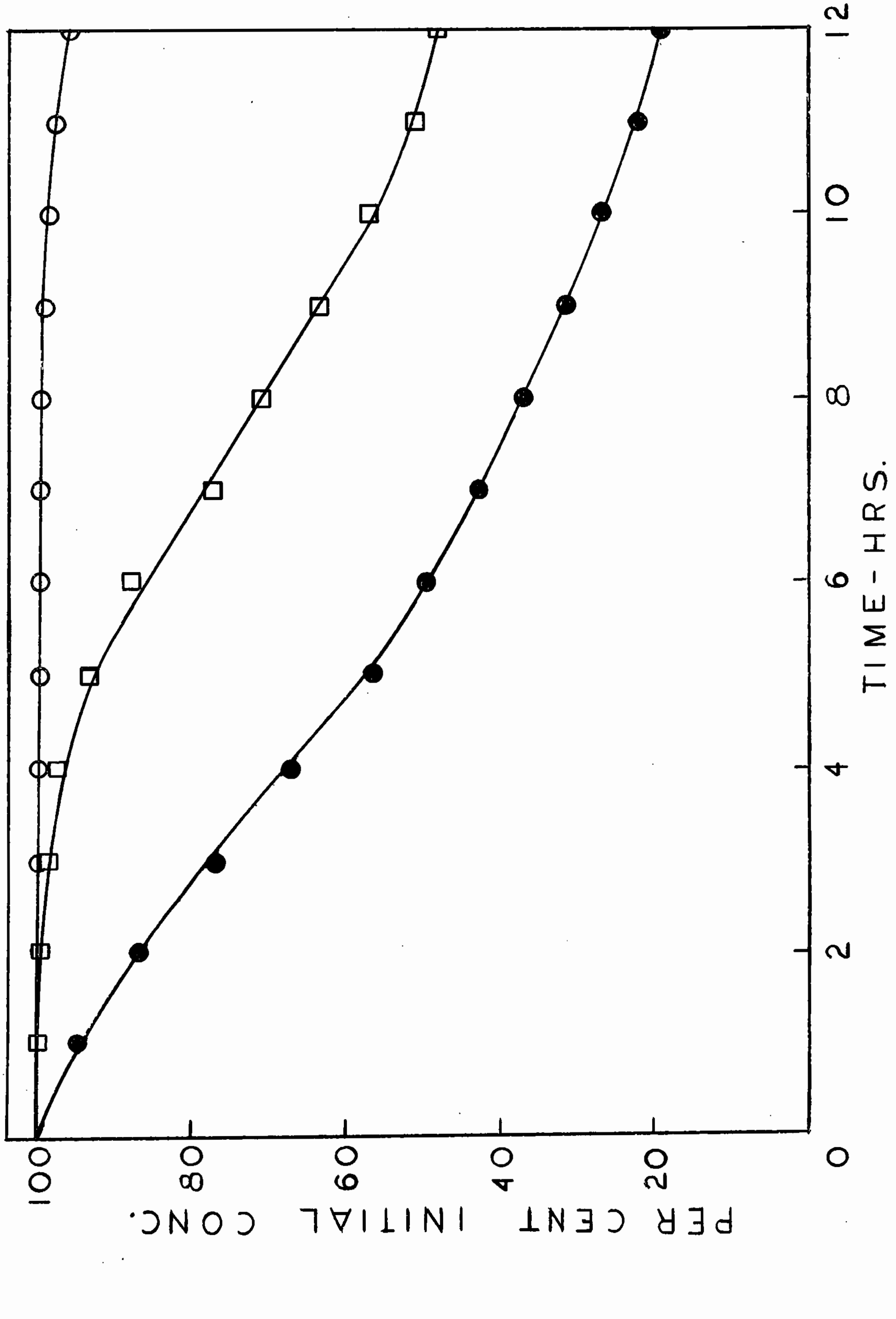
Figure 4.

Effect of Added Materials

● no addition

□ 5 g. ammonium chloride/l.

○ 10 g. ammonium chloride/l.



100
80
60
40
20
0
PER CENT INITIAL CONC.
2
4
6
8
10
12
TIME-HRS.

Figure 5.

Effect of Added Materials

● no addition

△ 5 g. magnesium sulphate/l.

○ 5 g. sodium or ammonium citrate/l.

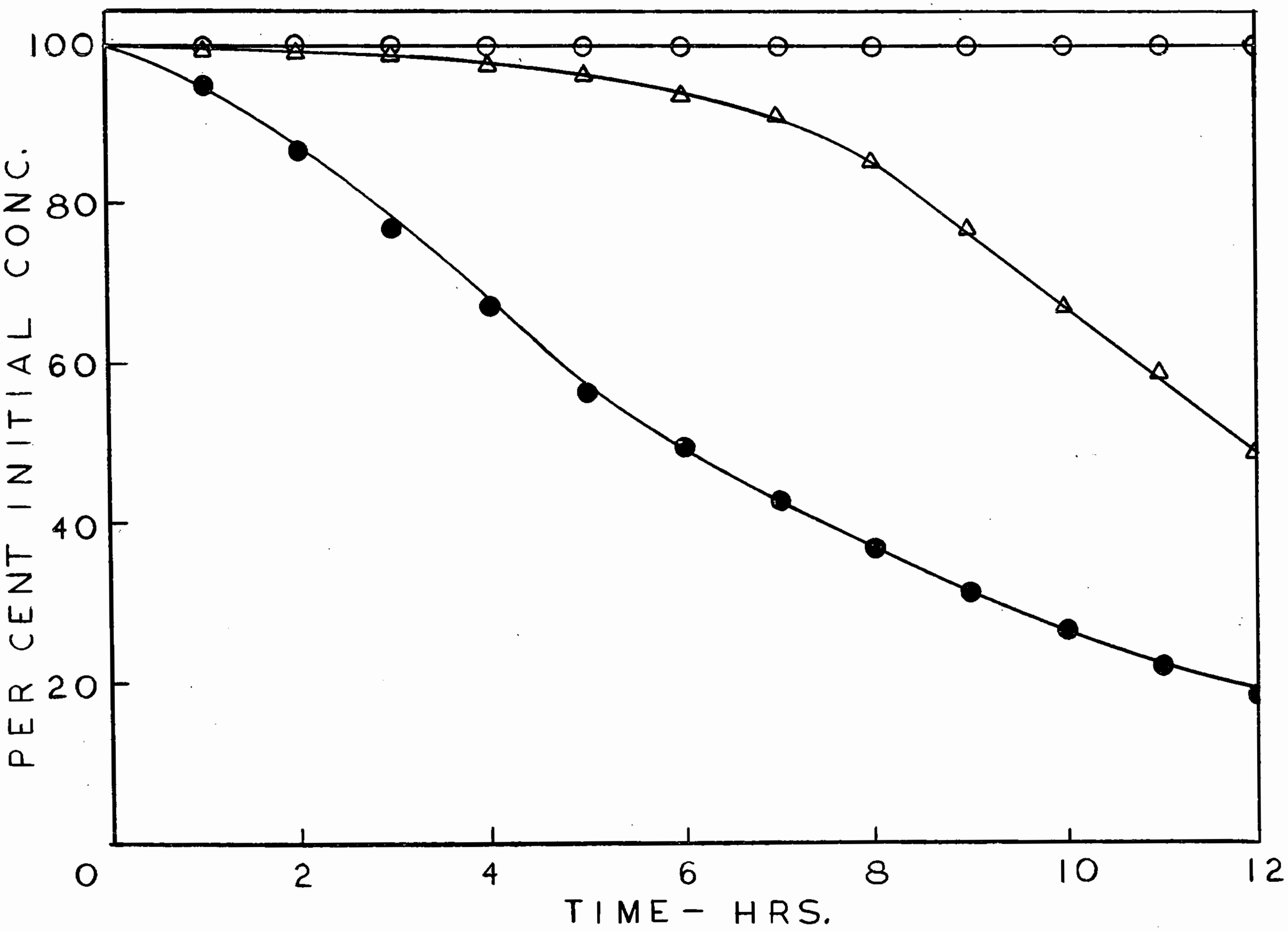

100
80
60
40
20
0
2
4
6
8
10
12
PER CENT INITIAL CONC.
TIME- HRS.

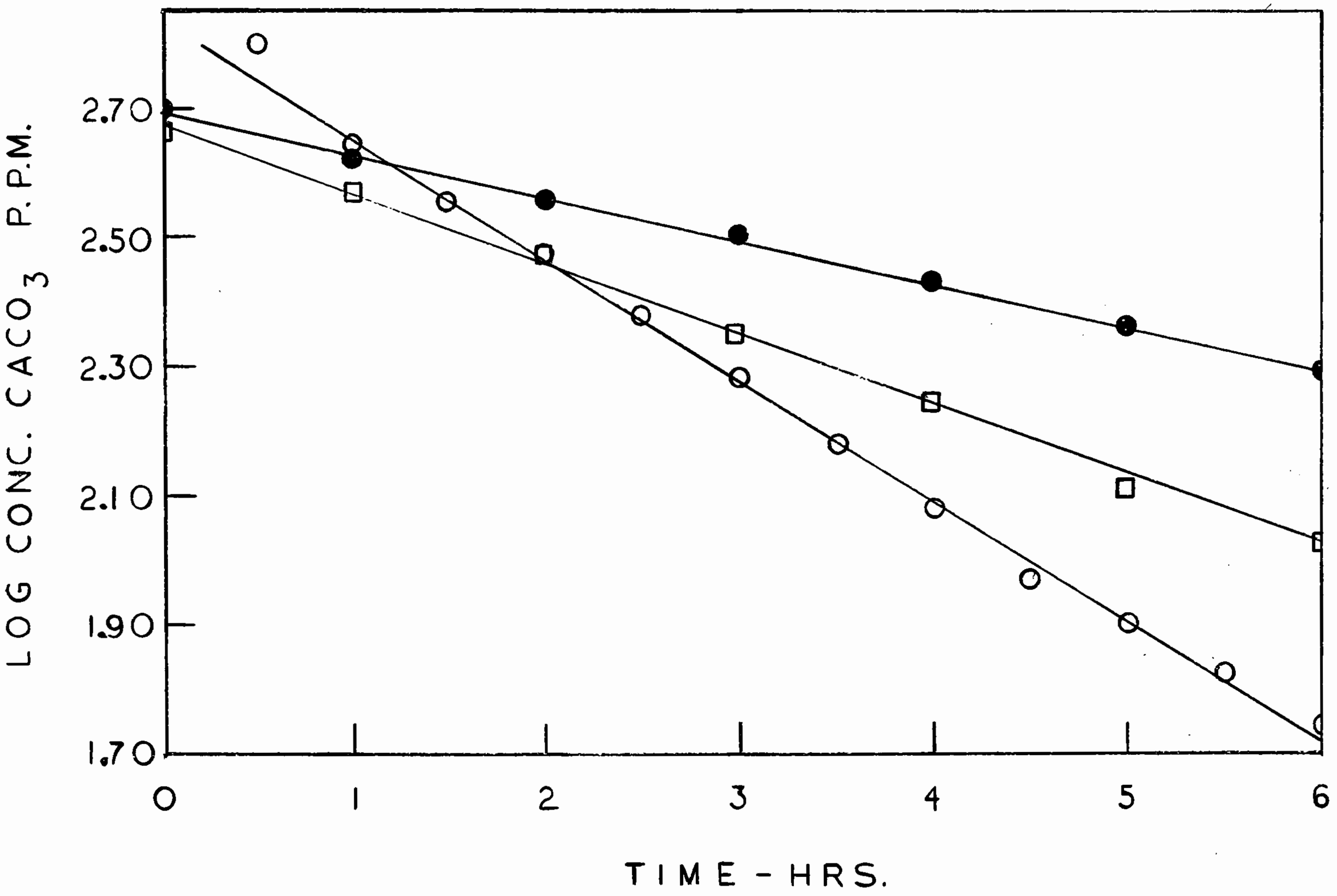
Figure 6.

First Order Plots for the Final Period

● 74°C.

□ 85°C.

○ agitated at 74°C.


LOG CONC. CACO$_3$ P.P.M.
2.70
2.50
2.30
2.10
1.90
1.70
0
1
2
3
4
5
6
TIME - HRS.

The rate of decomposition, measured by the slope of the linear portion of the curve, increases appreciably with temperature rise. From 6 per cent/hour at 61°C., it increases to 9 per cent/hour at 74°C. and 20 per cent/hour at 85°C.

The third period is affected in a similar manner.

Effect of Agitation

Agitation has a pronounced effect on all aspects of the decomposition (Fig. 2). At 74°C. the stirred reaction has no observable induction period and the initial slope, which may not be linear, is 65 per cent/hour. First order behaviour appears at a much earlier point in the reaction (Fig. 6).

Effect of Added Materials

Added materials generally increased the induction period but had little effect on the slope of the linear portion of the curve (Figs. 3,4,5). For the salts tested at 74°C. the general effectiveness increased from sodium chloride to ammonium chloride, magnesium sulphate and finally sodium and ammonium citrates. For a given salt the effectiveness increased with concentration, at least for those so tested (sodium chloride and ammonium chloride).

The curvature towards the end of the reaction containing 5 grams ammonium chloride suggests an effect on the final equilibrium of the system (Fig. 4). Also, the pronounced effect of citrates in extending the induction period to over 24 hours for the sodium salt and 48 hours for the ammonium salt may be associated with the final equilibrium in the system. Citrate ion is known to complex with calcium ion.

It is noteworthy that all of the added materials slowed down the precipitation of calcium carbonate primarily by increasing the induction period. Changes in the slopes of the linear portions of the curves were relatively insignificant.

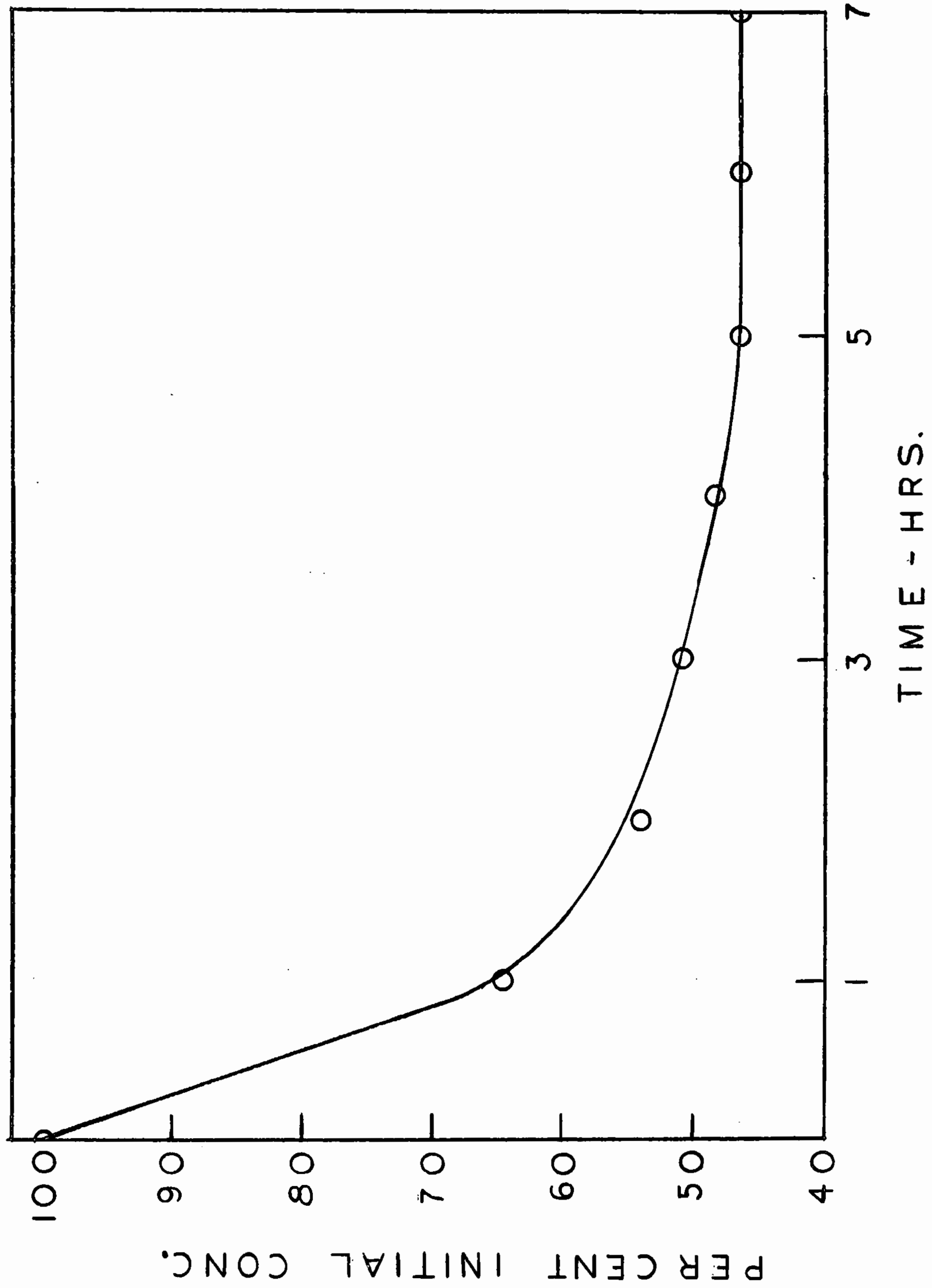
Precipitation of Calcium Carbonate

The precipitation of calcium carbonate from the solution containing 900 parts per million was immediate. The concentration had dropped to 100 parts per million by the time the first sample was taken. Henceforth the reaction slowed down as indicated in Fig. 7.

It is important to note that the precipitation is

Figure 7.

Variation of Per cent Initial Concentration with Time for the Precipitation of Calcium Carbonate at 74°C.

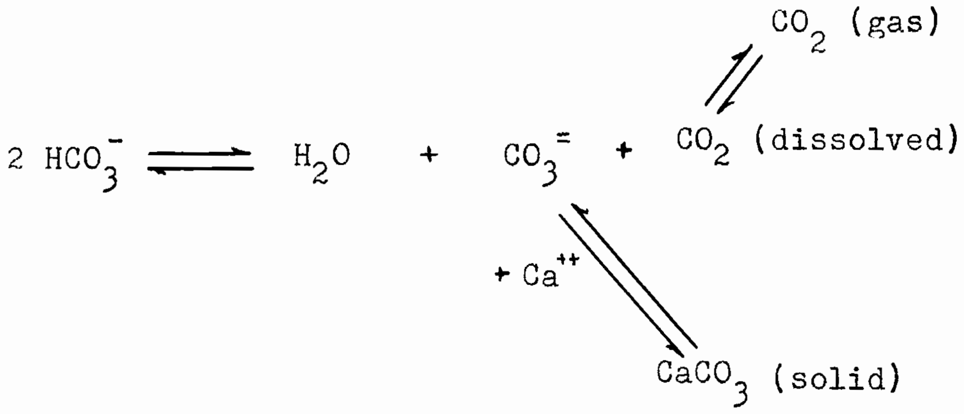


PER CENT INITIAL CONC.
100
90
80
70
60
50
40
1
3
5
7
TIME - HRS.

quite rapid compared with the decomposition of the bicarbonate; it is essentially complete in about 4 hours.

DISCUSSION

Aqueous calcium carbonate in contact with carbon dioxide establishes an equilibrium which may be represented as follows:



If the pressure of carbon dioxide is decreased or if the temperature is raised the solubility of carbon dioxide is decreased and the following sequence of reactions takes place:

$$CO_2\ (\text{dissolved}) \longrightarrow CO_2\ (\text{gas}) \qquad (2)$$

$$HCO_3^- \longrightarrow OH^- + CO_2\ (\text{dissolved}) \qquad (12)$$

$$HCO_3^- + OH^- \longrightarrow H_2O + CO_3^= \qquad (13)$$

$$Ca^{++} + CO_3^= \longrightarrow CaCO_3\ (\text{solid}) \qquad (6)$$

In this investigation the initial equilibrium was established at a temperature of about 0°C. and a carbon dioxide pressure of about 1000 mm. Hg. Decomposition of the bicarbonate was accomplished by raising the temperature to the desired level (74°C. in most cases) and opening the system to the atmosphere (partial pressure of CO_2 about 10 to 15 mm. Hg.).

The rate and general kinetic behaviour of such a process are governed by the slowest reaction in the sequence. Ionic reactions such as 12 and 13 are usually fairly rapid and will not be considered in the following discussion. Reactions 2 and 6 are heterogeneous and involve diffusion which is generally slow. The pronounced effect of agitation and the low activation energy are both characteristic of a diffusion controlled process and a qualitative explanation of the kinetics is based on reactions 2 and 6.

The Induction Period

Ordinary precipitation from slightly supersaturated solutions often involves an induction period which increases as the supersaturation is decreased. There is also a critical level of supersaturation below which spontaneous precipitation will not occur in any practical period of time. O'Rourke and Johnson (44) have explained the relationship between length of induction period and degree of supersaturation in terms of nucleation and growth of nuclei to some critical size sufficient to produce an observable change (Tyndall Effect).

The precipitation of calcium carbonate as accomplished in this investigation undergoes, in effect, a double induction. Initially the concentrations of Ca^{++} and $CO_3^{=}$ are at (or possibly slightly below) the saturation level. Thus, before nucleation can begin some time is required while the concentration of $CO_3^{=}$ builds up to the critical value at a rate governed by the evolution of carbon dioxide. Following this initial change, nucleation and growth as observed by O'Rourke and Johnson must occur and the total induction time is a combination of the two periods.

In principle, the effect of carbon dioxide supersaturation on induction can be calculated by finding the concentration of $CO_3^{=}$ as a function of time and using this in conjunction with the method of O'Rourke and Johnson. In practice this does not work because the functional relationship is too complex. Gas evolution is a first order process (41) and may be represented by

$$\frac{d\,[CO_2]}{dt} = k\,(CO_2) \qquad (14)$$

where $(\ \ )$ = concentration in solution
$[\ \ ]$ = concentration evolved from solution
k = rate constant

This expression can be integrated if converted to a single variable. Thus we note that

$$(CO_2) = (CO_2)_o - [CO_2] + \tfrac{1}{2}\left[(HCO_3^-)_o - (HCO_3^-)\right] \qquad (15)$$

where subscript zero denotes the initial value.

Also

$$(CO_3^=) = (CO_3^=)_o + \tfrac{1}{2}\left[(HCO_3^-)_o - (HCO_3^-)\right] \qquad (16)$$

Whence from (15) and (16)

$$[CO_2] = (CO_2)_o - (CO_3^=)_o + (CO_3^=) - (CO_2) \qquad (17)$$

Also, because we have assumed ionic reactions to be fast the bicarbonate - carbonate equilibrium is fairly closely maintained so that

$$K = \frac{(CO_2)\;(CO_3^=)}{(HCO_3^-)^2}$$

Now the initial ratio $(HCO_3^-) : (CO_3^=)$ is very large so that $(CO_3^=)$ can be increased several fold without significant change in (HCO_3^-). Thus for the induction period we may assume (HCO_3^-) to be constant whence

$$(CO_2) = \frac{K'}{(CO_3^=)} \qquad (18)$$

where $K' = K\;(HCO_3^-)_o^2$

Substituting from (18) in (17)

$$\left[CO_2\right] = (CO_2)_o - (CO_3^=)_o + (CO_3^=) - \frac{K'}{(CO_3^=)} \qquad (19)$$

and differentiating with respect to time

$$\frac{d\left[CO_2\right]}{dt} = \frac{d\;(CO_3^=)}{dt} - K'\;\frac{d\;\frac{1}{(CO_3^=)}}{dt}$$

$$= \frac{d\;(CO_3^=)}{dt} + \frac{K'}{(CO_3^=)^2}\;\frac{d(CO_3^=)}{dt} \qquad (20)$$

Combining (14), (18) and (20)

$$\frac{d(CO_3^=)}{dt} + \frac{K'}{(CO_3^=)^2}\frac{d(CO_3^=)}{dt} = \frac{k\,K'}{(CO_3^=)} \qquad (21)$$

Integration yields

$$\tfrac{1}{2}\,(CO_3^=)^2 + K' \ln\,(CO_3^=) = k\,K' t + \text{constant}$$

Or, since $(CO_3^=) = (CO_3^=)_o$ when $t = 0$

$$\tfrac{1}{2}\left[(CO_3^=)^2 - (CO_3^=)_o^2\right] + K' \ln \frac{(CO_3^=)}{(CO_3^=)_o} = k\,K' t \qquad (22)$$

This functional relationship is not adaptable to the treatment used by O'Rourke and Johnson. It does, however, permit a graphical representation of $(CO_3^=)$ with time, for the early stages of the decomposition. This is illustrated graphically in Fig. 8. No calcium precipitates during the induction period and the equilibrium concentration of $CO_3^=$ remains constant at $(CO_3^=)_o$. The actual $(CO_3^=)$ rises through stage 1 to

Figure 8.

Qualitative Decomposition Scheme

A - (Ca^{++}) concentration

B - actual ($CO_3^{=}$) concentration

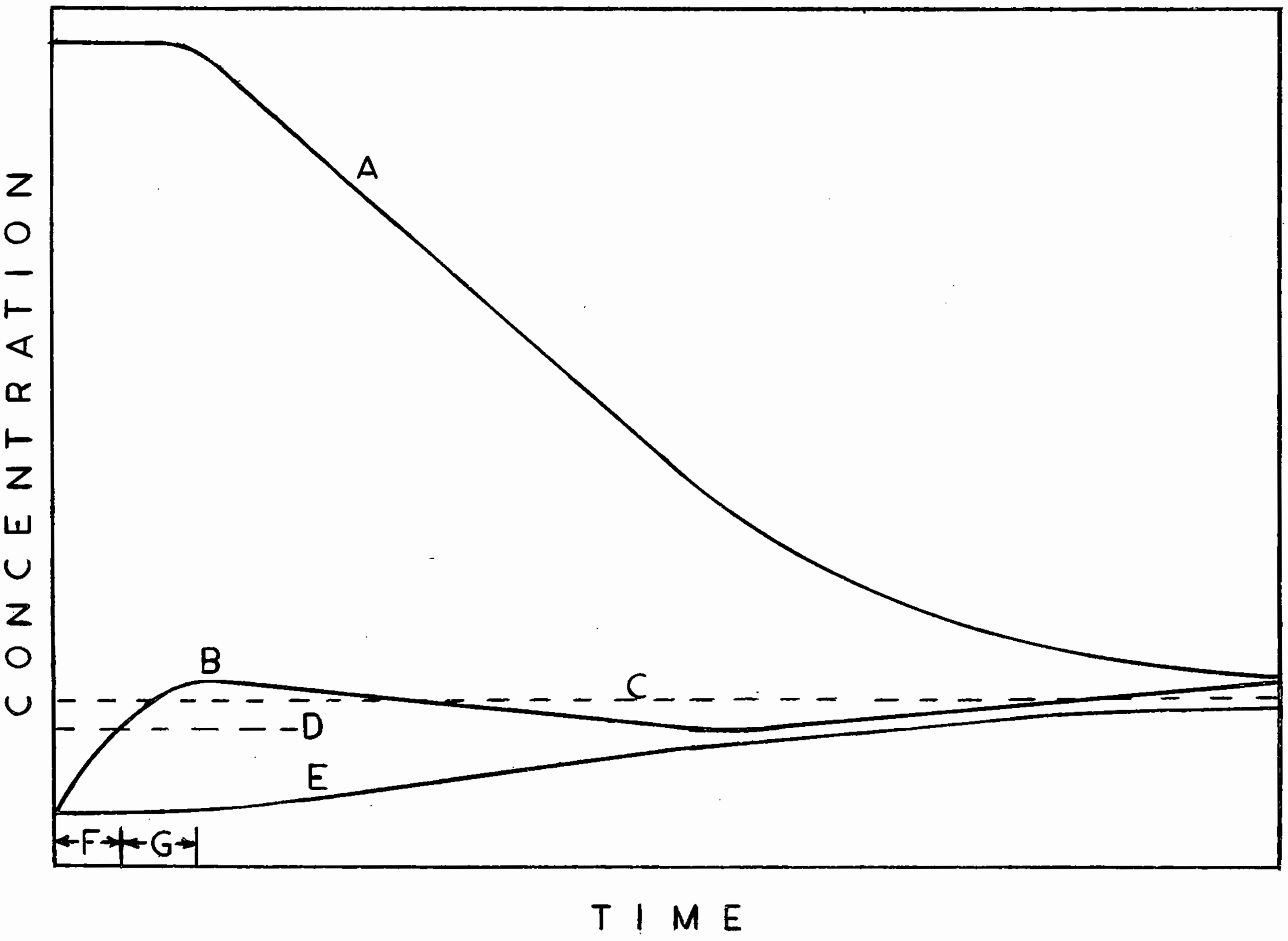
C - $\sqrt{K_{sp}}$ of $CaCO_3$

D - critical ($CO_3^{=}$) concentration

E - equilibrium ($CO_3^{=}$) concentration

F - stage 1 of induction period

G - stage 2 of induction period


CONCENTRATION
A
B
C
D
E
F
G
TIME

the critical level for nucleation. It continues to rise through stage 2 while nucleation and growth up to observable size take place. This point marks the end of the induction period.

The Linear Period

During this period the rate of precipitation remains constant. This rate is governed by the area of precipitate and some power of the degree of supersaturation. Since the area is constantly increasing the degree of supersaturation must steadily decrease. The concentration of Ca^{++} is large and decreasing linearly during this period so that $(CO_3^=)$, which is very small, will probably decrease only very slowly if at all. Hence carbonate ions, which are being removed at a constant rate, must be formed at an approximately constant rate. The formation of carbonate ions is governed largely by the evolution of carbon dioxide which is given by equation 14 . Hence (CO_2) must remain roughly constant, the amount evolved being replaced by decomposition of bicarbonate. Confirmation of this hypothesis would require measurement of carbon dioxide evolved which was, unfortunately, not possible with the apparatus available. A crude estimate of this period is indicated in the middle portion of Fig. 8.

The Final Period

As the concentration of bicarbonate becomes smaller the percentage change becomes greater and in order to maintain the carbonate-bicarbonate equilibrium the concentration of dissolved carbon dioxide must decrease. This causes a decrease in the rate of carbon dioxide evolution and hence on the rate of formation of carbonate ions. In turn, the precipitation of calcium carbonate becomes progressively slower as equilibrium is approached. This is seen in the final portion of Fig. 8.

The Effect of Added Salts

Added salts have a pronounced effect on the induction period. It is difficult to conceive a mechanism by which these materials would slow down the evolution of gas. If anything, the "salting out" effect should speed up the process. On the other hand added salts might readily affect the precipitation process itself in two ways:

(1) The adsorption of foreign ions on growing particles in the colloidal size range might

serve to stabilize them and inhibit, or even prevent, further growth.

(2) Ions capable of forming complexes with either Ca^{++} or $CO_3^=$ would change the equilibrium concentration of total calcium, thereby raising the critical concentration of $CO_3^=$ necessary to cause nucleation. It would be necessary to extend all experiments to final equilibrium to determine which of these mechanisms occurs. Only ammonium chloride appears to have affected the equilibrium, at least within the limits of the data obtained.

Very little change was noted in the slopes of the linear portions of the curves. This is further indication of control by gas evolution during this part of the decomposition.

Practical Applications

Calcium carbonate is the main component of scale formed in low temperature distillation of sea water. Its precipitation appears to be governed at least in part, by the evolution of carbon dioxide gas. If gas evolution promotes precipitation of calcium carbonate, it would be desirable to effect this evolution in a unit external to the evaporator. The precipitate may be removed by filtration and the filtrate returned to the evaporator. To obtain an appreciable fraction of precipitate formation in the external unit the rate of evolution of carbon dioxide gas can be accelerated by reduced pressure or increased temperature.

A reduction of the partial pressure of carbon dioxide in the gaseous phase decreases the solubility of carbon dioxide in solution and therefore the rate of carbon dioxide evolution is increased. The evolution rate is also increased by agitation. In still liquid, during gas evolution, there exists a concentration gradient of dissolved gas with the zones of highest concentration being furthest from the surface. Agitation will tend to transport these zones of higher concentration towards the surface, thus increasing the diffusion gradient. This, in effect, will result in an increase in the evolution rate.

If the temperature is increased, the solubility of carbon dioxide in solution is again decreased. The increased rate of evolution of carbon dioxide accelerates the rate of precipitation of calcium carbonate. Agitation increases the gas evolution rate as mentioned above and improves the heat transfer coefficient.

The precipitation of calcium carbonate can be retarded by citrate additions. This may be due to complexing of the citrate ions with calcium ions. Complexing changes the equilibrium concentration of total calcium and therefore raises the critical concentration of carbonate ion necessary to cause nucleation of the precipitate. Although citrates produce a marked effect in retarding precipitation the development of a stronger and inexpensive complexing agent is indicated.

The success of the seed recycle and contact stabilization methods proposed for the control of scale formation may be attributed to the effect of the seeds or contact materials on the induction period. In the second induction period, a certain supersaturation level must be attained in order to induce precipitation. However, in the presence of foreign seeds, supersaturation is destroyed and precipitation occurs rather rapidly on the seeds.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

(1) Decomposition of calcium bicarbonate solutions was followed by measuring the calcium concentration at hourly intervals.

(2) Generally, three characteristic periods were observed:

- (a) an induction period during which decomposition was not appreciable,
- (b) a linear period during which the reaction rate was generally constant,
- (c) a final period in which the rate decreased and the reaction approached completion.

(3) The induction period was increased by added materials and by decreasing temperatures but was decreased by agitation.

(4) The slope of the linear period was increased by both temperature rise and agitation but was not significantly altered by added materials.

(5) A possible explanation of the decomposition reaction was given on a qualitative basis in an attempt to show that in all three periods carbon dioxide gas evolution is rate-controlling.

SUGGESTIONS FOR FURTHER WORK

An alternative procedure is suggested to ascertain the validity of the qualitative decomposition scheme. A cylindrical reaction vessel rather than an Erlenmeyer flask should be used to eliminate the possibility of a change in the rate of carbon dioxide gas evolution by a change in the gas-liquid interface area as solution is withdrawn. The vessel should be equipped with suitable apparatus to determine as a function of time, (1) the carbon dioxide gas evolved from solution, (2) the calcium concentration and (3) either the bicarbonate, carbonate or carbon dioxide concentration in solution since these three are related by equations 15 and 16. These values can be used to determine the actual carbonate ion concentration (equation 22). If gas evolution is rate-controlling and if the assumptions presented are valid, the actual carbonate ion concentration curve should be similar to that in the qualitative decomposition scheme.

A closed system would be more desirable than a system open to the atmosphere since:

(1) the total pressure can be varied over a relatively wide range so that the effect of pressure on decomposition may be studied,

(2) the pressure can be kept constant whereas an open system is subject to fluctuations in atmospheric pressure,

(3) the composition of the gas phase can be controlled and

(4) measurements of the gas evolution rate can be performed.

A study of magnesium hydroxide precipitation in a manner similar to that described for calcium carbonate precipitation would be advantageous towards determining the mechanism of scale formation.

APPENDIX

Determination of Calcium in Bicarbonate Solutions

Effect of Temperature

Table II

Temperature 61°C.

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	866	866	873	868	100
1	866	873	866	868	100
2	860	856		858	99.0
3	851	854	854	853	98.3
4	834	840		837	96.5
5	804	807	810	807	93.6
6	761	764	761	762	87.7
7	718	720	716	718	82.7
8	664	660	660	661	76.1
9	605	605	605	605	69.7
10	545	543		544	62.6
11	478	478	476	477	55.0
12	410	412	414	412	47.4
13	345	346	347	346	39.8

Table III

Temperature 74°C.

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	860	860	856	859	100
1	808	828	808	815	95
2	741	750	741	744	86.6
3	660	662	660	661	74.4
4	575	576	570	574	66.8
5	480	489	489	486	56.6
6	423	423	425	424	49.4
7	366	366	368	367	42.7
8	314	316	320	317	36.9
9	271	271	271	271	31.6
10	228	232	232	231	26.9
11	191	194	195	193	22.5
12	159	162	164	162	18.8

Table IV

Temperature - 85°C.

Time hours	$CaCO_3$ concentration parts per million A	 B	 C	 Mean	Per cent initial concentration
0	776	768	767	770	100
0.5	712	704	703	706	91.8
1	618	619	615	617	80.3
1.5	537	537	537	537	69.9
2	470	464	464	466	60.5
3	358	360		359	46.6
4	290	288	285	288	37.4
4.5	254	257	257	256	33.2
5	221	222	222	222	28.8
6	153	153	153	153	19.9
7	115	115	112	114	14.8
8	85.4	85.4	92.0	87.6	11.4
9	69.1				8.99

Effect of Agitation

Table V

Temperature 74°C.

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0		871	871	871	100
0.5	610	635	661*	622	71.3
1	434	440	443	439	50.4
1.5	372	367	360	366	42.0
2	300	300	300	300	34.4
2.5	214*	242	264	253	29.0
3	195	193	198	195	22.4
3.5	154	156		155	17.8
4	120	120	121	120	13.9
4.5	95.3	99.1	110*	97.2	11.1
5	81.0	81.0	81.0	81.0	9.3
5.5	66.6	69.0	66.6	67.0	7.7
6	62.9*	57.2	58.6	57.9	6.65

* - rejected

Effect of Added Materials

Table VI

5 grams sodium chloride per litre

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0		856	856	856	100
1	849	843	855	849	99.1
2	807	804	807	806	94.2
3	782	792	789	788	92.0
4	741	738	735	735	85.9
5	680	675	675	677	79.2
6	625	621	625	624	72.9
7	541	548	548	546	62.8
8	480	480		480	56.1
9	429	429	426	428	50.1
10	354	356	355	355	41.3
11	306	300	296	301	35.2

Table VII

10 grams sodium chloride per litre

Time	$CaCO_3$ concentration parts per million				Per cent initial concentration
hours	A	B	C	Mean	
0	893	886	861*	890	100
1	866	866	866	866	97.5
2	857	865	849	857	96.4
3	839	839	855	844	94.7
4	831	816	810	819	92.0
5	770	766	755	764	85.8
6	716	715	709	713	80.1
7	646	652	652	650	73.0
8	579	582	585	582	65.4
9	520	517	515	517	58.2
10	456	456	456	456	51.3
11	390	387	387	388	43.6
12	328	332	332	331	37.2

* - rejected

Table VIII

15 grams sodium chloride per litre

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	884	884	889	886	100
1	876	866	861	868	98.0
2	867	855	851	858	96.8
3	855	855	861	857	96.8
4	848	845	842	845	95.4
5	826	823	816	822	92.7
6	796	791	791	793	89.4
7	765	765	754	761	85.9
8	728	721	705*	725	81.9
9	640	640	634	638	72.0
10	555	557	548	553	62.4
11	485	482	487	485	54.7
12	409	406	406	407	45.9

* - rejected

Table IX

23.476 grams sodium chloride per litre

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0		874	874	874	100
1	855	861	855	857	98.1
2	861	861	866	863	98.8
3	861	866	861	863	98.8
4	838	835	824	832	95.2
5	835	835	835	835	95.5
6	830	826	820	825	94.5
7	814	806	804	808	92.5
8	760	756	754	757	86.7
9	690	690	686	689	78.9
10	599	595	592	595	68.1
11	519	526	519	521	59.6
12	453	444	415*	449	51.4

* - rejected

Table X

150 grams sodium chloride per litre

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	874	868	866	869	100
1	862	850	880	864	99.4
2	868	856	868	864	99.4
3	870	870	870	870	100
4	872	870	868	870	100
5	871	869	869	870	100
6	874	874		874	100
7	874	865		870	100
8	837	831	837	835	97.2

Table XI

5 grams ammonium chloride per litre

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	856	864		860	98.6*
1	864	866	872	867	99.5*
2	869	869	875	871	100
3	869	869	853	864	99.1
4	853	853	850	852	97.8
5	816	816	816	816	93.6
6	756	756	756	756	86.8
7	684	684	684	684	78.5
8	617	617	617	617	70.9
9	554	554	554	554	63.5
10	500	500	496	499	57.3
11	447	447	447	447	51.4
12	424	421	421	422	48.4

* - rejected and concentration assumed to be 100 per cent.

Table XII

10 grams ammonium chloride per litre

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	861	861	856	859*	
1	884	892	875	884	100
2	875	870	870	872	98.6
3	884	884	884	884	100
4	884	884	884	884	100
5	884	887	887	889	100
6	887	887	879	884	100
7	879	882	885	882	99.9
8	884	884	884	884	100
9	886	870	878	878	99.5
10	875	865	884	875	99.1
11	865	865	865	865	98.0
12	855	855	846	852	96.5

* - rejected

Table XIII

5 grams magnesium sulphate per litre

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	890	896	896	894	100
1	909	892	896	892	99.6
2	896	898	876	890	99.5
3	890	874		882	98.6
4	876	885	879	880	98.4
5	860	856	860	859	96.0
6	856	830	830	839	93.8
7	824	807	807	813	90.9
8	774	765	760	766	85.6
9	695	688	685	689	77.0
10	597	597		597	66.8
11	536	526	518	527	59.0
12	442	442	435	440	48.2

Table XIV

5 grams sodium citrate per litre

Time hours	$CaCO_3$ concentration parts per million				Per cent initial concentration
	A	B	C	Mean	
0	880	880		880	100
1	880	875	888	874	99.3
2	875	888		881	100
3	886		880	883	100
4	880	863	880	874	99.3
5	856	875	886	872	99.0
6	884	884	878	882	100
7	878	880	884	881	100
8	876	875	875	875	99.3
9	878	878	878	878	99.7
10	875	881	888	881	100
11	851	851		851*	96.7
12	875	875	875	875	99.3

* - rejected

Table XV

5 grams ammonium citrate per litre

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	876	876	876	876	100
1	876	876	880	877	100
2	867	867	874	869	99.2
3	872	880	880	877	100
4	877	874	856	869	99.2
5	877	877	865	873	99.7
6	883	883	890	885	100
7	883	883	883	883	100
8	883	883	876	881	100
9	883	876	883	881	100
10	876	879	884	880	100
11	876	884	876	879	100
12	884	873		877	100

Determination of Calcium in Sodium Carbonate - Calcium Chloride Solution

Table XVI

Temperature - 74°C.

Time hours	$CaCO_3$ concentration parts per million A	B	C	Mean	Per cent initial concentration
0	96.6*	103	103	103	100
1	66.6	66.6		66.6	64.6
2	52.0*	56.0	55.2	55.6	54.0
3	52.8	52.0		52.4	50.8
4	50.0	50.0		50.0	48.5
5	48.0	48.0	48.0	48.0	46.5
6	48.0	48.0	48.0	48.0	46.5
7	48.0	48.0	48.0	48.0	46.5

* - rejected

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